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Standard Electrode Potentials Involving Radicals in Aqueous Solution: Inorganic Radicals

IUPAC Task Group on Radical Electrode Potentials

David A. Armstrong (deceased) (task group member)
Department of Chemistry, University of Calgary, Alberta, Canada

Robert E. Huie (task group member)
formerly of the Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Willem H. Koppenol (task group member)
Institute of Inorganic Chemistry, Swiss Federal Institute of Technology, CH-8093 Zürich, Switzerland

Sergei V. Lymar (task group member)
Chemistry Department, Brookhaven National Laboratory, Upton NY 11973, USA

Gábor Merényi (task group member)
Department of Applied Physical Chemistry, The Royal Institute of Technology, S-10044, Stockholm 70, Sweden

Pedatsur Neta (task group member)
Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Branko Ruscic
Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL, 60439, USA, and Computation Institute, University of Chicago, Chicago, IL, 60637, USA

David M. Stanbury (task group leader)

Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849, USA

Steen Steenken (task group member)
Mülheim, Germany

Peter Wardman (task group member)
formerly of the University of Oxford, Gray Cancer Institute, Department of Oncology, Old Road Campus Research Building, Roosevelt Drive, Oxford OX3 7DQ, U.K.

Abstract: Recommendations are made for standard potentials involving select inorganic radicals in aqueous solution at 25 °C. These recommendations are based on a critical and thorough literature review and also by performing derivations from various literature reports. The recommended data are summarized in tables of standard potentials, Gibbs energies of formation, radical pK_a's, and hemicolligation equilibrium constants. In all cases, current best estimates of the uncertainties are provided. An extensive set of Data Sheets is appended that provide original literature references, summarize the experimental results, and describe the decisions and procedures leading to each of the recommendations.

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1. Introduction

Radicals, both organic and inorganic, tend to be highly reactive. Nevertheless, they are widely encountered as intermediates in chemical reactions; their individual reactivities are central among the factors that determine the rates and products of the overall reactions in which they are involved. For reactions where the radicals are present in the aqueous phase, electrode potentials involving the radicals are among the most powerful indicators of reactivity. Electrode potentials involving radicals are often more directly related to reactivity than are electrode potentials of non-radicals, because the former more often correlate to specific steps in the reaction mechanisms.

The determination of radical electrode potentials has greatly expanded in the last three decades, largely through the application of pulse radiolysis and flash photolysis. These are techniques that are well suited to the generation of transient radicals and the measurement of their reaction equilibria. It is largely through the manipulation of the radical equilibrium constants that the current bounty of radical electrode potentials has been obtained.

In 1989 two comprehensive reviews on radical standard potentials appeared. Wardman's review emphasized organic radicals [1], while Stanbury's review considered inorganic radicals exclusively [2]. Both of those reviews are now rather dated. Another valuable compendium is Steenken's 1985 list of electron transfer equilibria involving radicals [3]. A related review emphasizing H-atom bond dissociation "free" (Gibbs) energies has also appeared [4]. The relevant primary literature has expanded greatly and numerous major corrections have been made. Moreover, with the benefit of these prior reviews, we are now in an improved position to appreciate the interconnected complexity of the various measurements. The work of the current IUPAC Task Group differs from those two prior reviews in that it doesn't attempt to make recommendations on all known radical electrode potentials but rather it focuses on a subset that has been judged to be of greater importance, and it makes a greater effort to apply the principles of error propagation in assessing the various potentials. This document presents the results of the IUPAC Task Group as they bear on inorganic radicals. Of necessity, some careful consideration of organic radicals is also included, because in some cases the inorganic radical potentials are derived from measurements of equilibrium constants for reactions with organic radicals. Some of the standard potentials discussed here were presented at the "Medicinal Redox Inorganic Chemistry" conference held at the University of Erlangen-Nürnberg in 2013 [5].

2. Definitions and Conventions

We limit the scope to those species, radical or otherwise, having sufficient lifetime to be vibrationally equilibrated with the solvent; this restriction allows the full forces of classical thermodynamics to be employed. We consider radicals to be species either neutral or ionic that bear an unpaired electron, and we exclude transition-metal complexes as a matter of convenience.

Use of the radical "dot" in chemical formulas to indicate radical species is redundant when the exact elemental composition and electronic charge of the species is specified, as is usually the case with the species in the current review. On the other hand, its use can be helpful for those who are not intimately familiar with the chemistry involved. In the present document, an effort has been made to use the dots consistently in the summary Tables, but in the supporting data sheets its use is less consistent. Both practices are in agreement with the current guidelines for inorganic nomenclature [6, 7].

By the term "standard electrode potential", $E°$, we refer to half reactions of the following type:

$$\mathrm{Ox} + n\mathrm{e}^- \rightleftharpoons \mathrm{Red} \qquad (1)$$

where n is an integer often 1, either Ox or Red can be a radical, and $E°$ is taken relative to the normal hydrogen electrode (NHE). On occasion we use here the shorthand expression "standard potential" to refer to standard electrode potentials. By convention, these reactions are always written as reductions – the associated potentials were previously known as "standard reduction potentials" – and they can be more complex than the simple example given above. Standard electrode potentials, rigorously speaking, refer to electrode potentials specified under conditions where all species are at unit activity. The standard state for such activities in the present review is usually the ideal 1 M aqueous solution. Species in solution that can also exist as gases, such as O_2, can be referred to the 1 M aqueous standard state or to the 100 kPa (~1 atm) pressure standard state, and in such cases we have taken care to designate the state explicitly. For water the standard state is the pure solvent (at unit activity, not 55.5 M). Standard electrode potentials are related to equilibrium constants (K_{eq}) through the relationship

$$E° = -(RT/nF)\ln K_{\mathrm{eq}} \qquad (2)$$

where $K_{\mathrm{eq}} = \Pi a_{\mathrm{prod}}{}^{\mathrm{x}}/\Pi a_{\mathrm{react}}{}^{\mathrm{y}}$, *i.e.*, the product of the equilibrium activities of the products (a_{prod}) divided by the product of the equilibrium activities of the reactants (a_{react}), all raised to the power of their appropriate stoichiometric coefficients x and y. In practice, when one is dealing with radicals, it is usually easier to determine equilibrium constants than it is to measure equilibrium electrode potentials directly.

It is often necessary to report formal potentials, $E^{\circ\prime}$, rather than standard potentials because of a lack of reliable means to estimate the activity coefficients (γ). This is typically the case when the reaction involves ionic species and the measurement is performed at high ionic strength. Formal potentials are defined in the IUPAC Green Book as in eq 3 [8]:

$$E_{\mathrm{eq}} = E^{\circ\prime} - (RT/nF)\Sigma \nu_{\mathrm{i}}\ln(c_{\mathrm{i}}/c^{\circ}) \qquad (3)$$

Here, c_{i} represents the concentration of species i, c° is a normalizing standard concentration (usually 1 M), and ν_{i} is that species stoichiometric coefficient. This definition is analogous to the Nernst equation except that it is expressed in terms of concentrations, and it allows for various species concepts. For example, in the case of S(IV) the species might be SO_3^{2-}, HSO_3^{-}, SO_2, or the sum of all. This definition also allows for $E^{\circ\prime}$ values to be defined at specific nonstandard pH values. To avoid ambiguity in the species definitions, in the present work we generally write out the relevant half-cell reaction, and for reactions involving the proton we normally refer to pH 0. Formal potentials for the species’ under consideration here can often be related to standard potentials through the activity coefficients:

$$E^{\circ} = E^{\circ\prime} + RT/nF\ln(\Pi\gamma_{\mathrm{prod}}{}^{\mathrm{x}}/\Pi\gamma_{\mathrm{react}}{}^{\mathrm{y}}) \qquad (4)$$

Likewise, it is often useful or necessary to report formal equilibrium quotients (K_{f}) rather than equilibrium constants. These are related through the expression

$$K_{\mathrm{eq}} = K_{\mathrm{f}}(\Pi\gamma_{\mathrm{prod}}{}^{\mathrm{x}}/\Pi\gamma_{\mathrm{react}}{}^{\mathrm{y}}) \qquad (5)$$

Even further removed from the thermodynamic ideal are “midpoint” potentials, E_{m}. These are E_{eq} values obtained when the oxidized and reduced species are at equal concentration. They are typically reported when the reaction is likely to be pH dependent and data are available at only a specific pH (often pH 7, E_7). Note that midpoint potentials will be strongly concentration dependent when the stoichiometric coefficients, ν_{i}, are not equal. In principle, midpoint potentials can be derived from standard potentials, but the derivation requires knowledge of the pK_{a} values involved. For a detailed discussion of these points the reader is referred to the introductory material in Wardman’s review on the potentials of radicals [1]. Related to midpoint potentials are apparent potentials, E°_{ap}. Apparent potentials are defined at a specific pH, like midpoint potentials, but the activities of the oxidized and reduced species in the

Nernst equation do not take the state of protonation into account. Thus, apparent potentials do not necessarily imply any knowledge of the pK_a's involved.

3. Methods for Determination of Standard Potentials

A wide variety of methods have been employed to determine standard potentials involving inorganic radicals, as has been reviewed elsewhere [9]. A brief summary is given here.

a) Electrochemical Methods.

a, i) Potentiostatic methods have been used only in a few special cases, such as in the chemistry of $ClO_2^{\bullet}$. The reason for this limitation is that inorganic radicals are usually highly reactive, so it is impossible to establish conditions where the concentrations are stable on the time frame of the measurements.

a, ii) Cyclic voltammetry (CV) shortens the time frame of the electrochemical methods, and it has been used successfully in a few cases. However, the lifetimes of most inorganic radicals are too brief even for CV.

a, iii) Pulse radiolysis provides an entry into very short time frames, and attempts have been made to apply electrochemical measurements to species generated by pulse radiolysis. Unfortunately, these efforts have not as yet provided reliable measurements or estimates of standard potentials involving inorganic radicals.

a, iv) An intriguing technique is to generate photoelectrons in solution by laser irradiation of an electrode and then to use the electrode to probe the electrochemistry of the radicals generated from the photoelectrons. The method, however, remains to be developed as a reliable source of thermodynamic data.

b) Equilibrium Constant Measurements. The vast majority of standard electrode potentials summarized in this review have been obtained by Hess' law methods where an equilibrium constant is measured somehow and combined with other thermodynamicchemical data to derive the reported potential. These derivations frequently make use of published values of $\Delta_f G°$, and this review normally makes the assumption that the values published in the NBS tables [10] are of reference quality. The various types of radical equilibrium constants used in these derivations are described below.

b, i) Solubilities. The solubilities of $ClO_2^{\bullet}$ and $NO^{\bullet}$ have been measured unambiguously because solutions of these radicals are stable. These solubility measurements then afford a method to determine the solution-phase standard potentials from the known gas-phase energetics of these species. The solubility of $NO_2^{\bullet}$ has also been measured, but in this case the method is complex and relies on an understanding of the kinetics of dissolution and of disproportionation of $NO_2^{\bullet}$(*aq*).

b, ii) Homolysis Equilibria. Homolysis at sigma bonds generally yields radicals, and determination of these equilibrium constants can lead rather directly to electrode potentials. In the case of $S_2O_4^{2-}$ it has been possible to measure the homolysis equilibrium constant by direct ESR detection of the $SO_2^{\bullet-}$ radicals. Homolysis equilibrium constants have been measured for unstable species such as N_2O_4 by use of transient methods such as flash photolysis and pulse radiolysis to establish the equilibria. A third method is to derive the equilibrium constant from the ratio of the forward and reverse rate constants ($K_{eq} = k_f/k_r$); an example of this method is provided by $S_2O_8^{2-}$, where k_f is determined from the kinetics of its oxidation of various substrates and k_r is obtained from transient measurements on the recombination of $SO_4^{\bullet-}$.

b, iii) Electron-Transfer Equilibria. Equilibrium constants for electron-transfer reactions are probably the most widely used data for deriving standard potentials involving radicals. A typical example is the reaction of O_3 with ClO_2^-:

$$O_3 + ClO_2^- \rightleftharpoons O_3^{\bullet-} + ClO_2^\bullet \qquad (6)$$

In this case the equilibrium constant was determined from the ratio of k_f and k_r, and it was used to determine the standard one-electron electrode potential of O_3 relative the well-established reference potential of $ClO_2^\bullet$. Equilibrium constants have also been measured for a substantial number of electron transfer reactions where neither of the component half reactions can be considered as having a reliable reference potential; nevertheless, such reactions are valuable in determining standard potentials, although the thermodynamicchemical derivations are necessarily more lengthy.

b, iv) Acid/Base Equilibria. Proton-transfer reactions can be crucial in understanding the reactivity of radicals, as is exemplified by superoxide. $HO_2^\bullet$ has a pK_a of 4.8. It is thermodynamically unstable with respect to disproportionation. Disproportionation via the reaction of $HO_2^\bullet$ with itself or $O_2^{\bullet-}$ is very fast. However, direct disproportionation via reaction of $O_2^{\bullet-}$ with itself is undetectably slow, so alkaline solutions of $O_2^{\bullet-}$ are remarkably persistent. Determinations of pK_a's have been performed for a significant number of radicals, and they have been performed by a large suite of techniques. These pK_a's have been used in a large number of derivations of radical standard potentials, and, because of their intrinsic importance, they are summarized below in Table 3.

b, v) Hemicolligation Equilibria. Reactions in which radicals bind to non-radical species are defined as hemicolligations. They can occur between a radical and its reduced form that produce a symmetrical radical adduct or between a radical and some other non-radical to form a non-symmetrical adduct. Two prominent such reactions are

$$I^{\bullet} + I^{-} \rightleftharpoons I_2^{\bullet -} \quad (7)$$

and

$$HO^{\bullet} + Cl^{-} \rightleftharpoons ClOH^{\bullet -} \quad (8)$$

Reactions of this type can have a profound effect on the net reactivity of the radicals, and they are often unavoidable in reactive systems. Equilibrium constants have been measured for a good number of hemicolligation reactions, have been used extensively in deriving radical standard potentials, and are summarized in Table 4.

b, vi) Nucleophilic Displacement Equilibria. In these reactions a nucleophile displaces another nucleophile from a radical. A typical example is

$$I^{-} + (SCN)_2^{\bullet -} \rightleftharpoons ISCN^{\bullet -} + SCN^{-} \quad (9)$$

Although these reactions can be considered as equivalent to the sum of two hemicolligations, their equilibrium constants often can be more easily measured than those of the component hemicolligations. These displacement equilibria are important in the present review primarily for their use in deriving standard potentials through thermodynamicchemical cycles.

c) Methods Involving Estimates. For certain important radicals there is no complete experimental thermodynamicchemical cycle available, and portions of the cycle must be obtained by making reasonable estimates. An important example is the hydrogen atom: although equilibrium constants have been measured for reactions that convert the aqueous hydrogen atom into other species (notably the hydrated electron), none of these reactions connects to a suitable reference redox couple. The best current solution to the problem is to make an estimate of the solvation energy of the hydrogen atom and then combine this estimate with other reliable data to derive the $H^{+}/H^{\bullet}$ electrode potential. There is good reason to believe that the uncertainties introduced in this example are relatively small. In general the current report relies on such thermodynamicchemical estimates only when direct experimental data are unavailable.

d) Quantum Calculations. It is becoming increasingly common to use quantum calculations to obtain radical electrode potentials. The methods typically entail a relatively accurate calculation of the energetics of the gas-phase radical and another calculation of the radical solvation energy. It has recently been shown that these computational methods can fail disastrously [11], so the present review makes little use of them.

4. Criteria for Selection of Recommended Data

The recommended values in the Tables of this report are based on results published in the peer-reviewed scientific literature. The Task Group has reviewed these primary publications to confirm their plausibility, scientific soundness, and adherence to established chemical principles. When there are multiple independent reports on the same results, the individual reports have been compared to determine the degree of agreement among them, and to identify outliers and assess whether there is just cause for rejecting them. Individual reports may be rejected because the experimental method or conditions are insufficiently documented and the method has been shown to be unreliable. Non-rectifiable errors have been identified in the data handling, or the results are not internally consistent. In cases where there are multiple acceptable reports of a given result, the reviewers have assigned a subjective weighting to each report based on an assessment of the care taken in the experiments and the typical accuracy of the method. These filtered results are then averaged, optimized, and their uncertainties assigned as described below.

5. Uncertainties

In the present review, all recommended data (E° values, pK_a's, $\Delta_f G^\circ$ values) are presented with associated uncertainties in two significant digits, up to 19. These uncertainties are given as $\pm 1\sigma$, and they are intended to indicate the best estimate of the overall uncertainty as arising from all contributions. Typically the least of these contributions are the statistical fluctuations in the direct measurements of a given quantity. Much more important are systematic errors, many of which are difficult to anticipate. Many of the recommended data are derived by combining various thermodynamicchemical quantities, and hence propagation of error must be taken into account. The level of uncertainty in the NBS $\Delta_f G^\circ$ values is frequently underappreciated in the broader chemical community. For some results there are multiple independent reports for the same quantity, for example as with the pK_a of $HO^\bullet$; in such situations each individual report is examined for plausibility and technical excellence, outliers are rejected, then remaining reports are averaged, and a subjective assessment of the uncertainty is assigned. The specific rationale for these assignments is provided in the detailed data sheets appended. In the language of metrology, these uncertainty estimates are of Type A (from statistical treatment of repeated measurements) and Type B (estimates from experience), and ISO standards mandate that both types of uncertainties are equally valid and can be freely combined; these concepts are briefly reviewed elsewhere [12].

6. Use of Thermodynamic Networks

As is discussed above, a large number of radical equilibrium constants of various types have been measured and combined with the standard potentials of reference couples to derive standard potentials of radicals through Hess' law-type calculations. Some of these equilibria share common radical species and hence lead to thermodynamicchemical networks. These networks can be very useful for determining radical standard potentials. When the networks are linear or branched it is a simple process to combine adjacent equilibrium constants with appropriate reference potentials to derive potentials of interest; in such calculations appropriate attention must be paid to the cumulative effects of error propagation. Occasionally there are loops in the networks, which form closed thermodynamicchemical cycles. These closed thermodynamicchemical cycles afford excellent tests of the data, because the associated Gibbs energy changes must sum to zero. Failure to meet this criterion within reasonable uncertainty limits is a signal that at least some of the data are seriously flawed. When this criterion is met, suitable adjustments of the individual equilibrium constants (within their uncertainties) can be made to achieve exact closure. Assessment and use of these thermodynamicchemical networks can be performed manually, although consistent results are difficult to achieve when the networks are large. Larger networks can be solved in an automated and consistent way through use of appropriate computerized approaches such as ATcT, Active Thermodynamicchemical Tables [13]. In the present review, some of the recommended data are the result of manual assessment while others have been generated by use of ATcT. In its standard format, the ATcT software is optimized for evaluation of gas-phase enthalpies; for the present purposes the ATcT software has been adapted to work with Gibbs energies in solution. The method thus consists of defining the reaction network, converting relevant reference potentials and equilibrium constants to ΔG° values and associated uncertainties, and localizing the thermodynamicchemical network by incorporating auxiliary values of $\Delta_f G^\circ$ (usually from the NBS tables) as network termini; the ATcT output then consists of a set of optimized $\Delta_f G^\circ$ values and uncertainties for the radicals of interest, and these are then combined with reference values of $\Delta_f G^\circ$ to derive the E° values. This method has been applied to a subset of the data presented here, as described in Data Sheet 7.

7. Important Reference Couples

There are a few redox couples that have attained particular significance, either because of their centrality as reference couples for determining other standard potentials or because of their general importance in inorganic radical chemistry. Aspects of these redox couples are highlighted here.

The $ClO_2^\bullet/ClO_2^-$ couple ($ClO_2^\bullet + e^- \rightleftharpoons ClO_2^-$) is of great importance in this review because it has been used extensively in establishing equilibria with other radicals and because its standard potential is known with unusually high accuracy. These characteristics are largely a consequence of the remarkable stability of both $ClO_2^{\bullet}$ and ClO_2^- in aqueous solution and the facile inter-conversions between them. As a result, it is not difficult to obtain reversible electrochemistry with this couple, perform classical equilibrium potentiostatic measurements, and extrapolate them to conditions of thermodynamicchemical ideality. The outcome is a reliable and genuinely *standard* value for $E°$.

The hydroxyl radical is of general importance because it is one of the three radicals intrinsic to water ($HO^{\bullet}$, $H^{\bullet}$, and e^-_{aq}), it is the only one of the three to have its electrode potential determined without extra-thermodynamic assumptions or approximations, and occupies a central position in the largest of the thermodynamicchemical networks in this review. Its potential has been determined by two independent routes. The first of these has its origins in thallium chemistry and rests specifically on the redox potentials of the unstable species Tl^{2+}, which are determined relative to the well-established Fe^{3+}/Fe^{2+} reference potential. The second route depends on the pK_a of $HO^{\bullet}$, the hemicolligation of $O^{\bullet-}$ with O_2, the electron-transfer equilibrium of $O_3^{\bullet-}$ with $ClO_2^{\bullet}$, and the use of the $ClO_2^{\bullet}/ClO_2^-$ redox couple as a reliable reference. The excellent agreement between these two routes provides strong support for the recommended potential of this important species.

$Br_2^{\bullet-}$ is widely used as an oxidant, and equilibrium constants have been measured for at least 12 of its reactions. Its electrode potential is considered well established because of the good agreement between several independent derivations. Notable among these are a derivation based on the equilibrium constants for 1) its reaction with OH^- to form $BrOH^{\bullet-}$ and bromide and 2) the dissociation of $BrOH^{\bullet-}$ to form Br^- and $HO^{\bullet}$.

The trinitrogen(•) radical, $N_3^{\bullet}$, is important generally because it is often used as a mild nonspecific oxidant. It holds special importance in this review because of its frequent use in establishing redox equilibria that can be used to establish electrode potentials that involve radicals. The standard electrode potential of the $N_3^{\bullet}/N_3^-$ redox couple has been determined in several ways with good agreement. It has been measured electrochemically (under irreversible conditions), and it has been derived from equilibria with four other reference redox couples ($[IrCl_6]^{2-}/[IrCl_6]^{3-}$, $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$, $ClO_2^{\bullet}/ClO_2^-$, and $Br_2^{\bullet-}/2Br^-$). Note that use of $N_3^{\bullet}/N_3^-$ as a reference potential at very high azide concentrations requires consideration of the association between $N_3^{\bullet}$ and N_3^- (Data Sheet 86).

There are also some organic radicals that are important in providing reference potentials for the inorganic radicals recommended here. These include species such as the phenoxyl radical, TEMPO, the tryptophan radical cation, and the promethazine (phenothiazine) radical. Evaluations of their electrode potentials are provided in the supplementary data sheets.

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Table 1: Inorganic Standard Electrode Potentials

Half-reaction	Electrode Potential / V	Data Sheet #
Table 1.1: Electron, Hydrogen and Oxygen		
$e^- \rightleftharpoons e^{\bullet -}(aq)$	–2.88 ± 0.02	1.1
$H^+ + e^- \rightleftharpoons H^\bullet(aq)$	–2.31 ± 0.03	1.3
$O(^3P) + e^- \rightleftharpoons O^{\bullet -}$	+1.6 ± 0.1	2
$O(^3P) + H^+ + e^- \rightleftharpoons HO^\bullet$	+2.3 ± 0.1	2
$O_2(g) + e^- \rightleftharpoons O_2^{\bullet -}$	–0.35 ± 0.02	3
$O_2(aq) + e^- \rightleftharpoons O_2^{\bullet -}$	–0.18 ± 0.02	3
$^1\Delta_gO_2(g) + e^- \rightleftharpoons O_2^{\bullet -}$	+0.64 ± 0.01	4
$^1\Delta_gO_2(aq) + e^- \rightleftharpoons O_2^{\bullet -}$	+0.81 ± 0.01	4
$O_2(g) + e^- + H^+ \rightleftharpoons HO_2^\bullet$	–0.07 ± 0.02	3
$O_2(aq) + H^+ + e^- \rightleftharpoons HO_2^\bullet$	+0.10 ± 0.02	3
$HO_2^\bullet + e^- + H^+ \rightleftharpoons H_2O_2$	+1.46 ± 0.01	5
$H_2O_2 + e^- + H^+ \rightleftharpoons HO^\bullet + H_2O$	+0.80 ± 0.01	6
$HO^\bullet + e^- + H^+ \rightleftharpoons H_2O$	+2.730 ± 0.017	7
$OH^\bullet + e^- \rightleftharpoons OH^-$	+1.902 ± 0.017	7
$O_3(g) + e^- \rightleftharpoons O_3^{\bullet -}$	+0.91 ± 0.02	23
$O_3(aq) + e^- \rightleftharpoons O_3^{\bullet -}$	+1.03 ± 0.02	23
Table 1.2: Halogens		
Table 1.2a: Chlorine		
$Cl^\bullet\,(aq) + e^- \rightleftharpoons Cl^-(aq)$	+2.432 ± 0.018	7
$Cl_2^{\bullet -}(aq) + e^- \rightleftharpoons 2Cl^-(aq)$	+2.126 ± 0.017	7
$Cl_2(aq) + e^- \rightleftharpoons Cl_2^{\bullet -}(aq)$	+0.666 ± 0.017	7
$ClOH^{\bullet -}(aq) + e^- \rightleftharpoons Cl^- + OH^-(aq)$	+1.912 ± 0.018	7
$ClOH^{\bullet -}(aq) + e^- + H^+(aq) \rightleftharpoons Cl^-(aq) + H_2O(l)$	+2.740 ± 0.018	7
$HOCl(aq) + e^- \rightleftharpoons ClOH^{\bullet -}(aq)$	+0.25 ± 0.08	7
$ClO_2^\bullet(aq) + e^- \rightleftharpoons ClO_2^-$	+0.935 ± 0.003	24
$ClO_3^\bullet(aq) + e^- \rightleftharpoons ClO_3^-(aq)$	+2.38 ± 0.03	7
$ClO^\bullet(aq) + e^- \rightleftharpoons ClO^-(aq)$	+1.39 ± 0.03	25
Table 1.2b: Bromine		
$Br_2^{\bullet -}(aq) + e^- \rightleftharpoons 2Br^-(aq)$	+1.63 ± 0.02	26
$Br_2(aq) + e^- \rightleftharpoons Br_2^{\bullet -}(aq)$	+0.55 ± 0.02	26
$Br^\bullet(aq) + e^- \rightleftharpoons Br^-(aq)$	+1.96 ± 0.02	26
$BrO_2^\bullet(aq) + e^- \rightleftharpoons BrO_2^-(aq)$	+1.290 ± 0.005	40
Table 1.2c: Iodine		
$I_2^{\bullet -} + e^- \rightleftharpoons 2I^-$	+1.05 ± 0.02	45
$I^\bullet + e^- \rightleftharpoons I^-$	+1.35 ± 0.02	45

$I_2(aq) + e^- \rightleftharpoons I_2^{\bullet -}$	+0.19 ± 0.02	45
Table 1.3: Chalcogens		
$SO_4^{\bullet -}(aq) + e^- \rightleftharpoons SO_4^{2-}(aq)$	+2.437 ± 0.019	7
$S_2O_8^{2-}(aq) + e^- \rightleftharpoons SO_4^{\bullet -}(aq) + SO_4^{2-}(aq)$	+1.44 ± 0.08	7
$SO_3^{\bullet -}(aq) + e^- \rightleftharpoons SO_3^{2-}(aq)$	+0.73 ± 0.02	59
$SO_5^{\bullet -}(aq) + e^- \rightleftharpoons SO_5^{2-}$	+0.81 ± 0.01	66
$S_2O_3^{\bullet -}(aq) + e^- \rightleftharpoons S_2O_3^{2-}$	+1.35 ± 0.03	71
$S_4O_6^{\bullet 3-}(aq) + e^- \rightleftharpoons 2S_2O_3^{2-}$	+1.10 ± 0.01	71
$HS^{\bullet}(aq) + H^+ + e^- \rightleftharpoons H_2S(aq)$	+1.54 ± 0.03	77
$S^{\bullet -} + e^- + H^+ \rightleftharpoons HS^-$	+1.33 ± 0.03	77
$S^{\bullet -} + e^- + 2H^+ \rightleftharpoons H_2S(aq)$	+1.74 ± 0.03	77
$HS^{\bullet}(aq) + e^- \rightleftharpoons HS^-$	+1.13 ± 0.03	77
$HS_2^- + e^- \rightleftharpoons HS_2^{\bullet 2-}$	–1.13 ± 0.05	77
$SeO_3^{\bullet -} + e^- \rightleftharpoons SeO_3^{2-}$	+1.68 ± 0.03	78
$SeO_3^{\bullet -} + H^+ + e^- \rightleftharpoons HSeO_3^-$	+2.18 ± 0.03	78
$TeO_3^{\bullet -} + e^- \rightleftharpoons TeO_3^{2-}$	+1.74 ± 0.03	79
$TeO_3^{\bullet -} + H^+ + e^- \rightleftharpoons HTeO_3^-$	+2.31 ± 0.03	79
Table 1.4: Group 5		
$NO_3^{\bullet}(aq) + e^- \rightleftharpoons NO_3^-(aq)$	+2.466 ± 0.019	7
$N_3^{\bullet}(aq) + e^- \rightleftharpoons N_3^-(aq)$	+1.33 ± 0.01	80
$NO^{\bullet}(\mathrm{aq}) + H^+ + e^- \rightleftharpoons HNO(aq)$	–0.15 ± 0.02	22
$HNO(\mathrm{aq}) + H^+ + e^- \rightleftharpoons H_2NO^{\bullet}(\mathrm{aq})$	+0.52 ± 0.04	87
$H_2NO^{\bullet} + 2H^+ + e^- \rightleftharpoons NH_3OH^+$	+1.253 ± 0.010	87
$H_2NO^{\bullet} + H^+ + e^- \rightleftharpoons NH_2OH$	+0.900 ± 0.010	87
$NO_2^{\bullet}(aq) + e^- \rightleftharpoons NO_2^-$	+1.04 ± 0.02	88
$PO_3^{\bullet 2-} + H^+ + e^- \rightleftharpoons HPO_3^{2-}$	+1.54 ± 0.04	96
$H_2PO_4^{\bullet} + e^- \rightleftharpoons H_2PO_4^-$	+2.75 ± 0.01	97
Table 1.5: Group 4		
$CO_2(aq) + e^- \rightleftharpoons CO_2^{\bullet -}$	–1.90 ± 0.02	98
$CO_3^{\bullet -}(aq) + e^- \rightleftharpoons CO_3^{2-}$	+1.57 ± 0.03	99
$CO_2^{\bullet -} + H^+ + e^- \rightleftharpoons HCO_2^-$	+1.52 ± 0.03	100
$SCN^{\bullet} + e^- \rightleftharpoons SCN^-$	+1.61 ± 0.02	101
$(SCN)_2^{\bullet -} + e^- \rightleftharpoons 2SCN^-$	+1.30 ± 0.02	101
Table 1.6: Group 3		
$Tl^{2+} + e^- \rightleftharpoons Tl^+$	+2.225 ± 0.007	21
$Tl^{3+}(aq) + e^- \rightleftharpoons Tl^{2+}(aq)$	+0.34 ± 0.08	7
$TlOH^+(aq) + e^- + H^+(aq) \rightleftharpoons Tl^+(aq) + H_2O(l)$	+2.507 ± 0.013	7

$TlOH^{2+}(aq) + e^- \rightleftharpoons TlOH^+(aq)$	+0.12 ± 0.08	7
$TlOH^{2+}(aq) + e^- + H^+(aq) \rightleftharpoons Tl^{2+}(aq) + H_2O(l)$	+0.40 ± 0.08	7
Table 1.7: Zn, Cd, Hg		
$HgCl_2(aq) + e^- \rightleftharpoons HgCl(aq) + Cl^-$	–0.55 ± 0.02	102

Table 2. Gibbs Energies of Formation, $\Delta_f G°$

Radical	$\Delta_f G°$ / kJ mol^{-1}	Data Sheet #
e^{-}_{aq}	+278 ± 2	1.1
$O^{\bullet-}$	+93.1 ± 1.7	2
$OH^{\bullet}$	+26.3 ± 1.6	7
$O_2^{\bullet-}$	+33.8 ± 1.9	3
$HO_2^{\bullet}(aq)$	+7 ± 2	3
$O_3^{\bullet-}$	+75 ± 2	23
$H^{\bullet}(aq)$	+223 ± 2	1.1
$Cl^{\bullet}(aq)$	+103.4 ± 1.7	7
$Cl_2^{\bullet-}(aq)$	–57.3 ± 1.6	7
$ClOH^{\bullet-}(aq)$	–104.0 ± 1.7	7
$ClO^{\bullet}(aq)$	+97 ± 3	25
$ClO_2^{\bullet}(aq)$	+110 ± 10	24
$ClO_3^{\bullet}(aq)$	+221.6 ± 3	7
$Br_2^{\bullet-}$	–51 ± 2	26
$Br^{\bullet}$	+85 ± 2	26
$BrO_2^{\bullet}(aq)$	+152 ± 4	40
$BrOH^{\bullet-}$	–93 ± 2	26
$BrSCN^{\bullet-}$	+129 ± 3	26
$I_2^{\bullet-}$	–2.1 ± 1.9	45
$I^{\bullet}$	+78.8 ± 2	45
$IOH^{\bullet-}$	–82.7 ± 2	45
$S^{\bullet-}$	+140 ± 3	77
$HS^{\bullet}$	+121 ± 3	77
$HSS^{\bullet 2-}$	+129 ± 4	77
$SO_3^{\bullet-}$	–416 ± 2	59
$SO_4^{\bullet-}(aq)$	–509.4 ± 1.8	7
$SO_5^{\bullet-}(aq)$	–506 ± 3	66
$S_2O_3^{\bullet-}$	–392 ± 8	71
$S_4O_6^{\bullet 3-}$	–939 ± 8	71
$SeO_3^{\bullet-}$	–202 ± 3	78
$HSeO_4^{\bullet 2-}$	–358 ± 3	78
$TeO_3^{\bullet-}$	–214 ± 3	79
$HTeO_4^{\bullet 2-}$	–394 ± 3	79
$TeO_4^{\bullet 3-}$	–319 ± 3	79
$N_3^{\bullet}(aq)$	+476 ± 8	80
$NO^{\bullet}(aq)$	+102.0 ± 0.2	90
$H_2NO^{\bullet}(aq)$	+66 ± 3	87
$NO_2^{\bullet}(aq)$	+62.3 ± 0.5	88
$NO_3^{\bullet}(aq)$	+126.7 ± 1.8	7
$CO_2^{\bullet-}$	–205 ± 2	98

$CO_3^{\bullet-}$	−373 ± 3	99
$SCN^{\bullet}$	+248 ± 2	101
$(SCN)_2^{\bullet-}$	+310 ± 2	101
$ISCN^{\bullet-}$	+152 ± 2	45
Tl^{2+}	+182.3 ± 1.2	7
$TlOH^{+}$	–27.6 ± 1.3	7

Table 3. Inorganic radical pK_as and related hydrolysis

Reaction	K_a / M	pK_a	Data Sheet #
$H^{\bullet}(aq) \rightleftharpoons e^{-}(aq) + H^{+}$	$(2.48 \pm 0.24) \times 10^{-10}$		1.2
$OH^{\bullet}(aq) \rightleftharpoons O^{\bullet -} + H^{+}$		11.7 ± 0.1	116
$HO_2^{\bullet}(aq) \rightleftharpoons O_2^{\bullet -} + H^{+}$		4.8 ± 0.1	3
$HO_3^{\bullet}(aq) \rightleftharpoons O_3^{\bullet -} + H^{+}$	No recommendation		23
$Cl^{\bullet}(aq) + H_2O(l) \rightleftharpoons ClOH^{\bullet -} + H^{+}$	5×10^{-6}, within a factor of 2		7
$Br^{\bullet}(aq) + H_2O(l) \rightleftharpoons BrOH^{\bullet -} + H^{+}$		10.50 ± 0.07	26
$I^{\bullet}(aq) + H_2O(l) \rightleftharpoons IOH^{\bullet -} + H^{+}$		13.3 ± 0.5	45
$HS^{\bullet}(aq) \rightleftharpoons S^{\bullet -} + H^{+}$		3.4 ± 0.7	77
$HS_4O_6^{\bullet 2-} \rightleftharpoons S_4O_6^{\bullet 3-} + H^{+}$		6.2	71
$NH_2OH^{\bullet +} \rightleftharpoons NH_2O^{\bullet} + H^{+}$		< -5	105
$NH_2O^{\bullet} \rightleftharpoons NHO^{\bullet -} + H^{+}$		12.6 ± 0.3	105
$HPO_3^{\bullet -} \rightleftharpoons PO_3^{\bullet 2-} + H^{+}$		5.75 ± 0.05	106
$H_2PO_3^{\bullet} \rightleftharpoons HPO_3^{\bullet -} + H^{+}$	1.1		107
$H_3PO_3^{\bullet +} \rightleftharpoons H_2PO_3^{\bullet} + H^{+}$	54		107
$H_2PO_4^{\bullet} \rightleftharpoons HPO_4^{\bullet -} + H^{+}$		5.7 ± 0.4	108
$HPO_4^{\bullet -} \rightleftharpoons PO_4^{\bullet 2-} + H^{+}$		8.9 ± 0.2	108
$HPO_5^{\bullet -} \rightleftharpoons PO_5^{\bullet 2-} + H^{+}$		3.4 ± 0.2	109
$As(OH)_4^{\bullet} \rightleftharpoons As(OH)_3O^{\bullet -} + H^{+}$		7.38 ± 0.06	110
$As(OH)_4^{\bullet} \rightleftharpoons HAsO_3^{\bullet -} + H_2O + H^{+}$		3.85 ± 0.05	110
$HAsO_3^{\bullet -} \rightleftharpoons AsO_3^{\bullet 2-} + H^{+}$		7.81 ± 0.04	110
$HCO_2^{\bullet} \rightleftharpoons CO_2^{\bullet -} + H^{+}$		NR	100
$HCO_3^{\bullet} \rightleftharpoons CO_3^{\bullet -} + H^{+}$		< 0	99
$SCN^{\bullet} + H_2O \rightleftharpoons HOSCN^{\bullet -} + H^{+}$		12.5 ± 0.1	111
$Tl^{2+} + H_2O(l) \rightleftharpoons TlOH^{+} + H^{+}$	$(1.7 \pm 0.3) \times 10^{-5}$		7

Table 4: Hemicolligation Equilibria

Reaction	K / M^{-1}	Data Sheet #
$O_2(aq) + O^{\bullet-} \rightleftharpoons O_3^{\bullet-}$	$(1.4 \pm 0.1) \times 10^6$	23
$Cl^{\bullet}(aq) + Cl^- \rightleftharpoons Cl_2^{\bullet-}$	$(1.4 \pm 0.2) \times 10^5$	10
$OH^{\bullet}(aq) + Cl^- \rightleftharpoons ClOH^{\bullet-}$	0.70 ± 0.13	12
$Br^{\bullet}(aq) + Br^- \rightleftharpoons Br_2^{\bullet-}$	$(3.9 \pm 1.2) \times 10^5$	33
$OH^{\bullet}(aq) + Br^- \rightleftharpoons BrOH^{\bullet-}$	$(3.2) \times 10^2$ within factor of 2	34
$I^{\bullet}(aq) + I^- \rightleftharpoons I_2^{\bullet-}$	1.35×10^5	52
$S^{\bullet-} + SH^- \rightleftharpoons HSS^{\bullet 2-}$	$(9 \pm 2) \times 10^3$	117
$S_2O_3^{\bullet-} + S_2O_3^{2-} \rightleftharpoons S_4O_6^{\bullet 3-}$	Log $K = 4.1 \pm 0.5$	71
$N_3^{\bullet}(aq) + N_3^- \rightleftharpoons N_6^{\bullet-}$	0.24 ± 0.08	85
$HAsO_3^{\bullet-} + H_2O \rightleftharpoons As(OH)_3O^{\bullet-}$	p$K = 3.53 \pm 0.11$	110
$SCN^{\bullet}(aq) + SCN^- \rightleftharpoons (SCN)_2^{\bullet-}$	$(2.0 \pm 0.3) \times 10^5$	101
$S_2O_3^{\bullet-} + SCN^- \rightleftharpoons SCNS_2O_3^{\bullet 2-}$	1.2×10^3 within a factor of 2	75
$Tl(aq) + Tl^+ \rightleftharpoons Tl_2^+$	140 ± 7	112
$Tl^+ + OH^{\bullet}(aq) \rightleftharpoons TlOH^+$	$(5.8 \pm 1.0) \times 10^3$	19
$Tl^{2+} + Cl^- \rightleftharpoons TlCl^+$	$(6.2 \pm 0.7) \times 10^4$	113
$TlCl^+ + Cl^- \rightleftharpoons TlCl_2$	$(1.9 \pm 0.4) \times 10^3$	114
$TlCl_2 + Cl^- \rightleftharpoons TlCl_3^-$	13 ± 3	115

Data Sheet 1

1.1 Reaction of e^-_{aq} with H_2O and NH_4^+

Chemical equilibrium: $e^-_{aq} + H_2O \rightleftharpoons H^\bullet + OH^-$ (1.1.1)

The equilibrium constant for this reaction can be obtained either through the direct study of the reaction, or indirectly through the study of a reaction of the electron with a protonated species, coupled with the protonation constant for that species.

List of reports:

Forward reaction

Fielden & Hart, 1967 [1].

Solution contains 0.7 mM H_2

$k_f = 890\ s^{-1}$ $E_a = 28 \pm 3$ kJ mol^{-1} (6.7 ± 0.7 kcal mol^{-1})

Swallow, 1968 [2].

$k_f = (1.2 \pm 0.3) \times 10^3\ s^{-1}$ (room temperature)

Pulse radiolysis of a solution containing $Ba(HO)_2$ and formate, at pH ~ 11. Hydrated electron decay monitored by absorption spectrophotometry. Rate constant determined by extrapolation to zero $[HCO_2^-]$, not corrected for the reaction of e^-_{aq} with H_2O_2.

Schwarz, 1992 [3].

Pulse radiolysis of H_2-saturated water and in deaerated formate solutions, following the optical absorption of the hydrated electron.

1. Results extrapolated to $[e^-_{aq}] = 0$ to remove second-order effects. Conditions: H_2-saturated, borate-buffered water, pH 8.27:

k_f= 1050 s^{-1} E_a = 30.7 kJ mol^{-1} (7.33 kcal mol^{-1})

Values in any solution were reproducible to ±5%; between solutions: ±10%.

2. Results extrapolated to [e^-_{aq}] = 0, to remove second-order effects. Conditions: de-aerated, borate-buffered formate solution, pH 9.16. Corrected for the reaction of e^-_{aq} with $C_2O_4^{2-}$, H_2O_2 and H^+, and for the reaction of $H^\bullet$ with HO^- and with HCO_2^-.

k_f= 1040 s^{-1} E_a = 31.7 kJ mol^{-1} (7.57 kcal mol^{-1})

The calculation of the rate constant involves an explicit correction for the reaction of e^-_{aq} with H_2O_2. These studies were more reproducible than those above, but no specific error limit was proposed.

Reverse reaction

Matheson & Rabani, 1965 [4].

k_r = (1.8 ± 0.6) x 10^7 M^{-1} s^{-1}

Pulse radiolysis and optical absorption on solutions in the pH range 7-14 with up to 10.1 MPa (100 atm) H_2

Hickel and Sehested, 1985 [5].

Formation of absorbance from e^-_{aq} in H_2-saturated solutions from 9.01 MPa to 10.1 MPa (90 – 100 atm); pH 11.7 and 12. t = (15 – 60) °C.

Activation parameters: $\Delta H^\ddagger$ = 23.8 ± 2.5 kJ mol^{-1} (5.7 ± 0.6 kcal mol^{-1}) and $\Delta S^\ddagger$ = −25 ± 8 kJ K^{-1} mol^{-1} (−6 ± 2 cal K^{-1} mol^{-1}) reported.

From these, $\Delta G^\ddagger$ = 31.4 kJ mol^{-1} (7.5 kcal mol^{-1}) and k_r = 2.0 × 10^7 M^{-1} s^{-1} at 298 K. But, Figure 4 [5] suggests that k_f = 2.9 × 10^7 M^{-1} s^{-1}. Total error estimate: < 20%

Buxton *et al.*, 1988 [6].

$k_r = 2.2 \times 10^7$ M^{-1} s^{-1} (selected value in compilation)

Han and Bartels, 1992 [7].

Pulse radiolysis of aqueous solutions containing 0.1 mol L^{-1} *t*-BuOH (EPR experiments) or 0.01 mol L^{-1} Na_2SO_3 (optical experiments).

Both optical and EPR free induction decay (FID) were utilized to follow e^-_{aq} decay after pulse radiolysis. Optical weighted at half of FID results. Na_2SO_3 added to remove O_2 and H_2O_2. T = (280 – 370) K. These values supplant earlier ones from the same laboratory.

$k_r = (2.51 \pm 0.44) \times 10^7$ M^{-1} s^{-1}
$A = (1.33 \pm 0.16) \times 10^{14}$ M^{-1} s^{-1}; $E_a = 38.38 \pm 0.31$ kJ mol^{-1}

Marin, *et al.* 2005 [8].

Optical spectrophotometry used to follow e^-_{aq} decay after pulse radiolysis of hydrogenated solutions at 25.0 MPa over the temperature range (100 to 300) ºC. At 100 ºC, the results were in good agreement with the earlier study from the same laboratory [5]. At the higher temperatures, the activation energy decreased to 25.4 ± 0.8 kJ mol^{-1}.

Renault, *et al.* 2008 [9].

A Density Functional, first-principles based molecular dynamics study of the fundamental mechanism of the reaction. The relatively low rate constant for the reaction is explained by the complexity of the mechanism, which involves proton transfers in the coordination sphere to the hydroxide ion and by diffusion of the hydrogen atom within its cavity. No quantitative results are given.

***Chemical equilibrium*:** $e^{-}_{aq} + NH_4^+ \rightleftharpoons H^\bullet + NH_3$ (1.1.2)

List of reports:

Schwarz, 1991 [10].

From measurements of the initial absorbance and the absorbance at equilibrium:

$K_{1.1.2} = 2.23$ corrected to zero ionic strength, thus $\Delta_r G^o = -1.99$ kJ mol^{-1}

$t = (4 – 87)$ °C

$\Delta H^o = -8.4 \pm 0.8$ kJ mol^{-1}; $\Delta S^o = -21 \pm 2$ J K^{-1} mol^{-1} and $\Delta C_p{}^o = 159 \pm 42$ J K^{-1} mol^{-1} where the reported error limits include the standard deviations from the fit and possible systematic errors in the correction required to derive the fraction of electrons in the $H^\bullet + e^{-}_{aq}$ pool. These uncertainties indicate a range of $\Delta_r G^o$ from (–0.7 to –3.5) kJ mol^{-1} and thus a range in $K_{1.1.2}$ at 298 K of 4.2 to 1.3.

$k_f = 1.5 \times 10^6$ M^{-1} s^{-1} (measured)

$k_r = 6.7 \times 10^5$ M^{-1} s^{-1} (calculated from K_{eq})

Chen *et al.*, 1994 [11].

From a study of the solvent effect on the reactivity of the solvated electron, rate constants were measured over the range (280 – 370) K.

$k_f = 1.5 \times 10^6$ M^{-1}s^{-1} $E_a = 20$ kJ mol^{-1} at 298 K

Shiraishi *et al.*, 1994 [12].

Pulse radiolysis of solutions containing ~0.1 mol L^{-1} NH_4^+.

$K_{1.1.2} = 2.12$ at 298K (from plot), so: $\Delta_r G^o = -1.86$ kJ mol^{-1}
$\Delta_r G^o = -0.47 \pm 0.04$ kcal mol^{-1} = -1.97 ± 0.17 kJ mol^{-1} reported in the paper, however.

A complex analysis due, in part, to an impurity problem, results in a complicated equation that was “examined by a curve-fitting method”. $t = (25 – 250)$ °C

Discussion

The results of Han and Bartels [7] for the reverse reaction (−1.1.1) and of Schwarz [3] for the forward reaction (1.1.1) are in very good agreement with the earlier published values. In both cases, however, they represent significant improvements to reduce uncertainties and ensure accurate values. Thus, these are the preferred values for these rate constants.

From the forward and reverse rate constants at 298 K, we obtain the equilibrium constant for the reaction:

$$e^{-}_{aq} + H_2O \rightleftharpoons H^{\bullet} + OH^{-} \qquad (1.1.1)$$

Thus, $K_{1.1.1} = k_f/k_r = 1040\ s^{-1}/2.51 \times 10^{7}\ L\ mol^{-1}\ s^{-1} = (4.1 \pm 0.8) \times 10^{-5}\ mol\ L^{-1}$. The estimated uncertainty, 20%, is based on the combined estimated uncertainties of 10% for k_f and 17.5% for k_r.

For the indirect determination of this value, the equilibrium constant reported by Schwarz [10] is preferred, $K_{1.1.2} = 2.23$ corrected to zero ionic strength. It is substantiated by the somewhat less certain study of Shiraishi, *et al.* [12] and by the kinetic result of Chen, *et al.* [11] on the forward rate constant. An examination of the results and the good agreement with the other measured value, suggest an uncertainty range of no more than ± 0.5. for reaction 1.1.2

$$K_{1.1.2} = 2.2 \pm 0.5 \qquad (1.1.2)$$

Combination with the ionization constant for aqueous ammonia:

$$NH_3 + H_2O \rightleftharpoons NH_4^{+} + OH^{-} \quad K_i = (1.77 \pm 0.03) \times 10^{-5} \text{ at 298 K [13]}$$

leads to the equilibrium constant for reaction (1.1.1)

$$K_{1.1.1} = K_i \times K_{1.1.2} = (3.95 \pm 0.53) \times 10^{-5}\ mol\ L^{-1}$$

The values derived for $K_{1.1.1}$ are quite close. Thus, we simply average to get $K_{1.1.1} = (4.0 \pm 0.5) \times 10^{-5}$ mol L^{-1} as the recommended value and $\Delta_r G(1.1.1) = +(25.1 \pm 0.3)$ kJ mol^{-1}.

The value for the Gibbs energy change associated with this reaction can be converted to the standard potential of the electron by making use of the solubility of the hydrogen atom:

$e^-_{aq} + H_2O \rightleftharpoons H^\bullet(aq) + OH^-$ $\Delta_r G(1.1.1) = +25.1 \pm 0.3$ kJ mol^{-1}

$H^\bullet(aq) \rightleftharpoons H^\bullet(g)$ $\Delta_{solv} G^o = -19.99 \pm 2.22$ kJ mol^{-1} (see Data Sheet 1.3)

$H^\bullet(g) \rightleftharpoons \frac{1}{2} H_2(g)$ $\Delta_r G^o = -203.278$ kJ mol^{-1} [14]

$H^+ + OH^- \rightleftharpoons H_2O$ $\Delta_r G^o = -79.89$ kJ mol^{-1} (from $K_i = 1.008 \times 10^{-14}$)

$e^-_{aq} + H^+ \rightleftharpoons \frac{1}{2} H_2(g)$ $\Delta_r G^o = -278.1 \pm 2.2$ kJ mol^{-1} $E^o = -(2.88 \pm 0.02)$ V

Correspondingly,
$\Delta_f G^\circ = 278 \pm 3$ kJ mol^{-1} for e^-_{aq}.
$\Delta_f G^\circ = 223 \pm 3$ kJ mol^{-1} for $H^\bullet(aq)$.

1.2 pK_a of $H^\bullet$

Chemical equilibrium: $H^\bullet \rightleftharpoons e^-_{aq} + H^+$ (1.2)

List of reports:

Forward reaction

Alcorn *et al.* 2014 [15].

Reaction of muonium with water studied from 200 °C to 425 °C as a surrogate for the hydrogen atom. DFT calculations augmented with single-point MP4 energy calculations, were used to model the reaction, particularly the abstraction channel, $H^\bullet + H_2O \rightleftharpoons H_2 + {}^\bullet OH$. These were combined with higher-level calculations on $H_3O^{\bullet}\cdot(H_2O)_n$ clusters. These clusters were found to be charge-separated species, corresponding to the products of reaction (1.2), separated by some number of water molecules. Reaction 1.2, then, can be considered the reaction of $H^{\bullet}$ with an exterior water molecule to form $H_3O^{\bullet}$, which can either rapidly dissociate back to a hydrogen atom and a water molecule, or ionize to an electron and a hydronium ion. (The work of Sobolweski ea al.2002a,b [16a,b] is cited, but see also Uhlig *et al.* 2011 [17] and Chulkov *et al.* 2009 [18].)

From this analysis, Alcorn *et al.* concluded that the abstraction reaction only became significant at 190 °C, where it made up 10% of the reaction. Below that, the reaction leading to the solvated proton and electron becomes more and more dominant.

Reverse reaction

Buxton *et al.*, 1988 [6].

Review of the literature.

$k_r = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}$ (selected value)

Elliot *et al.*, 1990 [19].

Pulse radiolysis measurement of the decay of the absorption due to the hydrated electron in the presence of perchloric acid. The activation energy is about the same as that for diffusion, but the observed rate constant is about five times lower. $T = 20 – 200$ °C.

$k_r = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}$
$E_a = 14.5\ kJ\ mol^{-1}$

Chen *et al.*, 1994 [11].

Pulse radiolysis measurement of the decay of the absorption due to the hydrated electron in the presence of 1 – 7 × 10^{-5} mol L^{-1} perchloric acid. Measurements were made in isobutanol/water solutions that containined 0 – 100% water.

k_r = 2.4 × 10^{10} L mol^{-1} s^{-1}
E_a = 12 kJ mol^{-1}

Wu *et al.*, 2002 [20].

Contains a graphical presentation over the temperature range 25° – 400°C of k_r, the reaction of e^-_{aq} with H^+; the results are in good agreement with those of Shiraishi *et al.* [11]. Relative to e^-_{aq} + benzophenone.

k_r = 2.3 × 10^{10} L mol^{-1} s^{-1}

Shiraishi *et al.*, 1994 [12].

Value taken from graph. E_a = 11 kJ/mol at 298 – 373 K (linear part of curved plot, Fig. 8). The forward rate constant, k_f, is too small to be measured at 25 °C, according to Shiraishi *et al.* These authors give only K derived from the equilibrium $e^-_{aq} + NH_4^+ \rightleftharpoons H^\bullet + NH_3$ below 392 K:

$pK_a = 9.59 \pm 0.03$ at 298 K, thus $K_{1.2} = (2.6 \pm 0.2) \times 10^{-10}$ mol kg^{-1}.

Stevenson *et al.*, 1991 [21].
Hovath *et al.*, 1992 [22].

k_r = 1.3 to 0.6 × 10^{10} L mol^{-1} s^{-1} for μ = 0.5 to 5 mol L^{-1}

These data were obtained from a flash photolysis study; there is good agreement with other works when corrected for ionic strength.

Marsalek et al, 2010 [23]; Uhlig *et al.* 2011 [17]; Uhlig & Jungwirth 2013 [24].

The reverse reaction was subjected to an ab initio – molecular dynamics study in a cluster of 32 water molecules. The results indicate that the reacion involves proton transfer, not electron transfer. The fact that the reaction is significantly slower than diffusion controlled is ascribed to the energy required for desolvation of the two charge species. No evidence for the intermediate formation of $H_3O^\bullet$ was found. It was also determined that when starting the calculation with $H_3O^\bullet$, solvent-separated ions were formed with as few as three water molecules.

Discussion

Equilibrium 1.2 has only been observed above 100 °C [11]. Values at room temperature can be obtained from Reaction 1.1.1:

$$e^-_{aq} + H_2O \rightleftharpoons H^\bullet + OH^- \qquad (1.1.1)$$

by $K_{1.2} = K_w/K_{1.1.1}$, with $K_w = 10^{-14}$ M^2.

With $K_{1.1.1} = (4.04 \pm 0.5) \times 10^{-5}$ mol L^{-1}, this leads to $K_{1.2} = (2.48 \pm 0.24) \times 10^{-10}$ mol L^{-1} and $\Delta_r G^o = 54.8 \pm 0.3$ kJ mol^{-1}.

1.3 Gibbs energy of solvation of $H^\bullet$

List of reports:

Chemical equilibrium: $H^\bullet(g) \rightleftharpoons H^\bullet(aq)$ (1.3.1)

There are no actual experimental determinations of the Henry's Law constant for the hydrogen atom, which would lead to the Gibbs energy of the hydrogen atom in water. This quantity has been estimated by comparison with the solubility of other gases – primarily He, due to the similarity in size, and H_2. Parker [25a,b] has expanded upon the first approach by pointing out that the Δ_{solv} values for the rare gases are correlated with their Van der Waals radii. On the other hand, Rodun*G*er and Bartels [26a,b] have argued that H_2 is a much better surrogate for $H^\bullet$ due to their similar polarizability values.

Rare gas solubility

The first question that arises is what set of Van der Waals radii to use for the rare gases and for the hydrogen atom. Zefirov [27] has argued that a consistent set of radii must be taken from a single experimental approach, for example crystallography, and not mixed with other approaches, like equilibrium and gas-kinetic. Crystallographic values for the rare gases have been reviewed recently [28], leading to a set showing a very good linear trend of radii with atomic number (a quadratic fit is even better). This same general trend is shown in other data sets, but the correlation in this set is much better.

For the hydrogen atom, the radii from 15 data sets in the literature were averaged to yield a value of (114 ± 6) pm in this recent review [28]. Other, non-crystallographic values not included are (100 ± 10) pm from an extrapolation to zero dipole moment in hydrogen halides [29] and 92 pm from an analysis of the hyperfine coupling by EPR spectroscopy [30].

Taking the rare gas radii from Hu, *et al.* [28] and solubility Gibbs energies from the IUPAC Solubility Data Series [31-34], along with a radius value of 114 pm for $H^\bullet$, we derive $\Delta_{\mathrm{solv}}G$ = (22.18 ± 0.84) kJ mol^{-1} for standard states of one bar and one mol L^{-1}, where the error limit is the standard error in the intercept, taking 114 pm as the origin. With $H^\bullet$ radii of 120 pm and 108 pm, we obtain (21.57 and 22.80) kJ mol^{-1}, respectively. For comparison, if we use a recent analysis of Van der Waals radii based on gas-phase structural data, [35] we obtain $\Delta_{\mathrm{solv}}G = 21.99$ kJ mol^{-1}.

H_2 solubility

If we assume the solubility of H_2 as a surrogate for that of $H^\bullet$ due to the similar polarizability values, the calculation is straightforward. Taking the solubility from the IUPAC Solubility Data Series, [36] we obtain $\Delta_{\mathrm{solv}}G$ = (17.74 ± 0.09) kJ mol^{-1}, for standard states of one bar and one mol L^{-1}. The error limit is from the reported standard deviation of the solubility fit.

Difference in rate constants

There is an alternate, somewhat more complicated, method for estimating the solubility of $H^\bullet$(g) and thus the Gibbs energy of $H^\bullet$(aq) introduced by Roduner and Bartels [26a,b]. This approach compares the rate constant for a reaction in the gas phase with its rate constant in solution. The reaction must have the same mechanism in both phases; an electron transfer reaction would be ruled out, for example, as the reaction would not take place that way in the gas phase. Also the rate constant should not be too close to the diffusion rate constant in either phase. The approach makes use of the well-known thermodynamic formulation of transition-state theory, which gives for the rate constant for a bimolecular reaction

$$k = \mathrm{Q} \bullet T \bullet \exp(-\Delta G^{\#}/\mathrm{R}T)$$

where Q is the ratio of the Boltzman constant to Planck's constant and $\Delta G^{\#}$ is the Gibbs energy of activation, that is the Gibbs energy change in going from the reactants to the transition state. The ratio of the rate constant in the aqueous phase, k(aq), and that in that in the gas phase, k(g), is then simply

$$k(\mathrm{aq})/k(\mathrm{g}) = \exp([-\Delta_{\mathrm{solv}}G(\mathrm{TS}) + \Delta_{\mathrm{solv}}G(\mathrm{C_6H_6}) + \Delta_{\mathrm{solv}}G(\mathrm{H^{\bullet}})]/\mathrm{R}T)$$

The reaction of the hydrogen atom with benzene appears to be ideally suited for this purpose. In both phases, it has been studied by several groups with reasonable agreement. Taking the solution results of Roduner and Bartels [26a] and the gas results of Nicovich and Ravishankara [37], we obtain an enhancement of a factor of 40.

Solving the equation for the Gibbs energy of solvation of the hydrogen atom requires knowledge of $\Delta_{\mathrm{solv}}G$ for both benzene and the transition state. A recent determination of the Henry's Law constant for benzene, $K_{\mathrm{H}} = \mathrm{C_{aq}/C_g} = 4.44$, [38] is in good agreement with most previous measurements. This leads to $\Delta_{\mathrm{solv}}G(\mathrm{C_6H_6}) = -3.79$ kJ mol^{-1}. (We use dimensionless units for K_{H} since the units used for the rate constants are the same in both phases and thus cancel.) The addition of a hydrogen atom to benzene would be expected to reduce the solubility. For example, for cyclohexene, $K_{\mathrm{H}} = 0.57$ [38]. A cyclohexadiene would probably be a good surrogate for the transition state of the reaction. Unfortunately, there are no reported Henry's Law constants for these, but the value for 1,4-cyclohexadiene (cyclohexa-1,4-diene) can be estimated from its water solubility ((0.0117 mol L^{-1} [39]) and vapor pressure (0.089 atm [40]) to be 3.20. Thus, we estimate $\Delta_{\mathrm{solv}}G(1,4\text{-C}) = \Delta_{\mathrm{solv}}G(\mathrm{TS}) = -2.88$ kJ mol^{-1}. With the above equation, the Gibbs energy of $\mathrm{H^{\bullet}}$(aq) is calculated to be $\Delta_{\mathrm{solv}}G(\mathrm{H^{\bullet}}) = 10.06$ kJ mol^{-1}, if the standard states are the same in both phases. Converting to the normal standard-state convention, one bar and one M^{-1}, this becomes $\Delta_{\mathrm{solv}}G(\mathrm{H^{\bullet}}) = 17.99$ kJ mol^{-1}.

The uncertainty in the Gibbs energy value will arise from both the uncertainty in the enrichment factor and the uncertainty in the Gibbs energy of the transition state. An uncertainty factor of ±1.7 kJ mol^{-1} would represent a doubling or halving the enhancement factor. This uncertainty range is chosen because values for the gas phase rate constant for the reaction of the hydrogen atom with benzene range from half to twice the value used here [41] and some question has been raised about the possibility that the reaction is not at the high-pressure limit [42]. A more recent laser photolysis study, however, supports the rate constant chosen here [43]. The value is solution also is uncertain, having been reported as 50% lower than the value used here [44]. An enhancement factor in this range is supported by studies on other reactions. From data taken from databases [41,44], we find ratios of 43 (benzonitrile), 22 (naphthalene), 36 (toluene), 15 (chlorobenzene), 28 (nitrobenzene), 9.5 (aniline), and 27 (methoxybenzene). (None of these molecules have been studied as thoroughly as benzene in either phase.) The uncertainty in the Gibbs energy of the transition state is at least 1 kJ mol^{-1}, the difference between the values for benzene and cyclohexa-1,4-diene. Thus, we estimate:

$\Delta_{\text{solv}}G(\text{H}^\bullet) = +18.0 \pm 2.7$ kJ mol^{-1}.

Computational

There has been a theoretical determination of the Helmholtz and Gibbs solvation energies of the hydrogen atom employing path integral Monte Carlo methods that also should be considered. [45] The procedure involved determining the equilibrium solvation in a cubic simulation cell of one solute and108 water molecules. For the Gibbs energy, the value $\Delta_{\text{solv}}G = (21.44 \pm 1.46)$ kJ mol^{-1} was obtained.

Discussion

There are four values of the Gibbs energy of solvation to chose among: $\Delta_{\text{solv}}G = (17.77 \pm 0.09)$ kJ mol^{-1}, from the solubility of H_2; $\Delta_{\text{solv}}G = (18.0 \pm 2.7)$ kJ mol^{-1} from the reaction of $\text{H}^\bullet$ with C_6H_6; $\Delta_{\text{solv}}G = (21.44 \pm 1.46)$ kJ mol^{-1} from a theoretical calculation; and $\Delta_{\text{solv}}G = (22.21 \pm 0.84)$ kJ mol^{-1} from the solubility of the rare gases.

The use of H_2 as a surrogate for $\text{H}^\bullet$ is supported by the observation that the Gibbs energy of solvation of a non-polar solute in water is proportional to its polarizability. Indeed, both the entropies and the enthalpies of solvation of the rare gases, along with H_2 and N_2 are smoothly related to this parameter [46]. On the other hand, whereas O_2 is less polarizable than N_2, it is twice as soluble [47]. This was due to the difference in solvation enthalpy and was ascribed to the energy required for cavity formation, with the observation from theoretical analysis that the interaction between N_2 and water was about twice that of O_2. It should be pointed out that the difference in polarizability between N_2 and O_2 is only about 20%, while that between $\text{H}^\bullet$ and He is a factor of three [46].

The use of the Van der Waals radii of $H^•$ and the rare gases to derive a value for the solubility of $H^•$ is based on the observation that the Gibbs energies of solvation of the rare gases are correlated with the radii. The value obtained in this way is supported by the one theoretical calculation addressing this matter. In addition, there have been a number of theoretical studies which also may provide some insight into the solubility, even though they mostly deal with the diffusion of $H^•$. The diffusion coefficient of $H^•$ is surprisingly high [48], close to that of the proton, H^+, which has a mechanism for diffusion unavailable to the uncharged atom [49]. He diffuses similarly rapidly, with H_2 and Ne a bit slower. The behavior of $H^•$ has been addressed in molecular dynamics studies [49-52]. Pure water is characterized by hydrophobic cavities that are spontaneously created and destroyed. These cavities have the right size to host a small solute such as $H^•$. The rapid diffusion arises from an exchange of water molecules, structural diffusion, which is unlike the behavior of small hydrated cations which will travel with their hydration shell attached [50]. Of particular interest is that $H^•$ does not seem to exhibit any particular interactions with the solvent shell, except some repulsion. The hydrogen atom also participates in some intercavity hopping, essentially tunneling, which also explains the even greater diffusion coefficient of muonium [52].

The Gibbs energies of solution derived from the solubility of H_2 and from the rare gases probably represent two extreme cases: one in which the solubility depends primarily on interactions with the solvent, and one in which the size of the solute is the primary parameter. The correct picture is probably somewhere in between. Thus, we have averaged these two values and obtain (19.99 ± 2.22) kJ mol^{-1} where the uncertainty represents the range of the two values. Of great importance is that this value is very close to that derived from the enhancement of the rate constant for the addition to benzene in solution over that in the gas phase.

This value can be converted to the standard potential of $H^•$ by making use of the known enthalpy of dissociation of H_2 in the gas phase and the defined Gibbs energy of the normal hydrogen electrode, as follows:

$$\begin{array}{ll}
H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2} H_2(g) & \Delta_r G^o = 0 \\
\tfrac{1}{2} H_2(g) \rightleftharpoons H^•(g) & \Delta_r G^o = +203.278 \text{ kJ mol}^{-1} \text{ [14]} \\
H^•(g) \rightleftharpoons H^•(aq) & \Delta_{solv} G^o = +19.99 \text{ kJ mol}^{-1} \\
\hline
\end{array}$$

$$H^+(aq) + e^- \rightleftharpoons H^•(aq) \qquad \Delta_r G^o = +223.27 \text{ kJ mol}^{-1}, E^o = -2.31 \text{ V}$$

The Gibbs energy for the dissociation of H_2 decreases as the temperature is raised; the Gibbs energy of solution of $H^\bullet$(g) increases. As a result, at least for (0 – 70) °C, the standard potential for $H^\bullet$(aq) is independent of temperature, based on this derivation.

The range that arises from the two competing models for the Gibbs energy of solvation, ± 2.2 kJ mol^{-1}, probably best represents the uncertainty in the standard potential or the Gibbs energy of the hydrogen atom. Thus, the recommended values are as follows:

Recommended values:

$\Delta_{solv}G = +20 \pm 2$ kJ mol^{-1}
$E^o = -2.31 \pm 0.03$ V
$K_h = 0.313 \times 10^{-4}$ mol L^{-1} MPa^{-1} (3.1×10^{-4} mol L^{-1} atm^{-1}) with a range of $(0.131 - 0.778) \times 10^{-4}$ mol L^{-1} MPa^{-1} $\{(1.3 - 7.7) \times 10^{-4}$ mol L^{-1} $atm^{-1}\}$.

Nomenclature

The recommended name of $H^\bullet$ is hydrogen or, to avoid confusion, mono-hydrogen. There is no recommended name for e^-_{aq}. $HClO_4$, hydroxidotrioxidochlorine; perchloric acid is accepted.

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1.4 Hydration Gibbs energies for the electron and the proton

The electrode potential of the electron is connected to well-known gas-phase dissociation and photoionization values through the hydration Gibbs energies of the electron and the proton.

$$\begin{aligned} &\tfrac{1}{2}\, H_2(g) \rightleftharpoons H^{\bullet}(g) && \Delta_r G^\circ = +203.278 \text{ kJ mol}^{-1} \text{ [1]} \\ &H^{\bullet}(g) \rightleftharpoons e^-(g) + H^+(g) && \Delta_r G^\circ = +1310.075 \text{ kJ mol}^{-1} \text{ [2]} \\ &H^+(g) \rightleftharpoons H^+(aq) && \Delta_r G^\circ = X \end{aligned}$$

$e^-(g) \rightleftharpoons e^-(aq) \qquad \Delta_r G^\circ = Y$

$e^-(aq) + H^+(aq) \rightleftharpoons \frac{1}{2} H_2(g) \qquad \Delta_r G^\circ = -278.1\ \text{kJ mol}^{-1} \quad E^\circ = -2.88\ \text{V}$

(from section 1.1. of Data Sheet 1)

From these equations, X + Y = −1235.2 kJ mol^{-1} for a standard state of 1 bar in the gas phase and 1 mol L^{-1} in solution. High-level solvent-induced electronic structure calculations by Zhan & Dixon have resulted in values of X = −1097.9 kJ mol^{-1} [3] and Y = −140.6 kJ mol^{-1} [4] which yields X + Y = −1238.5 kJ mol^{-1}, in excellent agreement. Note that X and Y refer to reactions that violate charge conservation in the individual phases and, hence, the X and Y values are "absolute" rather than conventional thermodynamicchemical quantities.

Unfortunately, even though there has been a great deal of interest in the value of the hydration energy of the proton, its value is still contentious [5-17]. Bryantsev, *et al.* [18] argue that the Zhan & Dixon [3] calculation for the proton should have included concentration corrections for the water clusters. This would lower their value by about −5.4 kJ mol^{-1}. It is not clear what iMPact this correction would have on the electron hydration energy.

The value for the proton hydration Gibbs energy obtained from an analysis of cluster-ion solvation data is $\Delta_r G^\circ$ = −1104.5 kJ mol^{-1} [19]. This value has been widly accepted. A more recient cluster correlation method has led to a "best" value of $\Delta_r G^\circ$ = −1102.1 kJ mol^{-1}, even closer to the theoretical value [20]. This more recient cluster correlation value for the proton hydration Gibbs energy [20] leads to a value for the hydration Gibbs energy of the electron of $\Delta_r G^\circ$ = −136.4 kJ mol^{-1}. This is about 4.2 kJ mol^{-1} higher than the theoretical value, without including any concentration corrections for clusters. That correction, applied only to the calculation for the proton, suggests an agreement to within 1.2 kJ mol^{-1}.

Thus, the sum of the electron and proton hydration Gibbs energies, X + Y, that results from theoretical and experimental studies is very close to the sum derived from the hydration Gibbs energies recommended here. This clearly supports the electrode potential for the hydrated electron recommended here, E° = –2.88 V.

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Data Sheet 2

$E°(\mathrm{O/O^{\bullet-}})$

List of reports:

No direct determinations of this standard potential have been made.

Henglein, 1980 [1].
Henglein used $\Delta_f G°(\mathrm{O^{\bullet-}})$ = +103 kJ $\mathrm{mol^{-1}}$, an estimated $\Delta_s G°(\mathrm{O})$ of +10 kJ $\mathrm{mol^{-1}}$, and $\Delta_f G°(\mathrm{O})$g = +232 kJ $\mathrm{mol^{-1}}$ [2] and arrived at $E°(\mathrm{O/O^{\bullet-}})$ = +1.4 V.

Stanbury, 1989 [3].
Use of more recent values, $\Delta_f G°(\mathrm{O^{\bullet-}})$ = +94 kJ $\mathrm{mol^{-1}}$ and $\Delta_s G°(\mathrm{O})$ = +19 kJ $\mathrm{mol^{-1}}$ yielded $E°(\mathrm{O/O^{\bullet-}})$ = +1.63 V.

Discussion

A Gibbs energy of formation of 251 kJ $\mathrm{mol^{-1}}$ has been estimated for $\mathrm{O}(^3P)$ in water[3]. The standard potentials $E°(\mathrm{O/O^{\bullet-}})$ and $E°(\mathrm{O, H^+/HO^\bullet})$ are calculated from this value and $\Delta_f G°(\mathrm{O^{\bullet-}})$ = +(93.1 ± 1.7 kJ) $\mathrm{mol^{-1}}$, which follows from $\Delta_f G°(\mathrm{HO^\bullet})$ = +(26.3 ± 1.7) kJ $\mathrm{mol^{-1}}$ (Data Sheet 7), and a $\mathrm{p}K_\mathrm{a}$ of (11.7±0.1) [4-12] (see Data Sheet 116 for a discussion of this $\mathrm{p}K_\mathrm{a}$).

Recommended values:

$E°(\mathrm{O/O^{\bullet-}})$ = +(1.6 ± 0.1) V
$E°(\mathrm{O, H^+/HO^\bullet})$ = +(2.3 ± 0.1) V. The errors are conservative estimates.

Nomenclature

The recommended name of O is oxygen or, to avoid confusion, mono-oxygen, of $\mathrm{O^{\bullet-}}$ oxide(•1−) or oxidanidyl, that of $\mathrm{HO^\bullet}$ is hydridooxygen(•) or oxidanyl, while hydroxyl is allowed.

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Data Sheet 3

$E°(O_2/O_2^{\bullet-})$

List of reports:

Chemical equilibrium: $DQ + O_2^{\bullet-} \rightleftharpoons O_2 + DQ^{\bullet-}$ (3.1)

DQ is duroquinone, 2,3,5,6-tetramethylbenzo-1,4-quinone.
IUPAC PIN: 2,3,5,6-tetramethylcyclohexa-2,5-diene-1,4-dione

Wood, 1974 [1].
Review, value based on $E°(DQ/DQ^{\bullet-}) = -0.25$ V, calculated, and $K(3.1) = 2.3 \times 10^{-2}$ [2].
$E°(O_2/O_2^{\bullet-}) = -0.15$ V or -0.32 V ($pO_2 = 0.100$ MPa)

Meisel and Czapski, 1975 [3].
Based on $E°(DQ/DQ^{\bullet-}) = -0.235$ V, calculated, and $K(3.1) = 4.6 \times 10^{-2}$, determined. Conditions: pH 7, $\mu = 25$ m*M* (5 mM phosphate and 10 mM formate) or 15 mM (5 mM phosphate with 10 mM 2-propanol as $HO^{\bullet}$ scavenger), ambient temperature.
$E°(O_2/O_2^{\bullet-}) = -0.16$ V or -0.33 V ($pO_2 = 0.100$ MPa)

Wardman, 1991 [4].
Based on $E°(DQ/DQ^{\bullet-}) = -264 \pm 5$ mV, determined against a revised value for $E°(MV^{2+}/MV^{\bullet+})$, -0.450 V, and the average of the two $K(3.1)$'s given above. MV^{2+} is the 1,1'-dimethyl-4,4'-bipyridinium(2+) cation (paraquat). Conditions: pH 7.7, $\mu = 0.12$ M, $T = 296$ K.
$E°(O_2/O_2^{\bullet-}) = -(0.179 \pm 0.011)$ or $-(0.350 \pm 0.011)$ V ($pO_2 = 0.100$ MPa)

Chemical equilibrium: $DMBQ + O_2^{\bullet-} \rightleftharpoons O_2 + DMBQ^{\bullet-}$ (3.2)

DMBQ is 2,5-dimethylbenzo-1,4-quinone.
IUPAC PIN: 2,5-dimethylcyclohexa-2,5-diene-1,4-dione

Ilan, Meisel and Czapski, 1974 [5].
$K(3.2) = 54$, determined at $\mu \approx 105$ mM, T not stated. $E°(DMBQ/DMBQ^{\bullet-})$ is calculated from the energetics of the comproportionation reaction, $E°(DMBQ/DMBQ^{2-})$ and the dissociation constants of $DMBQH_2$, $DMBQH^-$ and $DMBQH^{\bullet}$, but not explicitly stated. The authors conclude that $E°(O_2/O_2^{\bullet-}) = -0.33$ V ($pO_2 = 0.100$ MPa).

Ilan, Czapski and Meisel, 1976 [6].
Based on $E°(\mathrm{DMBQ}/\mathrm{DMBQ}^{\bullet-}) = -67$ mV, calculated as described above, and $K(3.2)$ values of 56 and 53, based on equilibrium measurements, and $K(3.2) = 37$ based on the ratio of the forward and backward rate constants of Reaction 3.2. The latter value is considered less reliable by the authors. The error in $E°(\mathrm{DMBQ}/\mathrm{DMBQ}^{\bullet-})$ is not given; we estimate 10 mV.
$E°(O_2/O_2^{\bullet-}) = -(0.169 \pm 0.011)$ or $-(0.340 \pm 0.011)$ V ($pO_2 = 0.100$ MPa). The authors list –0.33 V for $E°(O_2/O_2^{\bullet-})$.

Chemical equilibrium: $\mathrm{MQ} + O_2^{\bullet-} \rightleftharpoons O_2 + \mathrm{MQ}^{\bullet-}$ (3.3)

MQ is menadione, 2-methylnaphtho-1,4-quinone
IUPAC PIN: 2-methylcyclohexa-2,5-diene-1,4-dione

Meisel and Czapski, 1975 [3].
Based on $E°(\mathrm{MQ}/\mathrm{MQ}^{\bullet-}) = -0.203$ V, determined against DQ, and $K(3.3) = 0.16$, determined. Conditions, see above.
$E°(O_2/O_2^{\bullet-}) = -0.16$ V or –0.33 V ($pO_2 = 0.100$ MPa)

Chemical equilibrium: $\mathrm{IDS} + O_2^{\bullet-} \rightleftharpoons O_2 + \mathrm{IDS}^{\bullet-}$ (3.4)

IDS is indigodisulfonate, *(E)*-2,2'-bis(2,3-dihydro-3-oxoindolylidene)-5,5'-disulfonate
IUPAC PIN: (*E*)-3,3'-dioxo-1,1',3,3'-tetrahydro-2,2'-bi(indolylidene)-5,5'-disulfonate

Meisel and Czapski, 1975 [3].
Based on $E°(\mathrm{IDS}/\mathrm{IDS}^{\bullet-}) = -0.247$ V [7], and $K(3.4) = 2.9 \times 10^{-2}$, determined. Conditions, see above.
$E°(O_2/O_2^{\bullet-}) = -0.16$ V or –0.33 V ($pO_2 = 0.100$ MPa).

Chemical equilibrium: $\mathrm{BQ} + O_2^{\bullet-} \rightleftharpoons O_2 + \mathrm{BQ}^{\bullet-}$ (3.5)

BQ is benzo-1,4-quinone
IUPAC PIN: cyclohexa-2,5-diene-1,4-dione

Sawada *et al.*, 1975 [8].

Based on $E^\circ(\mathrm{BQ}/\mathrm{BQ}^{\bullet-}) = +0.10$ V.[9], k(forward) $9.8 \times 10^{8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ [10] and k(backward) $= 4.5 \times 10^{4}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, determined indirectly. Conditions: pH 5.0, 0.05 M acetate buffer, $\mu = 0.05$ M, and pH 7, 0.05 M phosphate buffer, $\mu = 0.13$ M, $T = 298$ K.

$E^\circ(\mathrm{O_2}/\mathrm{O_2}^{\bullet-}) = +0.10–0.257 = –0.16$ V or –0.33 V ($p\mathrm{O_2} = 0.100$ MPa)

Chemical equilibrium: iron(III)cytochrome c + $\mathrm{O_2}^{\bullet-} \rightleftharpoons$ iron(II)cytochrome c + $\mathrm{O_2}$ (3.6)

Sawada *et al.,* 1975 [8].

Based on E°(iron(III)-/iron(II)-cytochrome c) = +0.255 V, k(forward) $= 2.5 \times 10^{4}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and k(backward) $= 0.03\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, estimated. Conditions: pH 7.0, (25 ± 2) ºC, 0.05 M phosphate, $\mu = 0.13$ M, $T = 298$ K.

$E^\circ(\mathrm{O_2}/\mathrm{O_2}^{\bullet-}) = +0.255–0.35 = –0.095$ V or –0.27 V ($p\mathrm{O_2} = 0.100$ MPa).

Chemical equilibrium:

$[\mathrm{Ru(NH_3)_5}\text{isonicotinamide}]^{3+} + \mathrm{O_2}^{\bullet-} \rightleftharpoons \mathrm{O_2} + [\mathrm{Ru(NH_3)_5}\text{isonicotinamide}]^{2+}$ (3.7)

Isonicotinamide (isn) is pyridine-4-carboxamide.

Stanbury *et al.,* 1980 [11], [12].

Based on $E^\circ([\mathrm{Ru(NH_3)_5isn}]^{3+}/[\mathrm{Ru(NH_3)_5isn}]^{2+}) = +0.387$ V, k(forward) $= (2.2 \pm 0.2) \times 10^{8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$and k(backward) $= 1.08 \times 10^{-1}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, determined. Conditions: pH 4.5, $T = (296 \pm 2)$ K, 0.1 M $\mathrm{NaHCO_2}$, $\mu = 0.1$ M.

$E^\circ(\mathrm{O_2}/\mathrm{O_2}^{\bullet-}) = +0.387–0.551 = –0.164$ V, or –0.335 V ($p\mathrm{O_2} = 0.100$ MPa).

Chemical equilibrium: TBQ + $\mathrm{O_2}^{\bullet-} \rightleftharpoons \mathrm{TBQ}^{\bullet-} + \mathrm{O_2}$ (3.8)

TBQ is 2-*tert*-butyl-1,4-benzosemiquinone

IUPAC PIN: 2-*tert*-butyl-4-hydroxyphenoxyl or 3-*tert*-butyl-4-hydroxyphenoxyl

Dohrmann and Bergmann, 1995 [13].

Based on $E^\circ(\mathrm{TBQ}/\mathrm{TBQ}^{\bullet-}) = –(0.032 \pm 0.006)$ V, k(forward) $= (1.1 \pm 0.2) \times 10^{8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and k(backward) $= (1.6 \pm 0.5) \times 10^{6}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ (log $K = 1.85 \pm 0.1$), determined by pulse radiolysis. Conditions: 22 °C and $\mu = 0.1$ M

$E^\circ(\mathrm{O_2}/\mathrm{O_2}^{\bullet-}) = –(0.140 \pm 0.012)$ V, or –(0.31 ± 0.01) V ($p\mathrm{O_2} = 0.100$ MPa).

Discussion

Due to the high content of organic solvents, the concentration of dioxygen in the studies of Patel and Willson [2] is likely to be much higher than the 1.25 mM they assumed. Based on the literature [14] the concentration may have been twice as high. Indeed, we determined 2.01 mM O_2 in 6 M 2-propanol (Latal, Kissner, Koppenol, 2002, unpublished). This leads to a larger equilibrium constant, and the value determined by Meisel and Czapski[3] should be used. When combined with the revised value for the DQ/$DQ^{\bullet-}$ electrode potential from Wardman [4], one arrives at –264 + 79 = –185 mV (–357 mV, pO_2 = 0.100 MPa).

The revised value of the electrode potential of DQ/$DQ^{\bullet-}$, 29 mV more negative than that used by Meisel and Czapski [3], has consequences for the determination based on menadione, eq. 3.3. The corrected value for $E°(O_2/O_2^{\bullet-})$ is –0.356 V (pO_2 = 0.100 MPa).

A value of 0.078 V for $E°(BQ/BQ^{\bullet-})$ has been recommended by Wardman [15]. Applied to the determination based on eq. 3.5 by Sawada *et al.* [8] one arrives at $E°(O_2/O_2^{\bullet-})$ = +0.078–0.257 = –0.179 V or –0.350 V (pO_2 = 0.100 MPa).

$E°(DMBQ/DMBQ^{\bullet-})$, –0.067 V at μ = 0.1 M [6], can be corrected for ionic strength (DMS) and yields –0.080 V, with an estimated error of 0.02 V. Equilibrium 3.2 is not ionic strength dependent, even when the difference in radii of the reactants and products are taken into account. Thus, at μ = 0, $E°(O_2/O_2^{\bullet-})$ = –(0.35 ± 0.02) V.

The value obtained by Sawada *et al.* [8] from eq. 3.6 can also be corrected. The rate constant *k*(forward) is $(5.6 \pm 0.5) \times 10^5\ M^{-1}\ s^{-1}$ [16] under conditions similar to those of Sawada *et al.* [8] (except in 0.15 M formate). Combined with their *k*(backward) of 0.03 $M^{-1}\ s^{-1}$, and an electrode potential of 0.26 ± 0.01 V [17,18], one arrives at –0.17 V, or –0.34 V (pO_2 = 0.100 MPa). Given the unknown quality of the cytochrome *c* used, more weight is given to the values obtained with the quinones.

The determination of the electrode potential of the couple TBQ/$TBQ^{\bullet-}$ has been evaluated (Data Sheet S-1), which led to a correction and increased uncertainties: $E°(TBQ/TBQ^{\bullet-})$ = –(0.014 ± 0.016) V. Based on this value $E°(O_2/O_2^{\bullet-})$ = –(0.122 ± 0.016) V, or –(0.29 ± 0.02) V (pO_2 = 0.100 MPa). Given the increased uncertainties, this value is of limited use and is not used in the recommendation.

Overall, the large majority of the values cited above are in reasonable agreement. Because of the various weaknesses noted above in several of the reports, we place greatest confidence in the results derived from the DMBQ and BQ reactions. These two reports yield identical values for *E*°. The uncertainty in the DMBQ result is suggested to be ±20 mV, while none is specified for the BQ .

Recommended values:

$E°(O_2/O_2^{\bullet-})$ is –(0.18 ± 0.02) V, or –(0.35 ± 0.02) V (pO_2 = 0.100 MPa).
$\Delta_f G°(O_2^{\bullet-})$ = +(8.1 ± 0.5) kcal mol^{-1}, or +(33.8 ± 1.9) kJ mol^{-1}.
Given a pK_a of (4.8 ± 0.1) for $HO_2^{\bullet}$ [19], $E°(O_2, H^+/HO_2^{\bullet})$ is +(0.10 ± 0.02) V, or –(0.07 ± 0.02) V (pO_2 = 0.100 MPa).
$\Delta_f G°(HO_2^{\bullet})$ = +(1.7 ± 0.5) kcal mol^{-1}, or +(7 ± 2) kJ mol^{-1}

List of auxiliary thermodynamic data:

Baxendale *et al.* [20] derived a value of +8.2 kcal mol^{-1}, or +34.3 kJ mol^{-1}, for $\Delta_f G°(O_2^{\bullet-})$ via the Gibbs energy of formation of $HO_2^{\bullet}$ in the gas phase, +34.7 kJ mol^{-1}, an estimate for the Gibbs energy of solvation of –28.5 kJ mol^{-1} (identical to that of hydrogen peroxide) and a pK_a of 4.88. The resulting Gibbs energy of formation is in very good agreement with the recommended value.

Chevalet *et al.* [21] reported a value of –0.27 V for $E°(O_2/O_2^{\bullet-})$, determined by electrochemistry. This value has been corrected to –0.29 V [22]. A very similar value, –0.284 V, was obtained by Divišek and Kastening [22]. There are two fundamental problems with the electrochemical determination of $E°(O_2/O_2^{\bullet-})$. On a metal surface, catalysis of the dismutation of superoxide proceeds vigorously, and when surfactants are used to suppress this catalysis, one may not achieve an equilibrium. For that reason we prefer the data obtained by pulse radiolysis.

Zhuravleva and Berdnikov [23] calculated a electrode potential of –0.33 V from the equilibrium between iron(II) and hydrogen peroxide.

The electrode potential of 0.15 V reported by Rao and Hayon[10] is in error, as discussed by Wood [1] and Ilan *et al.* [6].

Petlicki and Van de Ven [24] have argued that the electrode potential of the $O_2/O_2^{\bullet-}$ couple is –0.14 V, instead of –0.33 V. They drew attention to the fact that there is a discrepancy between the electrode potential of the O_2/H_2O_2 couple derived from the NBS compilation [25] and that determined experimentally. They argue that this discrepancy proves that there is an equilibrium between superoxide on one side and dioxygen and hydrogen peroxide on the other side, which requires a substantial increase in the electrode potential of the $O_2/O_2^{\bullet-}$ couple. Given the many consistent determinations of $E°(O_2/O_2^{\bullet-})$ we dismiss the value reported by these authors.

Nomenclature

The systematic name of $O_2^{\bullet-}$ is dioxide(•1−) or dioxidanidyl, of $HO_2^{\bullet}$ hydrogen dioxide or dioxidanyl, and of O_2, dioxygen or dioxidanediyl. The venerable name superoxide is allowed.

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Data Sheet 4

$E°(^1\Delta_gO_2/O_2^{\bullet-})$

List of reports:

No direct determinations of this standard potential have been made.

Koppenol, 1976 [1].
A value of 0.65 V is calculated for $E°(^1\Delta_gO_2/O_2^{\bullet-})$ relative to a $p^1\Delta_gO_2$ = 0.100 MPa. It is based on $E°(O_2/O_2^{\bullet-}) = -0.33$ V, a difference in energy of 22.6 kcal between $^3\Sigma_g^-O_2$ and $^1\Delta_gO_2$, and a Gibbs energy of solution of singlet dioxygen identical to that of triplet dioxygen.
$E°(^1\Delta_gO_2/O_2^{\bullet-})$ is +0.82 V, or +0.65 V ($p^1\Delta_gO_2$ = 0.100 MPa). $\Delta_fG°(^1\Delta_gO_2) = +111$ kJ mol^{-1} or +26.5 kcal mol^{-1}.

Stanbury, 1989 [2].
A Gibbs energy of formation of +112 kJ mol^{-1} for 1 *m* $^1\Delta_gO_2$ is derived from a quantum-chemically derived Gibbs energy of formation of $^1\Delta_gO_2$ in the gas phase and a Gibbs energy of solution of singlet dioxygen identical to that of triplet dioxygen.
$E°(^1\Delta_gO_2/O_2^{\bullet-})$ is +0.83 V, or +0.66 V ($p^1\Delta_gO_2$ = 0.100 MPa). $\Delta_fG°(^1\Delta_gO_2) = +112$ kJ mol^{-1} or +26.8 kcal mol^{-1}.

Discussion

A reliable standard potential can be calculated from the recommended $\Delta_fG°(O_2^{\bullet-}) = +(33.8 \pm 0.8)$ kJ mol^{-1} (Data Sheet 3) and $\Delta_fG°(^1\Delta_gO_2) = +112$ kJ mol^{-1} or +26.8 kcal mol^{-1}.

Recommended values:

$E°(^1\Delta_gO_2/O_2^{\bullet-})$ is $+(0.81 \pm 0.01)$ V, or $+(0.64 \pm 0.01)$ V ($p^1\Delta_gO_2$ = 0.100 MPa).
$\Delta_fG°(^1\Delta_gO_2) = +(112 \pm 1)$ kJ mol^{-1}.

Nomenclature

The systematic name of $O_2^{\bullet-}$ is dioxide(•1−) or dioxidanidyl, of $HO_2^{\bullet}$ hydrogen dioxide or dioxidanyl, and of O_2, dioxygen or dioxidanediyl. The venerable name superoxide is allowed.

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Data Sheet 5

$E°(HO_2^•, H^+/H_2O_2)$

List of reports:

No direct determinations of this standard potential have been made.

Discussion

A value can be calculated from the Gibbs energy of formation of hydrogen dioxide ($HO_2^•$), +(7 ± 2) kJ mol^{-1} (see Data Sheet 3), and that of hydrogen peroxide. The Gibbs energies of formation of hydrogen peroxide are summarized in Table 1. The present recommendation from the National Institute of Standards and Technology [1], is the value obtained by Kern [2], −134.1 kJ mol^{-1}, which dates from 1963; a value also found in the compilation by Hoare in *Standard Potentials in Aqueous Solution* [3]. The standard potentials derived from this value are $E°(HO_2^•/H_2O_2) = +1.461$ V, $E°(O_2/H_2O_2) = 0.695$ V ($pO_2 = 0.100$ MPa) and $E°(H_2O_2/H_2O) = 1.763$ V.

There appears to be a distinct difference between the thermodynamic estimates and the electrochemical determinations, the latter yielding more negative values than the former, see Table 1. Given the perceived uncertainties of the electrochemical determinations, it was decided to stay with the existing recommendation.

Table 1 Gibbs energies of formation of H_2O_2

Authors	Year	Value / (kJ mol^{-1})	Remarks
Lewis and Randall [4]	1914	−129.6	sum of 9 Gibbs energies involving barium oxide and peroxide[a]
Lewis and Randall [5]	1923	−131.7	sum of 8 Gibbs energies involving barium oxide and peroxide[a]
Berl [6]	1943	−138.3	electrochemistry, C|O_2, HO_2^-, HO^-|calomel. $E°(O_2/HO_2^-)$= −0.0416 V
Yablokova and Bagotskii [7]	1952	−137.7	electrochemistry, Hg|O_2, HO_2^-, HO^-|HgO $E°(O_2/HO_2^-)$= −0.045 V
Kern [2]	1954	−134.1	electrochemistry, Hg|O_2, HO_2^-, HO^-|calomel. $E°(O_2/H_2O_2)$= +0.695 V. Expts. pH 6-14
Schumb *et al.* [8]	1955	−133.7	calculated from $\Delta_fG°$ of H_2O_2(l) and H_2O_2(g) and dissolution in H_2O
Yeager *et al.* [9]	1964	−137.0	electrochemistry, C|O_2, HO_2^-, HO^-|HgO|Hg. $E°(O_2/HO_2^-)$= −0.048 V. pO_2-range
Tikhomirova *et al.* [10]	1965	−137.0	electrochemistry, Pt|O_2, H_2O_2, H^+|H_2|Pt. $E°(O_2/H_2O_2)$= +0.71 V
Rotinyan [11]	1969	−141.0	electrochemistry, C|O_2, H_2O_2, H^+|SO_4^{2-}|Hg_2SO_4, Hg. $E°(O_2/H_2O_2)$= +0.73 V

[a] Lewis and Randall calculated the Gibbs energies involved in the dissolution of barium oxide and its oxidation by dioxygen to barium peroxide. When added to the formation of water from dihydrogen and dioxygen, the formation of hydrogen peroxide results. The slight difference between the calculations from 1914 and 1923 results from a better approximation of the activity coefficients involved; furthermodynamicre, one reaction was eliminated.

Recommended value:

$E°(HO_2^\bullet, H^+/H_2O_2) = (1.46 \pm 0.02)$ V.

Nomenclature

The systematic name of $HO_2^\bullet$ is hydrogen dioxide or dioxidanyl, of H_2O_2 dihydrogen dioxide or dioxidane, and of O_2, dioxygen or dioxidanediyl. The name hydrogen peroxide is allowed.

References

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Data Sheet 6

$E°(HO^{\bullet}, H^+/H_2O)$

Discussion

The calculation of $E°(HO^{\bullet}, H^+/H_2O)$ is based on evaluations presented in Data Sheets 19-21. Chemical equilibria

$$HO^{\bullet} + Tl^+ \rightleftharpoons TlOH^+ \qquad (19.1)$$

$$TlOH^+ + H^+ \rightleftharpoons Tl^{2+} + H_2O \qquad (-20.1)$$

$$Tl^{2+} + e^- \rightleftharpoons Tl^+ \qquad (21.9)$$

Use of the K_{eq} for the Equilibrium 19.1, $K_{eq} = (5.8 \pm 1.0) \times 10^3\ M^{-1}$ at 25 °C , the K_a of Tl^{2+} from reaction 20.1, $(1.7 \pm 0.3) \times 10^{-5}$ M, $E° = +(2.221 \pm 0.003)$ V for Tl^{2+}/Tl^+ (Equilibrium 21.9), and the NBS value [1] of $\Delta_f G°$ for $H_2O(l)$ (= –237.129 ± 0.08 kJ mol^{-1}) leads to $\Delta_f G° = +(25.9 \pm 0.5)$ kJ mol^{-1} for $HO^{\bullet}$. Use of the NBS value [1] of $\Delta_f G°$ for $OH^-(aq)$ (= –157.244 ± 0.08 kJ mol^{-1}) leads to $E° = +(1.898 \pm 0.005)$ V for the $HO^{\bullet}/HO^-$ redox couple.

Chemical equilibria

$$O_3(aq) + ClO_2^- \rightleftharpoons O_3^{\bullet-} + ClO_2^{\bullet}(aq) \qquad (2.07)$$

$$O_3^{\bullet-} \rightleftharpoons O_2(aq) + O^{\bullet-} \qquad (-6.02)$$

$$O^{\bullet-} + H^+ \rightleftharpoons HO^{\bullet} \qquad (-4.02)$$

Kläning, Sehested and Holcman, 1985 [2].
The calculation of the standard potential involves $K(2.07) = (22 \pm 6)$ at low ionic strength (from determinations of the forward and backward rate constants at 22°C), $K(-6.02) = 1.1 \times 10^{-6}$ M (from published forward and backward rate constants [3,4]), the ionization constant of $HO^{\bullet}$, 11.9 [5], and a new determination of $E°(ClO_2^{\bullet}/ClO_2^-) = +(0.934 \pm 0.002)$ V. No explicit error in $E°$ is given. Note: the authors refer to $E°(HO^{\bullet}, H^+/H_2O)$ incorrectly as an oxidation potential.
These workers reported the following results: $E°(HO^{\bullet}, H^+/H_2O) = +2.74$ V. $E°(HO^{\bullet}/HO^-) = +1.91$ V. $\Delta_f G°(HO^{\bullet}) = +(26.8 \pm 1.0)$ kJ mol^{-1}.

Recommended values:

$E°(HO^{\bullet}, H^+/H_2O) = +(2.72 \pm 0.01$ V.

$E°(HO^•, HO^–) = +1.89 ± 0.01)$ V.
$E°(H_2O_2, H^+/HO^•, H_2O) = +(0.80 ± 0.01)$ V (based on the NIST Gibbs energy of –134.1 kJ mol^{-1} for hydrogen peroxide).
$\Delta_f G°(HO^•) = +26 ± 1$ kJ mol^{-1}, and $\Delta_f G°(O^{•–}) = +(92 ± 3)$ kJ mol^{-1}.

List of auxiliary thermodynamic data

Gibbs energies of formation of +(6.2 and +22.3) kcal mol (+25.9 and +93.3 kJ mol^{-1}) were derived for $HO^•$ and $O^{•–}$, respectively, from the gas phase Gibbs energy of formation of $HO^•$, +34.7 kJ mol^{-1} (+8.3 kcal mol^{-1}), an assumed Gibbs solvation energy of +(8.8 kJ mol^{-1}) (–2.1 kcal mol^{-1}) for $HO^•$ and a pK_a of 11.8 [6].

An estimate of $E°(HO^•/HO^–) = +1.77$ V, and a brief discussion of earlier standard potentials are found in Koppenol and Liebman [7].

Nomenclature

The systematic name of $HO^•$ is hydridooxygen(•) or oxidanyl, of $O^{•–}$ oxide(•–) or oxidanidyl, and of H_2O oxidane. The venerable names hydroxyl and water are allowed.

References

1. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttal. *J. Phys. Chem. Ref. Data* **11 (Suppl. 2)**, 37-38 (1982).

2. U. K. Kläning, K. Sehested, J. Holcman. *J. Phys. Chem.* **89**, 760-763 (1985).

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7. W. H. Koppenol, J. Liebman. *J. Phys. Chem.* **88**, 99-101 (1984).

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Data Sheet 7

An optimization of a subset of the radical equilibria was performed using the Active Thermodynamicchemical Tables approach (see main document, section 6). It is based on the following evaluated data.

Table 7.1. Input equilibrium data for optimization

rxn #	reaction	equilibrium constant	uncertainty	Data Sheet #
8.1	$HO^{\bullet} + Cl^{-} + H^{+} \rightleftharpoons Cl^{\bullet} + H_2O$	9×10^{4} M^{-2}	within a factor of 2	8
9.1	$Cl_2^{\bullet-} + H_2O \rightleftharpoons HO^{\bullet} + H^{+} + 2Cl^{-}$	6.1×10^{-11} M^{3}	± 10%	9
10.1	$Cl^{\bullet} + Cl^{-} \rightleftharpoons Cl_2^{\bullet-}$	1.4×10^{5} M^{-1}	± 15%	10
11.1	$Cl^{\bullet} + H_2O \rightleftharpoons HOCl^{\bullet-} + H^{+}$	5×10^{-6} M	within a factor of 2	11
12.1	$HO^{\bullet} + Cl^{-} \rightleftharpoons HOCl^{\bullet-}$	0.70 M^{-1}	± 0.13	12
13.1	$SO_4^{\bullet-} + Cl^{-} \rightleftharpoons SO_4^{2-} + Cl^{\bullet}(aq)$	1.2	± 17%	13
14.1	$SO_4^{\bullet-} + NO_3^{-} \rightleftharpoons SO_4^{2-} + NO_3^{\bullet}$	0.3	± 36%	14
15.1	$SO_4^{\bullet-} + HNO_3 \rightleftharpoons HSO_4^{-} + NO_3^{\bullet}$	5×10^{2}	± 40%	15
16.1	$NO_3^{\bullet} + Cl^{-} \rightleftharpoons NO_3^{-} + Cl^{\bullet}$	3.3	± 7%	16
17.1	$NO_3^{\bullet} + ClO_3^{-} \rightleftharpoons NO_3^{-} + ClO_3^{\bullet}$	3×10	± 67%	17
18.1	$SO_4^{\bullet-} + H_2O \rightleftharpoons HSO_4^{-} + HO^{\bullet}$	1.4×10^{-3} M	± 29%	18
19.1	$HO^{\bullet}(aq) + Tl^{+}(aq) \rightleftharpoons TlOH^{+}(aq)$	5.8×10^{3} M^{-1}	± 15%	19
20.1	$Tl^{2+}(aq) + H_2O(l) \rightleftharpoons TlOH^{+}(aq) + H^{+}(aq)$	1.7×10^{-5} M	± 15%	20
21.1	$Tl^{2+}(aq) + 1/2H_2(g) \rightleftharpoons Tl^{+}(aq) + H^{+}(aq)$	2.225 V	± 0.007 V	21

	$HNO_3(aq) \rightleftharpoons NO_3^-(aq) + H^+(aq)$	20 M	± 20%	15

The above equilibrium constants were supplemented with the standard data in Table 7.2, all of which come from the NIST tables except for NO_3^-; the value for NO_3^- in the NBS tables is incorrect, and the correct value is the value given for dissociated HNO_3, as explained in Data Sheet 103. Data Sheet 103 also includes an evaluation of the $NO_3^•$ radical that is independent of the Active Thermodynamicchemical Tables optimization.

Nomenclature (venerable names in italics): $Cl^•$, chlorine atom; $Cl_2^{•-}$, dichloride(•1−); $ClO_3^•$, trioxidochlorine(•); $HO^•$, *hydroxyl*, oxidanyl or hydridooxygen(•); $HOCl^{•-}$, hydroxidochlorate(•1−); $NO_3^•$, trioxidonitrogen(•); $SO_4^{•-}$, tetraoxidosulfate(•1−); $TlOH^+$, hydroxidothallium(•1+)

Table 7.2. Input standard Gibbs energies for optimization

species	$\Delta_f G°$ / kJ mol^{-1}	uncertainty/ kJ mol^{-1}
$H^+(aq)$	0	
$H_2O(l)$	−237.13	± 0.080
$Cl^-(aq)$	−131.23	± 0.080
$SO_4^{2-}(aq)$	−744.53	± 0.80
$NO_3^-(aq)$	−111.25	± 0.80
$HSO_4^-(aq)$	−755.91	± 0.80
$ClO_3^-(aq)$	−7.95	± 0.80
$Tl^+(aq)$	−32.40	± 0.80

/

The result of the optimization is

Table 7.3. Optimized Gibbs energies

species	$\Delta_f G°$ kJ mol^{-1}	Uncertainty / kJ mol^{-1}
$HO^•(aq)$	+26.3	± 1.6
$Cl^•(aq)$	+103.4	± 1.7
$Cl_2^{•-}(aq)$	−57.3	± 1.6
$HOCl^{•-}(aq)$	−104	± 1.7
$SO_4^{•-}(aq)$	−509.4	± 1.8
$NO_3^•(aq)$	+126.7	± 1.8
$ClO_3^•(aq)$	+222	± 3

$Tl(OH)^+(aq)$	–27.6	± 1.3
$Tl^{2+}(aq)$	+182.3	± 1.2
$HNO_3(aq)$	–104.1	± 0.9

Standard potentials can be derived from these optimized $\Delta_f G^\circ$ data by combining them with the standard Gibbs energies of formation given above plus the following additional standard Gibbs energies of formation:

Table 7.4. Auxiliary Gibbs energies

species	$\Delta_f G°$ / kJ mol^{-1}	Uncertainty / kJ mol^{-1}
$Cl_2(aq)$	+6.9	± 0.8
$HOCl(aq)$	–80	± 8
$(S_2O_8)^{2-}(aq)$	–1115	± 8
$Tl^{3+}(aq)$	+215	± 8
$TlOH^{2+}(aq)$	–16	± 8

[a] Data at 25 °C and from NBS.

Table 7.5. Derived standard potentials

Reaction	$E°$ / V vs NHE	Uncertainty / V
$HO^{\bullet}(aq) + e^- \rightleftharpoons HO^-(aq)$	+1.902	± 0.017
$HO^{\bullet}(aq) + e^- + H^+(aq) \rightleftharpoons H_2O(l)$	+2.730	± 0.017
$Cl^{\bullet}(aq) + e^- \rightleftharpoons Cl^-(aq)$	+2.432	± 0.018
$Cl_2^{\bullet-}(aq) + e^- \rightleftharpoons 2Cl^-(aq)$	+2.126	± 0.017
$Cl_2(aq) + e^- \rightleftharpoons Cl_2^{\bullet-}(aq)$	+0.666	± 0.017
$ClOH^{\bullet-}(aq) + e^- \rightleftharpoons Cl^-(aq) + HOH(aq)$	+1.912	± 0.018
$HOCl^{\bullet-}(aq) + e^- + H^+(aq) \rightleftharpoons Cl^-(aq) + H_2O(l)$	+2.740	± 0.018
$HOCl(aq) + e^- \rightleftharpoons HOCl^{\bullet-}(aq)$	+0.25	± 0.08
$SO_4^{\bullet-}(aq) + e^- \rightleftharpoons SO_4^{2-}(aq)$	+2.437	± 0.019
$S_2O_8^{2-}(aq) + e^- \rightleftharpoons SO_4^{\bullet-}(aq) + SO_4^{2-}(aq)$	+1.44	± 0.08
$NO_3^{\bullet}(aq) + e^- \rightleftharpoons NO_3^-(aq)$	+2.466	± 0.019
$ClO_3^{\bullet}(aq) + e^- \rightleftharpoons ClO_3^-(aq)$	+2.38	± 0.03
$Tl^{3+}(aq) + e^- \rightleftharpoons Tl^{2+}(aq)$	+0.34	± 0.08
$Tl^{2+}(aq) + e^- \rightleftharpoons Tl^+(aq)$	+2.225	± 0.012
$TlOH^+(aq) + e^- + H^+(aq) \rightleftharpoons Tl^+(aq) + H_2O(l)$	+2.507	± 0.013
$TlOH^{2+}(aq) + e^- \rightleftharpoons TlOH^+(aq)$	+0.12	± 0.08
$TlOH^{2+}(aq) + e^- + H^+(aq) \rightleftharpoons Tl^{2+}(aq) + H_2O(l)$	+0.40	± 0.08

Data Sheet 8

Chemical equilibrium: $HO^{\bullet} + Cl^{-} + H^{+} \rightleftharpoons Cl^{\bullet} + H_2O$ (8.1)

List of reports:

$K_{eq} = (2.0 \pm 1.0) \times 10^{5}\ M^{-2}$, $\mu = 0.01$ M [1]. Result obtained from UV/vis data on the equilibrium attained during pulse-radiolysis. The reported value includes the concentration of water; the value given here has been corrected to reflect water having unit activity.

$K_{eq} = 9.1 \times 10^{4}\ M^{-2}$, no specified uncertainty but probably correct within a factor of 2, μ = 0.01 M [2]. The basis for this result is unclear from the published paper, but a letter from Kläning to Stanbury (21 Feb 1990) states that the result was obtained by recalulation from the optical/pulse-radiolysis data of Jayson *et al.* [1] with a correction for the optical density due to chlorine atoms.

Discussion

McElroy [3] has argued that the decay of chlorine atoms is more complex than indicated by the models of Jayson *et al.* [1] and Kläning *et al.* [2], and he has specifically introduced the equilibrium hydration of chlorine atoms: $Cl^{\bullet}(aq) + H_2O(l) \rightleftharpoons HOClH^{\bullet}$ [3]. However, Buxton *et al.* have argued persuasively that McElroy's suggestion is unsupported by data [4].

We accept the equilibrium constant of Kläning *et al.* [2], with the understanding that it has not been checked directly, and that it is likely to be dependent on ionic strength.

Recommended value:

$K_{eq} = 9.1 \times 10^{4}\ M^{-2}$ within a factor of two at $\mu = 0.01$ M.

List of auxiliary thermodynamic data: none

References

1. G. G. Jayson, B. J. Parsons, A. J. Swallow. *J. Chem. Soc., Faraday Trans. I* **69,** 1597-1607 (1973).

2. U. K. Kläning, T. Wolff. *Ber. Bunsenges. Phys. Chem.* **89,** 243-245 (1985).
3. W. J. McElroy. *J. Phys. Chem.* **94,** 2435-2441 (1990).
4. G. V. Buxton, M. Bydder, G. A. Salmon, J. E. Williams. *Phys. Chem. Chem. Phys.* **2,** 237-245 (2000).

Data Sheet 9

Chemical equilibrium: $Cl_2^{\bullet-} + H_2O \rightleftharpoons HO^{\bullet} + H^{+} + 2Cl^{-}$ (9.1)

List of reports:

$K_{eq} = 3.6 \times 10^{-8}$ M^3, no specified uncertainty, μ unspecified, but apparently less than 0.1 M [1]. Data obtained from flash photolysis with conductivity detection. Result obtained from ratio of forward and reverse rate constants (k(19) and k(19')) in Table 2, p. 865) given in the paper.

$K_{eq} = (7.7 \pm 0.8) \times 10^{-11}$ M^3, $\mu \sim 0.01$ M. Result obtained from ratio of forward and reverse rate constants, which were obtained from flash photolysis with optical detection [2]. The forward rate constant used is k^{I}_{-4}/K_5 given on the bottom left of p. 1321 (also in Table 4), and the reverse rate constant is k_4K_3 from Table 2 (note that the dimensions in the paper are incorrect).

Discussion

Given the gross discrepancy between the two reports, careful evaluation is required. Note that the forward and reverse rate constants given in the two papers have different dimensions and apparently pertain to systems having different rate-limiting steps. The first report, by Wagner *et al.* [1], gives a forward first-order rate constant k(19) of 7.2×10^3 s^{-1} for the direct reaction of $Cl_2^{\bullet-}$ with water. The second report, by Yu and Barker [2], gives a forward rate constant of 1.4 M s^{-1}, the dimensions reflecting an inverse dependence on [Cl$^-$] and thus implying a mechanism proceeding via dissociation of $Cl_2^{\bullet-}$ followed by hydrolysis of Cl atoms. Yu and Barker claim that their data set an upper limit of (100 s^{-1}) for the direct reaction of $Cl_2^{\bullet-}$ with water. They cite several prior reports in support of their slow rate constant. They also cite good literature support for their measured value for the forward rate constant. In view of the great difficulty in measuring the very slow rate constant for the direct reaction of $Cl_2^{\bullet-}$ with water and the apparently incorrect value obtained by Wagner *et al.* [1], we recommend the result of Yu and Barker [2].

Yu and Barker [2] note that their rate constant k_4 can be corrected to zero ionic strength by applying a factor of 1/0.8. As the other components of K_{eq} (K_5, K_3, and k^{I}_{-4}) are expected to be independent of ionic strength, we can correct K_{eq} to 6.1×10^{-11} M^3 at zero ionic strength.

Recommended value:

$K_{eq} = (6.1 \pm 0.7) \times 10^{-11}$ M^3, $\mu = 0$ M.

List of auxiliary thermodynamic data: none.

References

1. I. Wagner, J. Karthauser, H. Strehlow. *Ber. Bunsen-Ges. Phys. Chem.* **90,** 861-867 (1986).
2. X.-Y. Yu, J. R. Barker. *J. Phys. Chem. A* **107,** 1313-1324 (2003).

Data Sheet 10

Chemical equilibrium: $Cl^{\bullet}(aq) + Cl^{-} \rightleftharpoons Cl_2^{\bullet-}$ (10.1)

List of reports:

$K_{eq} = (1.9 \pm 0.5) \times 10^5\ M^{-1}$, $\mu = 0.01$ M [1]. Result obtained from UV/vis data of equilibrium observed during pulse-radiolysis.

$K_{eq} = 1.77 \times 10^1\ M^{-1}$, $\mu = 0.1$ M [2]. Obtained by UV/vis evaluation of equilibrium obtained by flash photolysis.

$K_{eq} = (4.7 \pm 0.4) \times 10^3\ M^{-1}$, $\mu = ?$ M [3]. Data obtained by pulse radiolysis.

$K_{eq} = (1.4 \pm 0.1) \times 10^5\ M^{-1}$, μ unspecified, but is rather low [4]. Result obtained from UV/vis data on the forward and reverse rate constants determined by pulse-radiolysis.

$K_{eq} = (1.4 \pm 0.2) \times 10^5\ M^{-1}$, μ unspecified, but presumed to be unimportant [5]. Result obtained from the ratio of forward and reverse rate constants, the forward one being a literature value and the reverse being measured by Yu *et al.* [5].

Discussion

The low value of Wu *et al.* [2] is discounted because of internal inconsistency of the data, as pointed out by Wagner *et al.* [6] The low value of Adams *et al.* [3] is discounted because of an incorrect approximation, as pointed out by Buxton *et al.* [4]. Deviations of the values of Buxton *et al.* [4] and Yu *et al.* [5] from the result of Jayson *et al.* are attributed to neglect of the absorption due to chlorine atoms by Jayson *et al.* [1]. Thus, we recommend the averaged results of Buxton *et al.* [4] and Yu *et al.* [5].

Recommended value:

$K_{eq} = (1.4 \pm 0.2) \times 10^5\ M^{-1}$, μ unspecified and presumed to be unimportant.

List of auxiliary thermodynamic data: none

References

1. G. G. Jayson, B. J. Parsons, A. J. Swallow. *J. Chem. Soc., Faraday Trans. I* **69,** 1597-1607 (1973).
2. D. Wu, D. Wong, B. Di Bartolo. *J. Photochem.* **14,** 303-310 (1980).
3. D. J. Adams, S. Barlow, G. V. Buxton, T. M. Malone, G. A. Salmon. *J. Chem. Soc., Faraday Trans.* **91,** 3303-3305 (1995).
4. G. V. Buxton, M. Bydder, G. A. Salmon. *J. Chem. Soc., Faraday Trans.* **94,** 653-657 (1998).
5. X.-Y. Yu, J. R. Barker. *J. Phys. Chem. A* **107,** 1313-1324 (2003).
6. I. Wagner, J. Karthauser, H. Strehlow. *Ber. Bunsen-Ges. Phys. Chem.* **90,** 861-867 (1986).

Data Sheet 11

Chemical equilibrium: $Cl^{\bullet}(aq) + H_2O \rightleftharpoons HOCl^{\bullet-} + H^+$ (11.1)

List of reports:

$K_{eq} = 3.4 \times 10^{-6}$ M, within a factor of 2 [1]. Actually, Jayson *et al.* did not really measure this equilibrium constant but rather derived it from their measured equilibrium constants for reactions 8.1 and 12.1 (electron transfer from Cl^- to $HO^{\bullet}$, and addition of $HO^{\bullet}$ to Cl^-). Moreover, the value they calculate takes the concentration of water into account; the value given here has been corrected to reflect water having unit activity.

$pK_a = 5.1$ [2]. The basis for this result is unclear from the published paper, but a letter from Kläning to Stanbury (21 Feb 1990) states that the result was obtained by recalculation from the optical/pulse-radiolysis data of Jayson *et al.* [1] with a correction for the optical density due to chlorine atoms. Thus, the actual equilibria measured directly are reactions 8.1 and 12.1.

$K_a = 5 \times 10^{-6}$ M, ionic strength unspecified but quite low, uncertainty unspecified [3]. Forward rate constant obtained from flash photolysis of aqueous chloroacetone. Reverse rate constant taken as the usual value for protonation reactions; Buxton (private communication) cites the reaction of $H^+ + O_2^{\bullet-}$ [4] and a host of similar rate constants tabulated in Table 12.1 of Caldin's book [5].

$K_{eq} = (6.3 \pm 1.6) \times 10^{-6}$ M, extrapolated to zero ionic strength [6]. Result obtained by flash photolysis. It is obtained from a ratio of measured rate constants and is directly dependent on the value of the equilibrium constant for reaction 12.1; they actually obtained the equilibrium constant for reaction 9.1.

Discussion

As all of the literature reports, except from Buxton *et al.* [3], actually present results derived from other equilibrium constants, we make no recommendation based on these.

The report from Buxton *et al.* [3] is based on an assumed diffusion-controlled reverse rate constant, and thus is not highly accurate; we assign an uncertainty of a factor of 2. As the forward rate constant was obtained at quite low ionic strength and the reverse rate constant was appropriate for zero ionic strength, the derived equilibrium constant reasonably approximates the value at zero ionic strength.

Recommended value:

$K_a = 5 \times 10^{-6}$ M ± factor of 2, at low ionic strength.

List of auxiliary thermodynamic data: none

References

1. G. G. Jayson, B. J. Parsons, A. J. Swallow. *J. Chem. Soc., Faraday Trans. I* **69,** 1597-1607 (1973).
2. U. K. Kläning, T. Wolff. *Ber. Bunsenges. Phys. Chem.* **89,** 243-245 (1985).
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5. E. F. Caldin. *Fast Reactions in Solution***,** John Wiley & Sons Inc., New York 263 (1964).
6. X.-Y. Yu, J. R. Barker. *J. Phys. Chem. A* **107,** 1313-1324 (2003).

Data Sheet 12

Chemical equilibrium: $HO^{\bullet} + Cl^{-} \rightleftharpoons HOCl^{\bullet-}$ (12.1)

List of reports:

$K_{eq} = 0.70 \pm 0.13\ M^{-1}$, $\mu = 1.0$ M [1]. Result obtained from optical data on the equilibrium position in pulse radiolysis experiments.

Discussion

The experiments appear to have been done quite well, and there are no conflicting data. Thus, we accept the result. It is to be expected that the equilibrium constant is not substantially affected by ionic strength.

Recommended value:

$$K_{eq} = 0.70 \pm 0.13\ M^{-1}$$

List of auxiliary thermodynamic data: none

References

1. G. G. Jayson, B. J. Parsons, A. J. Swallow. *J. Chem. Soc., Faraday Trans. I* **69,** 1597-1607 (1973).

Data Sheet 13

Chemical equilibrium: $SO_4^{\bullet-} + Cl^- \rightleftharpoons SO_4^{2-} + Cl^{\bullet}(aq)$ (13.1)

List of reports:

$K_{eq} = 1.9$ at $\mu = 0.1$ M. No uncertainty specified. Result obtained from ratio of forward and reverse rate constants [1].

$K_{eq} = 2.9 \pm 0.2$ at $\mu = 0.3$ M, and $K_{eq} = 1.2$ at $\mu = 0$ M. Results obtained from ratio of forward and reverse rate constants, with extrapolation of the ionic-strength dependent data to get the result at $\mu = 0$ [2].

Discussion

The good agreement between the two determinations of this equilibrium constant gives confidence in its value. We recommend the more recent result of Buxton *et al.* [2], because of its experimental extrapolation to $\mu = 0$ M.

Recommended value:

$K_{eq} = 1.2 \pm 0.2$ at $\mu = 0$ M

List of auxiliary thermodynamic data: none

References

1. R. E. Huie, C. L. Clifton, P. Neta. *Radiat. Phys. Chem.* **38,** 477-481 (1991).
2. G. V. Buxton, M. Bydder, G. A. Salmon. *Phys. Chem. Chem. Phys.* **1,** 269-273 (1999).

Data Sheet 14

Chemical equilibrium: $SO_4^{\bullet-} + NO_3^- \rightleftharpoons SO_4^{2-} + NO_3^{\bullet}(aq)$ (14.1)

List of reports:

$K_{eq} = (0.5 \pm 0.1)$ at ionic strength of 0.1 M to 0.2 M was determined directly from the equilibrium absorbance measurements by Løgager *et al.* [1]. They employed the same correction as Exner *et al.* [2] to extrapolate to zero ionic strength, which resulted in $K_{eq} = 0.28$ at $\mu = 0$ M.

Discussion

The determination of K_{eq} from the equilibrium absorbance relies upon the knowledge of spectra of the radicals. Although significant, the uncertainties in molar absorptivity are unlikely to bring the errors in K_{eq} outside the stated uncertainty for this value. For the extrapolated K_{eq}, Løgager *et al.* [1] have not indicated the error margins. However, error margins of no more than 30% appear reasonable in this type of extrapolations.

Recommended value:

$K_{eq} = (0.28 \pm 0.1)$, at $\mu = 0$ M.

List of auxiliary thermodynamic data: none

References

1. T. Løgager, K. Sehested, J. Holcman. *Radiat. Phys. Chem.* **41,** 539-543 (1993).
2. M. Exner, H. Herrmann, R. Zellner. *Ber. Bunsen-Ges. Phys. Chem.* **96,** 470-477 (1992).

Data Sheet 15

Chemical equilibrium: $SO_4^{\bullet-} + HNO_3 \rightleftharpoons HSO_4^- + NO_3^{\bullet}(aq)$ (15.1)

List of reports:

Løgager *et al.* [1] measured the ratio $[SO_4^{\bullet-}]/[NO_3^{\bullet}]$ as a function of $[HSO_4^-]/([NO_3^-] + [HNO_3])$ at three different H_2SO_4 concentrations, namely (0.5, 1.0, and 2.0) M. By taking $K_a(HNO_3) = 20$ M, reportedly from the work of Hood and Reilly [2], they calculated the apparent K_{eq} to be 492, 462, and 440 at (0.5, 1.0, and 2.0) M H^+, respectively.

Discussion

The K_a of HNO_3 is somewhat uncertain. The work of Hood and Reilly [2] actually does not report $K_a(HNO_3) = 20$ M; instead it reports two K_a values of 27.5 and 25 obtained with slightly different assumptions, both values are dimensionless and expressed through activities. Recalculation of the data from Løgager *et al.* [1] with the former number gives $K_{eq} = 670$, 630, and 590 at (0.5, 1.0, and 2.0) M $[H^+]$, respectively. However, the K_a value of 20 has indeed been reported by Redlich *et al.* [3]. With such an uncertainty in $K_a(HNO_3)$, the equilibrium constant of reaction 15.1 is probably not better known than within $\pm 2 \times 10^2$. Combining $K_a(HNO_3) = 20$ with $pK_a(HSO_4^-) = 1.99$ and $(K_{eq})_{14.1} = 0.28$, one obtains $(K_{eq})_{15.1} = 5.5 \times 10^2$, which is about the average of all the values above.

Recommended value:

$K_{eq} = (5 \pm 2) \times 10^2$

List of auxiliary thermodynamic data: none

References

1. T. Løgager, K. Sehested, J. Holcman. *Radiat. Phys. Chem.* **41,** 539-543 (1993).
2. G. C. Hood, C. A. Reilly. *J. Chem. Phys.* **32,** 127-130 (1960).
3. O. Redlich, R. W. Duerst, A. Merbach. *J. Chem. Phys.* **49,** 2986-2994 (1968).

Data Sheet 16

Chemical equilibrium: $NO_3^{\bullet}(aq) + Cl^- \rightleftharpoons NO_3^- + Cl^{\bullet}(aq)$ (16.1)

List of reports:

$K_{eq} = (3.3 \pm 0.2)$ at $\mu = 0$ M, calculated from the ratio of the rate constants; $k_f = (3.40 \pm 0.11) \times 10^8$ M^{-1} s^{-1} was obtained by Buxton *et al.* from pulse radiolysis, and $k_r = (1.02 \pm 0.04) \times 10^8$ M^{-1} s^{-1} from flash photolysis experiments with chloroacetone, both rate constants extrapolated to zero ionic strength [1]. The reported uncertainty in K_{eq} is conservative, as ± 0.17 for K_{eq} follows from the propagation of uncertainties in k_f and k_r.

$K_{eq} = (3.5 \pm 0.5)$ at $\mu = 0.1$-1 M, obtained from the ratio of the rate constants. Only $k_f = (3.5 \pm 0.5) \times 10^8$ M^{-1} s^{-1} was measured; the value is obtained by fitting pulse radiolysis kinetic data to a complex mechanism [2]. The literature value [1] used for k_r was rounded up to 1×10^8 M^{-1} s^{-1}; without the round-up, $K_{eq} = (3.43 \pm 0.51)$.

Discussion

Only one measurement of k_r has been reported [1]. However, this measurement is straightforward (obtained from linear dependence of $Cl^{\bullet}$ decay upon $[NO_3^-]$ in chloride-free solution) and appears to be reliable. In contrast, several earlier k_f evaluations that have been reported (1×10^8 [3], 8.8×10^6 [4], 7.1×10^7 [5], and 9.1×10^6 M^{-1} s^{-1} [6]) are most likely in error. The probable reasons for errors in the first two of these measurements have been discussed [1]. The last two values are not accompanied by sufficient details to assess their reliability. Nearly perfect agreement between k_f in the two most recent reports [1, 2] and the explanations for the complex kinetic concentration dependencies (upon $[NO_3^-]$ and $[Cl^-]$) provide good confidence in the results. We select the data of Buxton *et al.* [1] because of the smaller error, simultaneous determination of both k_f and k_r, transparent data analysis, and careful extrapolation to zero ionic strengths.

Recommended value:

$K_{eq} = (3.3 \pm 0.2)$ at $\mu = 0$ M.

List of auxiliary thermodynamic data: none

References

1. G. V. Buxton, G. A. Salmon, J. Wang. *Phys. Chem. Chem. Phys.* **1,** 3589-3593 (1999).
2. G. A. Poskrebyshev, R. E. Huie, P. Neta. *J. Phys. Chem. A* **107,** 1964-1970 (2003).
3. K.-J. Kim, W. H. Hamill. *J. Phys. Chem.* **80,** 2320-2325 (1976).
4. M. Exner, H. Herrmann, R. Zellner. *Ber. Bunsen-Ges. Phys. Chem.* **96,** 470-477 (1992).
5. P. Neta, R. E. Huie. *J. Phys. Chem.* **90,** 4644-4648 (1986).
6. Z. Zuo, Y. Katsumura, K. Ueda, K. Ishigure. *J. Chem. Soc., Faraday Trans.* **93,** 1885-1891 (1997).

Data Sheet 17

Chemical equilibrium: $NO_3^{\bullet}(aq) + ClO_3^- \rightleftharpoons NO_3^- + ClO_3^{\bullet}(aq)$ (17.1)

List of reports:

$K_{eq} = (42 \pm 6)$ at $\mu = (1\text{-}1.4)$ M (1 M HNO_3 + 0.02-0.4 M $NaClO_3$), obtained from the measurements of absorption at equilibrium as a function of $[ClO_3^-]/[NO_3^-]$ by Katsumura and co-workers [1]. The $NO_3^{\bullet}$ radical has been generated by flash photolysis of cerium nitrate. The forward and reversed rate constants are reported as $k_f = (9.0 \pm 1.2) \times 10^3$ M^{-1} s^{-1} and $k_r = (8.3 \pm 1.0) \times 10^2$ M^{-1} s^{-1}, which corresponds to $K_{eq} = 11 \pm 2$ from the ratio of the rate constants. The medium effects (high ionic strength) have not been considered.

Discussion

The authors are of the opinion that the value of K_{eq} obtained from the equilibrium position is more reliable than that obtained from the rate constants. However, this may not be the case because the equilibration is slow (milliseconds) and there is likely to be a significant net loss of radicals during that time. Such a possibility is of particular concern because of the occurrence of an unexplained first-order decay of $NO_3^{\bullet}$ in the absence of added ClO_3^- that is observed on this timescale [1, 2], and because of the fast second-order self-recombination ($2k \approx 9 \times 10^8$ M^{-1} s^{-1}) observed for $ClO_3^{\bullet}$ [1]. The latter should be very significant with the large concentration of radicals (*ca.* 15 μM) present. Furthermore, the dose dependence of K_{eq} obtained from the equilibrium position was not investigated. The net loss of radicals would tend to increase the apparent K_{eq} value, such that $K_{eq} = 42$ is probably close to an upper limit.

The determination of K_{eq} from the ratio of the rate constants is also somewhat worrisome, because the first-order decay of $NO_3^{\bullet}$ was ignored and because of the possibility that the reverse reaction is actually not with NO_3^-, but with undissociated HNO_3 present at (20-30) mM in 1 M nitric acid. By analogy with the oxidation of HNO_3/NO_3^- by $SO_4^{\bullet -}$ [3], the oxidation of HNO_3 could occur much more rapidly than that of NO_3^-. Although this possibility has not been considered, it is not unlikely that the observed equilibration (by both methods) was applied to reaction 17.2, instead of 17.1.

$$NO_3^{\bullet}(aq) + ClO_3^- + H^+ \rightleftharpoons HNO_3 + ClO_3^{\bullet}(aq) \quad (17.2)$$

With $pK_a(HNO_3) = -1.3$, one obtains $K_{eq} = K_a(HNO_3) \times K_{eq}' \approx 20K_{eq}'$.

Recommended value:

K_{eq} = 10-50, in 1 M HNO_3 (can be approx. 20 times larger, if the reverse reaction is with HNO_3)

List of auxiliary thermodynamic data: none

References

1. Z. Zuo, Y. Katsumura, K. Ueda, K. Ishigure. *J. Chem. Soc., Faraday Trans.* **93,** 533-536 (1997).
2. P. H. Wine, R. L. Mauldin, R. P. Thorn. *J. Phys. Chem.* **92,** 1156-1162 (1988).
3. T. Løgager, K. Sehested, J. Holcman. *Radiat. Phys. Chem.* **41,** 539-543 (1993).

Data Sheet 18

Chemical equilibrium: $SO_4^{\bullet-} + H_2O \rightleftharpoons HSO_4^- + HO^\bullet(aq)$ (18.1)

List of reports:

No *K* has been reported,, but Wine and co-workers [1] report measurements of both forward, (3.6 ± 0.9) × 10^2 s^{-1}, and reverse, (3.5 ± 0.5) × 10^5 M^{-1} s^{-1}, rate constants, from which K_{eq} = (1.0 ± 0.3) × 10^{-3} M is calculated.

Discussion

Four laboratories have determined the rate constant of the forward reaction, k_f, with good internal consistency. In all cases, very similar rate constants were obtained by producing the $SO_4^{\bullet-}$ radical from $S_2O_8^{2-}$ and by measuring the disappearance of the characteristic absorption of SO_4^- around 450 nm. The reported values are as follows: (360 ± 90) s^{-1} [1], (500 ± 60) s^{-1} [2], (660 ± 40) s^{-1} [3], and (440 ± 50) s^{-1} [4]. Bao and Barker have found that simulations with the last value together with the rate constant for self-recombination of $SO_4^{\bullet-}$ reproduce very well the experimental traces at low ionic strength [4]. They also report low impurity contents. A much higher value for k_f, namely (9.4 ± 3.7) × 10^3 s^{-1}, is reported by Ivanov *et al.* [5]. However, as the primary aim of the authors was not the determination of this value, they did not take special precautions to avoid impurities. In fact, they attribute their high k_f value to impurities and to the high ionic strengths of about 1 M employed. Excluding this value, the average of k_f comes out as (4.9 ± 1.3) × 10^2 s^{-1} and this number is selected.

Three direct determinations for the reverse reaction rate constant, k_r, are known: 6.9 × 10^5 [6], (3.5 ± 0.5) × 10^5 [1], and 4.7 × 10^5 M^{-1} s^{-1} [7]. The agreement is satisfactory. The first and last values are obtained by pulse radiolysis under conditions where radical-radical reactions may play a role. In addition, the last determination has been made in concentrated H_2SO_4, where the reaction $HO^\bullet + H_2SO_4$ dominated the $HO^\bullet$ decay. The second value, obtained by Tang *et al.* [1] using flash photolysis of H_2O_2 to generate $HO^\bullet$, appears to be more accurate and is selected, because of the special care taken to minimize radical-radical and other interfering reactions.

Recommended value:

$K_{eq} = (1.4 \pm 0.4) \times 10^{-3}$ M, from the selected $k_f = (4.9 \pm 1.3) \times 10^2$ s^{-1} and $k_r = (3.5 \pm 0.5) \times 10^5$ M^{-1} s^{-1}

List of auxiliary thermodynamic data: none

References

1. Y. Tang, R. P. Thorn, R. L. Maudlin, P. H. Wine. *J. Photochem. Photobiol., A* **44,** 243-258 (1988).
2. W. J. McElroy, S. J. Waygood. *J. Chem. Soc., Faraday Trans.* **86,** 2557-2564 (1990).
3. H. Herrmann, A. Reese, R. Zellner. *J. Mol. Struct.* **348,** 183-186 (1995).
4. Z.-C. Bao, J. R. Barker. *J. Phys. Chem.* **100,** 9780-9787 (1996).
5. K. L. Ivanov, E. M. Glebov, V. F. Plyusin, Y. V. Ivanov, V. P. Grivin, N. M. Bazhin. *J. Photochem. Photobiol. A* **133,** 99-104 (2000).
6. E. Heckel, A. Henglein, G. Beck. *Ber. Bunsen-Ges. Phys. Chem.* **70,** 149-154 (1966).
7. P.-Y. Jiang, Y. Katsumura, R. Nagaishi, M. Domae, K. Ishikawa, K. Ishigure, Y. Yoshida. *J. Chem. Soc., Faraday Trans.* **88,** 1653-1658 (1992).

Data Sheet 19

Chemical equilibrium: $HO^{\bullet}(aq) + Tl^{+}(aq) \rightleftharpoons TlOH^{+}(aq)$ (19.1)

List of reports:

$K_{eq} = (5.8 \pm 1.0) \times 10^{3}\ M^{-1}$ at 25 °C and $\mu = 0.01$ M; $K_{eq} = (3.4 \pm 0.5) \times 10^{3}\ M^{-1}$ at 25 °C and $\mu = 1.00$ M ($LiClO_4$) [1]. Data obtained by pulse radiolysis with optical detection. Result obtained from the ratio of the forward and reverse rate constants and also from the position of the equilibrium. Data analysis required the simultaneous determination of the pK_a of Tl^{2+} (reaction 20.1).

Discussion

These sole determinations of the equilibrium constant appear to be reliable and accurate. It is not expected to be significantly dependent on ionic strength, and this expectation is supported by the data of Schwarz and Dodson at $\mu = 1.0$ and 0.01 M [1].

Indiscriminate use of this equilibrium constant with the pK_a of Tl^{2+} can lead to a flawed value for $E°(HO^{\bullet}/HO^{-})$ if it is assumed that the pK_a of Tl^{2+} is independent of ionic strength. To avoid this problem we follow Schwarz *et al.* and use $E°' = +(2.217 \pm 0.003)$ V for the Tl^{2+}/Tl^{+} couple in 1 M ionic strength (see data sheet for reaction 21.1), combine it with the $K_a = (1.2 \pm 0.2) \times 10^{-5}$ M of Tl^{2+} in the same medium (reaction 20.1) and the above K_{eq} in the same medium to derive $E°' = +(2.718 \pm 0.006)$ V at $\mu = 1.00$ M for $HO^{\bullet}(aq) + H^{+}(aq) + e^{-} \rightleftharpoons H_2O(l)$. With the approximation that $HO^{\bullet}(aq)$ and $H_2O(l)$ have activity coefficients of unity while $H^{+}(aq)$ has an activity coefficient of 0.85, we then derive $E° = +(2.722 \pm 0.006)$ V for $HO^{\bullet}(aq) + H^{+}(aq) + e^{-} \rightleftharpoons H_2O(l)$. Use of the NBS value for $\Delta_f G°(H_2O(l))$ then yields $\Delta_f G° = +(25.5 \pm 0.6)\ kJ\ mol^{-1}$ for $HO^{\bullet}(aq)$. Use of the NBS value [2] of $\Delta_f G°$ for $OH^{-}(aq)$ ($= -157.244 \pm 0.08\ kJ\ mol^{-1}$) leads to $E° = +(1.894 \pm 0.006)$ V for the OH/OH^{-} redox couple. We view the approximations and uncertainties introduced by this method to be superior to those involved in methods that use $E°(Tl^{2+/+})$ and equilibrium constants extrapolated to zero ionic strength.

Recommended values:

$HO^{\bullet}(aq) + Tl^{+}(aq) \rightleftharpoons TlOH^{+}(aq)$ $K_{eq} = (5.8 \pm 1.0) \times 10^{3}\ M^{-1}$
$HO^{\bullet}(aq) + Tl^{+}(aq) \rightleftharpoons TlOH^{+}(aq)$ $K_{eq} = (3.4 \pm 0.5) \times 10^{3}\ M^{-1}$ at $\mu = 1.00$ M

$HO^\bullet(aq) + H^+(aq) + e^- \rightleftharpoons H_2O(l)$ $E^{\circ\prime} = +(2.718 \pm 0.006)$ V at $\mu = 1.00$ M

$HO^\bullet(aq) + H^+(aq) + e^- \rightleftharpoons H_2O(l)$ $E^\circ = +(2.722 \pm 0.006)$ V

$HO^\bullet(aq) + e^- \rightleftharpoons HO^-(aq)$ $E^\circ = +(1.894 \pm 0.006)$ V

$HO^\bullet(aq)$ $\Delta_f G^\circ = +(25.5 \pm 0.6)$ kJ mol^{-1}

List of auxiliary thermodynamic data: $\Delta_f G^\circ$ for $HO^-(aq)$ and $H_2O(l)$, K_{eq} for reactions 20.1 and 21.1.

References

1. H. A. Schwarz, R. W. Dodson. *J. Phys. Chem.* **88,** 3643-3647 (1984).
2. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall. *J. Phys. Chem. Ref. Data* **11,** Suppl. No. 2 (1982).

Data Sheet 20

Chemical equilibrium: $Tl^{2+}(aq) + H_2O(l) \rightleftharpoons TlOH^{+}(aq) + H^{+}(aq)$ (20.1)

List of reports:

pK_a = (4.7 ± 0.2) at 21 °C, indeterminate ionic strength [1]. The result was obtained from pulse radiolysis, using both conductivity and optical detection.

pK_a = 4.65 probably at room temperature, unspecified ionic strength [2]. Result obtained from pulse radiolysis with conductivity detection.

$K_a = (1.7 \pm 0.3) \times 10^{-5}$ M at $\mu = 0.01$ M (pK_a = 4.70) at 25 °C; $K_a = (1.2 \pm 0.2) \times 10^{-5}$ M at μ = 1.00 M (pK_a = 4.93) at 25 °C [3]. Data obtained from pulse radiolysis with optical detection. Results obtained from both the ratio of forward and reverse rate constants and also from the equilibrium change in optical density. Both of the methods relied on analyses that adjusted the observed data by functions of the equilibrium constant for $Tl^{+} + HO^{\bullet} \rightleftharpoons TlOH^{+}$ (reaction 19.1).

Discussion

The two earlier determinations neglected the effects of reaction 19.1 and thus the result of Schwarz and Dodson [3] is to be preferred. By comparison with the ionic strength dependence of the pK_a of Ni^{2+}, the reaction is expected to be significantly affected by ionic strength [4].

In combination with the pK_a at 0.01 M, use of the NIST value [5] of $\Delta_f G°$ for H_2O and the $\Delta_f G°$ value (= 183.1 ± 0.7 kJ mol^{-1} from Longhi's Tl^{+} data [6]) for Tl^{2+} that we have recommended in the evaluation of reaction 21.1 (reaction of Tl^{2+} with Fe^{n+}) leads to $\Delta_f G°$ = –(26.8 ± 0.8) kJ mol^{-1} for $TlOH^{+}(aq)$ at μ = 0.01 M; this result is somewhat incorrect because it combines an ionic-strength dependent formal pK_a with an ideal Gibbs energy for Tl^{2+}. Use of the NBS value of $\Delta_f G°$ for $TlOH^{2+}(aq)$ leads to $E°$ = +0.113 ± 0.008 V for the $TlOH^{2+}/TlOH^{+}$ couple. Use of the NBS value of $\Delta_f G°$ for $TlOH(aq)$ leads to $E°$ = +(1.690 ± 0.008) V for the $TlOH^{+}/TlOH$ couple.

Recommended values:

$Tl^{2+}(aq) + H_2O(l) \rightleftharpoons TlOH^{+}(aq) + H^{+}(aq)$	$K_a = (1.7 \pm 0.3) \times 10^{-5}$ M at μ = 0.01 M
$Tl^{2+}(aq) + H_2O(l) \rightleftharpoons TlOH^{+}(aq) + H^{+}(aq)$	$K_a = (1.2 \pm 0.2) \times 10^{-5}$ M at μ = 1.00 M
$TlOH^{+}(aq)$	$\Delta_f G°$ = –26.8 ± 0.8 kJ mol^{-1} at μ = 0.01 M

$TlOH^{2+}(aq) + e^- \rightleftharpoons TlOH^+(aq)$ $E° = 0.113 \pm 0.008$ V
$TlOH^+(aq) + e^- \rightleftharpoons TlOH(aq)$ $E° = 1.690 \pm 0.008$ V

List of auxiliary thermodynamic data: NBS $\Delta_f G°$ for $H_2O(l)$, $TlOH^{2+}(aq)$, and $TlOH(aq)$; $\Delta_f G°$ for $Tl^{2+}(aq)$ (reaction 21.1).

References

1. P. O'Neill, D. Schulte-Frohlinde. *J. Chem. Soc., Chem. Commun.* 387-388 (1975).
2. M. Bonifacic, K.-D. Asmus. *J. Chem. Soc., Dalton Trans.* 2074-2076 (1976).
3. H. A. Schwarz, R. W. Dodson. *J. Phys. Chem.* **88,** 3643-3647 (1984).
4. D. D. Perrin. *J. Chem. Soc.* 3644-3648 (1964).
5. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall. *J. Phys. Chem. Ref. Data* **11,** Suppl. No. 2 (1982).
6. P. Longhi, T. Mussini, S. Rondinini, B. Sala. *J. Chem. Thermodynamicdynam.* **11**, 73-81 (1979).

Data Sheet 21

$E°(Tl^{2+}/Tl^{+})$

Chemical equilibrium: $Tl^{3+} + Fe^{2+} \rightleftharpoons Tl^{2+} + Fe^{3+}$ (21.1)

List of reports:

As all determinations of this equilibrium constant are based on the kinetics of the reaction of Fe^{2+} with Tl^{3+}, we present the mechanism of that reaction in order to define the rate constants involved. According to Ashurst and Higginson [1], the mechanism is

$$Tl^{3+} + Fe^{2+} \rightleftharpoons Tl^{2+} + Fe^{3+} \qquad k_1, k_{-1}, K_{eq} \qquad (21.1)$$
$$Tl^{2+} + Fe^{2+} \rightarrow Tl^{+} + Fe^{3+} \qquad k_2 \qquad (21.2)$$

As written, the reactions pertain to unhydrolyzed aqua ions. Ashurst and Higginson report that the apparent second-order forward rate constant is sensitive to $[H^+]$, and the overall rate law has two terms: one indicating a transition state having the composition $Fe^{2+}/Tl^{3+}/HO^-$ and the other being $Fe^{2+}/Tl^{3+}/2HO^-$. Thus, the use of forward and reverse rate constants obtained at different values of pH introduces a degree of error, as does the use of rate constants at different ionic strengths (see Discussion below). We will thus refer to the reported equilibrium constants as "apparent" K_{app}.

$K_{app} = 4.2 \times 10^{-8}$ at undefined ionic strength and pH was reported by Falcinella *et al.*, who obtained it from the ratio of the forward and reverse rate constants [2]. Flash photolysis was used to generate Tl^{2+} and observe the reverse reaction, for which a rate constant $k_{-1} = (1.1 \pm 0.15) \times 10^6$ M^{-1} s^{-1} at $\mu = 0.30$ M and $[H^+] = 0.25$ M was obtained. The forward rate constant k_1 was from the kinetic study by Ashurst and Higginson on the overall Tl^{3+} reaction with Fe^{2+} [1]. Falcinella *et al.* selected from Ashurst and Higginson a value for k_1 of 4.60×10^{-2} M^{-1} s^{-1} at $\mu = 3.0$ M and $[H^+] = 0.40$ M.

$K_{app} = (4.1 \pm 0.6) \times 10^{-8}$ in 1 M $HClO_4$ [3]. Schwarz *et al.* used pulse radiolysis to determine a rate constant $k_2 = (6.7 \pm 0.7) \times 10^6$ M^{-1} s^{-1}. The work of Ashurst and Higginson on the overall reaction of Tl^{3+} with Fe^{2+} was repeated, but in 1.1 M $HClO_4$; under these conditions, the values $k_1 = (1.39 \pm 0.02) \times 10^{-2}$ M^{-1} s^{-1} and $k_{-1}/k_2 = (0.051 \pm 0.005)$ were obtained from the Fe^{3+} inhibition of the kinetics. These measurements led to a value $k_{-1} = (3.4 \pm 0.5) \times 10^5$ M^{-1} s^{-1}, where we have inferred the indicated uncertainty from their data; hence, $K_{\text{app}} = k_{-1}/k_1 = (4.1 \pm 0.6) \times 10^{-8}$.

$K_{\text{app}} = 1.8 \times 10^{-7}$ at mixed ionic strength [4]. Falcinella *et al.* used flash photolysis to measure the rate constant of $(2.6 \pm 0.1) \times 10^6\ \text{M}^{-1}\ \text{s}^{-1}$ for k_2 at $\mu = 0.30$ M, $[\text{H}^+] = 0.25$ M. Then the pH-dependent data of Ashurst and Higginson were extrapolated to obtain $k_{-1}/k_2 = 0.10$ at 0.25 M $[\text{H}^+]$. These two pieces of data yielded $k_{-1} = 2.6 \times 10^5\ \text{M}^{-1}\ \text{s}^{-1}$ at $\mu = 0.30$ M and $[\text{H}^+] = 0.25$ M. Combination of this k_{-1} with Ashurst and Higginson's value for k_1 (at $\mu = 3.0$ M and $[\text{H}^+] = 0.40$ M) then yielded the indicated equilibrium constant; obviously, this equilibrium constant is based on two rate constants obtained under conditions of different ionic strength and $[\text{H}^+]$. Despite the four-fold discrepancy between k_{-1} determined in this way and that determined directly by Falcinella *et al.* [2], the two values were deemed "in reasonable agreement".

$K_{\text{app}} = 8 \times 10^{-8}$ in 1 M $HClO_4$ was obtained by Dodson from the ratio of the forward and reverse rate constants [5], the forward rate constant being the one determined by Schwarz *et al.* [3], and the reverse being obtained from the study of Fe(II)-induced radioactive label exchange between Tl(III) and *Tl(I).

$K_{\text{eq}} = 4.4 \times 10^{-8}$ at $\mu = 1.5$ and 3 M was derived by Nord through reanalysis of prior results in the literature [6]. Nord intended this value for equilibrium between purely aqua ions, hence K_{eq} notation. The reanalysis showed that in the actual reaction mechanism an important reaction pathway involves the hydrolyzed species, *i.e.*, the reaction

$$\text{TlOH}^{2+} + \text{Fe}^{2+} \rightleftharpoons \text{Tl}^{2+} + \text{FeOH}^{2+} \qquad (21.3)$$

The equilibrium constant for this reaction was derived to be 6.4×10^{-10} at $\mu = 1.5$, that is much smaller than for reaction 1. We note that: (i) Nord's interpretation of the acid dependence differs from that of Ashurst and Higginson and (ii) Nord's treatment entailed the use of literature values for the $\text{p}K_a$ of Fe^{3+} and Tl^{3+} as well as difficult assumptions concerning their change with ionic strength in the 1.5 M to 3 M region.

Discussion

All experimental evaluations of the equilibrium constant have three features in common. These evaluations: (1) are based on forward and reverse rate constants; (2) have been performed under conditions of partial Tl^{3+} and Fe^{3+} hydrolysis to TlOH^{2+} and FeOH^{2+}; (3) pertain to solutions with very high ionic strengths in excess of 1 M. The first and the second features imply that the estimated equilibrium constants are, in fact, the apparent parameters based on analytical concentrations of the reactants and products

$$K_{app} = [\mathrm{Tl(II)}][\mathrm{Fe(III)}]/[\mathrm{Tl(III)}][\mathrm{Fe(II)}] \qquad (21.4)$$

Only when forward and reverse rate constants are both measured in the same medium, will K_{app} be equal to their ratio, as both rate constants are strongly medium-dependent. The K_{app} value is related to the thermodynamic equilibrium constant, K_{eq}^0, through activity coefficients (γ) and fractions (F) of unhydrolyzed trivalent ions

$$K_{eq}^0 = K_{app} \times [F(\mathrm{Fe}^{3+})/F(\mathrm{Tl}^{3+})] \times [\gamma(\mathrm{Tl}^{2+})\gamma(\mathrm{Fe}^{3+})/\gamma(\mathrm{Tl}^{3+})\gamma(\mathrm{Fe}^{2+})] \qquad (21.5)$$

Hydrolysis of divalent ions is negligible under all reported conditions. The fractions F are also medium-dependent; for example, $F(\mathrm{Tl}^{3+}) = [\mathrm{H}^+]/(K_a(\mathrm{Tl}^{3+}) + [\mathrm{H}^+])$, where $K_a(\mathrm{Tl}^{3+})$ is the Tl^{3+} hydrolysis constant under prevailing medium conditions $K_a(\mathrm{Tl}^{3+}) = K_a^0\gamma(\mathrm{Tl}^{3+})/\gamma(\mathrm{TlOH}^{2+})\gamma(\mathrm{H}^+)$. The very high ionic strengths used in all studies makes rigorous derivation of K_{eq}^0 for reaction 1 under standard conditions unfeasible, because the activity coefficients at these ionic strengths are dependent upon specific ion interactions and are unavailable for all the ions involved. A useful estimate can, however, be made assuming that the activity coefficients ratio $\gamma(\mathrm{Tl}^{2+})\gamma(\mathrm{Fe}^{3+})/\gamma(\mathrm{Tl}^{3+})\gamma(\mathrm{Fe}^{2+})$ is close to unity; implicit in this assumption is the similarity between Fe and Tl cations with respect to their interactions with anions. Then $K_{eq}^0 = K_{app}\, F(\mathrm{Fe}^{3+})/F(\mathrm{Tl}^{3+})$. The only experimental study in which both forward and reverse rate constant have been measured in the same medium (1 M $\mathrm{HClO_4}$) is that by Schwarz *et al.* [3]. The hydrolysis constants are available at $\mu = 3.0$ M, $K_a(\mathrm{Fe}^{3+}) \approx 0.001$ and $K_a(\mathrm{Tl}^{3+}) \approx 0.073$ M. Assuming no significant change when the ionic strength is changed to $\mu = 1.0$ M, we compute $F(\mathrm{Fe}^{3+}) \approx 0.999$ and $F(\mathrm{Tl}^{3+}) \approx 0.932$ under the conditions of Schwarz *et al.* and using their $K_{app} = 4.1 \times 10^{-8}$, we calculate $K_{eq}^0 \approx 4.4 \times 10^{-8}$, which is identical to the value derived by Nord through a somewhat different and more involved procedure. An uncertainty of $\pm 1.0 \times 10^{-8}$ for K_{eq}^0 appears reasonable under the assumptions made.

Although Dodson's induced-exchange study [5] was done in 1 M $\mathrm{HClO_4}$, as had been the earlier work from the same group, it yielded an about 2 times larger K_{app}. However, this result depended upon both the detailed knowledge of mechanism for the exchange and the value of the quantum yield for photo induced exchange that was reported by Stranks and Yandell [7]. In the light of a subsequent work by Schwarz and Dodson [8], both the mechanism and the quantum yield require a revision. Specifically, it is now understood that the $\mathrm{HO}^\bullet$ radical is generated from

Tl(II), which sets up a chain reaction of radiolabel exchange [9]. This effect renders the exchange quantum yield by Stranks and Yandell [7] highly uncertain. This uncertainty propagates into Dodson's study [5], making the reported value of K_{app} much more uncertain than that in the previous study of Schwarz *et al.* [3] in the same medium.

By means of $K_{\mathrm{app}} = (4.1 \pm 0.6) \times 10^{-8}$ in 1 M $HClO_4$ and the standard potential of +0.738 ± 0.001 V for the Fe(III)/Fe(II) couple in the same medium [10], Schwarz *et al.* derived a value of +0.301 ± 0.003 V for the formal potential of Tl(III)/Tl(II) couple in 1 M $HClO_4$ [3]. Schwarz *et al.* then used the formal Tl(III)/Tl(I) potential (+1.259 ± 0.001 V) in the same medium from Stonehill [11] and from Sherrill and Hass [12] to derive $E°' = +(2.217 \pm 0.003)$ V for the Tl^{2+}/Tl^{+} potential in 1 M $HClO_4$.

By using $K_{\mathrm{eq}}^{0} = (4.4 \pm 1.0) \times 10^{-8}$ and the accurate $E°(Fe^{3+}/Fe^{2+}) = +0.770 \pm 0.002$ V [13], we obtain $E°(Tl^{3+}/Tl^{2+}) = +0.335 \pm 0.006$ V.

The two-electron potential $E°'(Tl^{3+}/Tl^{+}) = +(1.280 \pm 0.002)$ V has been reported by Biedermann [14]; this is actually the formal potential in 3 M $NaClO_4$. Stonehill used extrapolations to zero ionic strength and reported that the true standard potential is +1.280 V; we infer an uncertainty of ± 0.003 V from his data [11]. Apparently, the formal potential and standard potential are fortuitously identical. With this potential and $E°(Tl^{3+}/Tl^{2+})$ as selected above we calculate $E°(Tl^{2+}/Tl^{+}) = +2.225 \pm 0.007$ V. The NIST tables [15] give $-(32.40 \pm 0.4)$ kJ mol^{-1} for $\Delta_f G°$ of Tl^{+} that lead to $\Delta_f G°(Tl^{2+}) = (182.3 \pm 0.8)$ kJ mol^{-1}. This value is 6.6 kJ mol^{-1} higher than $\Delta_f G°(Tl^{2+})$ given by Schwarz *et al.* [3] mainly because these authors used older $\Delta_f G°$ values for Tl^{3+}, Fe^{3+}, and Fe^{2+} taken from Latimer [16] to arrive at $\Delta_f G°(Tl^{2+})$ from their $K_{\mathrm{app}} = 4.1 \times 10^{-8}$. Longhi *et al.* claim that the NBS value for $\Delta_f G°$ of Tl^{+} is significantly in error and should be corrected to $-(31.56 \pm 0.03)$ kJ mol^{-1} [17]. Use of the result of Longhi *et al.* in combination with our recommended value for $E°(Tl^{2+}/Tl^{+})$ (2.225 ± 0.007 V) leads to $\Delta_f G°(Tl^{+}) = +(183.1 \pm 0.7)$ kJ mol^{-1}; we are unsure whether to recommend this revised Gibbs energy because it depends on non-NIST data [15] and it is unclear to what extent other NIST data [15] are dependent on the $\Delta_f G°$ of Tl^{+}.

Recommended values:

$\mathrm{Tl(III)} + \mathrm{Fe(II)} \rightleftharpoons \mathrm{Tl(II)} + \mathrm{Fe(III)}$	$K_{\mathrm{app}} = (4.1 \pm 0.6) \times 10^{-8}$ (1 M $HClO_4$)	(21.6)
$Tl^{3+} + Fe^{2+} \rightleftharpoons Tl^{2+} + Fe^{3+}$	$K_{\mathrm{eq}}° = (4.4 \pm 1.0) \times 10^{-8}$	(21.7)
$Tl^{3+} + e^{-} \rightleftharpoons Tl^{2+}$	$E° = +0.335 \pm 0.006$ V	(21.8)
$Tl^{2+} + e^{-} \rightleftharpoons Tl^{+}$	$E° = +2.225 \pm 0.007$ V	(21.9)
$\mathrm{Tl(III)} + e^{-} \rightleftharpoons Tl^{2+}$	$E°' = +0.301 \pm 0.003$ V at $\mu = 1.00$ M ($HClO_4$)	(21.10)
$Tl^{2+} + e^{-} \rightleftharpoons Tl^{+}$	$E°' = +2.217 \pm 0.003$ V at $\mu = 1.00$ M ($HClO_4$)	(21.11)

$Tl^{2+}(aq)$ $\Delta_f G° = +182.3 \pm 0.8$ kJ/mol (NIST) (21.12)

$Tl^{2+}(aq)$ $\Delta_f G° = +183.1 \pm 0.7$ kJ/mol (Longhi) (21.13)

List of auxiliary thermodynamic data: K_a of Fe^{3+} (~ 0.001 M at $\mu = 3.0$ M) and Tl^{3+} (~ 0.073 M at $\mu = 3.0$ M); $E°(Fe^{3+}/Fe^{2+}) = +(0.770 \pm 0.002)$ V; $E°(Tl^{3+}/Tl^{+}) = +(1.280 \pm 0.002)$ V; $\Delta_f G°(Tl^{+}) = -(32.40 \pm 0.4)$ kJ mol^{-1}.

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Data Sheet 22

HNO and NO$^\bullet$

Chemical equilibrium: $HNO(g) \rightleftharpoons HNO(aq)$ (22.1)

List of reports:

$\Delta_h G° = –14$ kJ mol^{-1}, obtained from equating hydration Gibbs energy of HNO to that of HOCl [1].

$\Delta_h G° = –5.0$ kJ mol^{-1}, obtained from equating hydration Gibbs energy of HNO to that of HCN [2].

Discussion

Here we consider the HNO tautomer in its singlet ground state with the H atom attached to the N atom. Although the NOH tautomer with the H atom bound to the O atom, whose ground state is triplet, does exist, at least in the gas phase [3], this species is not evaluated here.

The enthalpy of HNO formation in the gas phase has been reviewed and the value of +107.1 kJ mol^{-1} has been recommended [4]. The uncertainty in the statistical sense was not given, but the "conservative" error limits were +(2.5 and –0.4) kJ mol^{-1}. Taking these limits into account, we will use $\Delta_f H°(HNO)_g = +(107.8 \pm 1.6)$ kJ mol^{-1} for the purposes of this evaluation. From this value and the tabulated entropy $S°(HNO)_g = 220.72$ J K^{-1} mol^{-1} [5], we calculate $\Delta_f G°(HNO)_g = +120.6 \pm 1.6$ kJ mol^{-1}.

Due to substantial instability of HNO toward recombination $HNO + HNO = N_2O + H_2O$ [6-8], its hydration energetics could not yet be evaluated experimentally, so that both reported values are analogy-based estimates. While Stanbury suggested HOCl as a proxy for HNO [1], Shafirovich and Lymar preferred HCN [2]. The latter appears to be a somewhat better choice because, unlike HOCl, both HNO and HCN do not contain an OH group that participates in three hydrogen bonds with water and thereby dominates the enthalpy of hydration [9, 10]. From this perspective, the unhydrolyzed formaldehyde, H_2CO, or acetaldehyde, CH_3CHO, appear to be as good of a model for HNO hydration as does HCN. From the overall hydration Gibbs energies that pertain to the equilibrium mixtures of hydrolyzed and unhydrolyzed forms of aldehydes in water $\Delta_h G°$(formaldehyde) = –20.5 and $\Delta_h G°$(acetaldehyde) = –6.69 kJ mol^{-1} [11], and the aldehyde hydrolysis $RCHO + H_2O = RCH(OH)_2$ equilibrium constants $K_{hyd}(H_2CO) = 1270$ [12] and $K_{hyd}(CH_3CHO) = 1.4$ [13] at 25 °C, we obtain $\Delta_h G° = –2.8$ kJ mol^{-1} for H_2CO and $\Delta_h G° = –$

4.5 kJ mol^{-1} for CH_3CHO. From the NBS Tables [14] $\Delta_f G°(HCN)_g$ = 124.7 kJ mol^{-1} and $\Delta_f G°(HCN)_{aq}$ = 119.7 kJ mol^{-1}, it follows that $\Delta_h G°(HCN)$ = –5.0 kJ mol^{-1}.

We thus adopt the average of hydration Gibbs energies for HCN, H_2CO and CH_3CHO; that is, –(4.1 ± 1.2) kJ mol^{-1} at 25 °C as the best estimate for $\Delta_h G°(HNO)$. With this value and using $\Delta_f G°(HNO)_g$ = +(120.6 ± 1.6) kJ mol^{-1} derived above, we calculate $\Delta_f G°(HNO)_{aq}$ = (116.5 ± 2.0) kJ mol^{-1}.

Recommended values:

$\Delta_h G°(HNO)$ = –(4.1 ± 1.2) kJ mol^{-1}.

$\Delta_f G°$ = (116 ± 2) kJ mol^{-1} for HNO(*aq*).

Electrode reaction: $NO^{\bullet} + H^+ + e^- \rightleftharpoons HNO$ (22.2)

List of reports:

$E°(NO^{\bullet}, H^+/HNO)$ = –0.14 V, obtained from an analogy-based estimate of the Gibbs energy of hydration of HNO [2].

Discussion

Here we consider the $NO^{\bullet}$ reduction to nitroxyl (HNO) in its singlet ground state with the H atom attached to the N atom.

At present, no redox equilibria involving HNO have been experimentally investigated. This potential can only be evaluated from the Gibbs energies of aqueous $NO^{\bullet}$ and HNO which are: $\Delta_f G°(NO^{\bullet})_{aq}$ = +(102.0 ± 0.2) kJ mol^{-1} (see Data Sheet 90) and $\Delta_f G°(HNO)_{aq}$ = (116.5 ± 2.0) kJ mol^{-1} (see above). Using these values, we obtain $E°(NO^{\bullet}, H^+/HNO)$ = –(0.145 ± 0.021) V.

Recommended value:

$E°(NO^{\bullet}, H^+/HNO)$ = –(0.15 ± 0.02) V.

Nomenclature: $NO^{\bullet}$, oxidonitrogen(•), oxoazanyl or nitrogen monoxide, nitric oxide is outdated. HNO, hydridooxidonitrogen, or azanone, nitrosyl hydride is outdated.

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Data Sheet 23

Ozone/Ozonide

Chemical equilibrium: $O_2(aq) + O^{\bullet-} \rightleftharpoons O_3^{\bullet-}$ (23.1)

Gzapski (1971) [1]
Review, $k_1 = (3.0 \pm 0.5) \times 10^9\ M^{-1}s^{-1}$ [2], $k_{-1} = (5.0 \pm 0.5)10^3\ s^{-1}$, $K = (0.6 \pm 0.1) \times 10^6\ M^{-1}$.

Elliot and McCracken (1989) [3]

Determination of K as a function of temperature from forward and backward rate constants, interpolated for 25°C. $K = (1.4 \pm 0.1) \times 10^6\ M^{-1}$.

Chemical equilibrium: $O_3(aq) + ClO_2^- \rightleftharpoons O_3^{\bullet-} + ClO_2^{\bullet}(aq)$ (23.2)

Kläning, Sehested and Holcman (1985) [4]
The calculation of the standard potential involves (i) $K(23.2) = (22 \pm 6)$, determined at low ionic strength and at (22 ± 1) °C from the forward and backward rate constants of $(4 \pm 1) \times 10^6\ M^{-1}s^{-1}$ and $(1.8 \pm 0.2) \times 10^5\ M^{-1}s^{-1}$, respectively, (ii) a new determination of $E°(ClO_2^{\bullet}/ClO_2^-) = +(0.934 \pm 0.002)$ V at 25 °C, and (iii) is based on $\Delta_fG°(O_3)aq = +174.9\ kJ\ mol^{-1}$.

$E°(O_{3aq}/O_3^{\bullet-}) = +(1.01 \pm 0.02)$ V. $\Delta_fG°(O_3^{\bullet-}) = +77.1\ kJ\ mol^{-1}$

Discussion

The first estimate of $E°(O_{3aq}/O_3^{\bullet-})$ [5] was based on the rate constants given in Ref. 1 and the following Gibbs energies: $\Delta_fG°(O_2)aq = +3.8\ kcal\ mol^{-1}$ ($+15.9\ kJ\ mol^{-1}$), $\Delta_fG°(O^{\bullet-}) = +22.4\ kcal\ mol^{-1}$ ($+93.7\ kJ\ mol^{-1}$), and $\Delta_fG°(O_3)aq = +41.6\ kcal\ mol^{-1}$ ($+174.1\ kJ\ mol^{-1}$), and resulted in a value of +1.00 V, and a standard Gibbs energy of formation of $O_3^{\bullet-}$ of $+18.5\ kcal\ mol^{-1}$ (+77.4 kJ/mol).

$\Delta_fG°(O_3)g$ is $+163.2\ kJ/mol^{-1}$ [6], and Henry's constant of O_3 is 1.03×10^{-2} M/0.100 MPa [7], from which a $\Delta_sG°$ of $+11.3\ kJ\ mol^{-1}$ follows; $\Delta_fG°(O_3)aq$ is therefore $+174.5\ kJ\ mol^{-1}$. Given a Gibbs energy change of $-35.1\ kJ\ mol^{-1}$ for Reaction 23.1, see above [3] and a $\Delta_fG°(O^{\bullet-})$ of +93.1 1.7 $kJ\ mol^{-1}$ (see Data sheet 2), $E°(O_3/O_3^{\bullet-}) = +(1.036 \pm 0.020)$ V and $\Delta_fG°(O_3^{\bullet-}) = +74.6\ kJ\ mol^{-}$

^{1}. The error is determined mainly by that of $\Delta_{f}G°(O^{\bullet -})$. This result is in good agreement with that of Kläning *et al.*[4], which has an estimated error in $E°(O_{3aq}/O_3^{\bullet -})$ of 0.02 V.

The pK_a of $HO_3^{\bullet}$ is not known with certainty, and an accurate determination may be precluded by rapid dissociation into $HO^{\bullet}$ and O_2. Values of 6.15 [8] and 8.2 [9] are found in the literature, while a value of −2 is expected on the basis of a rule that relates the pK_a to the ratio of O- to H-atoms (pK_a = 19 – 7[O]/[H]) [1]. Computational studies also support a pK_a near –2 [10]. No recommendation can be made.

Recommended values:

$K(23.1) = (1.4 \pm 0.1) \times 10^{6}\ M^{-1}$.
$\Delta_{f}G°(O_3^{\bullet -}) = +(75 \pm 2)$ kJ/mol^{-1}.
$E°(O_3/O_3^{\bullet -}) = +(1.03 \pm 0.02)$ V, or $+(0.91 \pm 0.02)$ V ($pO_2 = 0.100$ MPa).

Nomenclature

The systematic name of O_3 is trioxygen or trioxidanediyl, of $O_3^{\bullet -}$ trioxide(•1−) or trioxidanidyl, and of $HO_3^{\bullet}$ hydrogen trioxide or trioxidanyl. The trivial name ozone is allowed.

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Data Sheet 24

Reaction: $ClO_2^{\bullet}(aq) + e^{-} \rightleftharpoons ClO_2^{-}(aq)$ (24.1)

List of reports:

$E°$ = +(0.936 ± 0.003) V vs NHE at 298 K [1]. Determined by potentiometry vs SCE. Measurements were performed as a function of temperature and ionic strength. Analysis of the data in terms of Debye-Hückel theory led to a standard potential (at $\mu = 0$).

$E°$ = +(0.934 ± 0.002) V vs NHE at 298 K [2]. Determined by potentiometry vs SCE. Measurements were performed as a function of temperature. Analysis of the data in terms of Debye-Hückel theory led to a standard potential (at $\mu = 0$).

Discussion

The agreement between the two detailed reports of $E°$ cited above is excellent. A more recent detailed kinetic study of the electrode process [3] confirms the fundamental electrochemical reversibility assumed in these two studies. We recommend the average of the two results for $E°$.

As noted in *Standard Potentials* [4], by Kläning *et al.* [2], and discussed by Stanbury [5], the measured $E°$ values differ (by ~130 mV) from that (+1.067 V) calculated from the values of $\Delta_f G°$ given in the NIST tables [6]: $\Delta_f G°$ = +120.1 kJ mol^{-1} for $ClO_2(aq)$ and $\Delta_f G°$ = +17.2 kJ mol^{-1} for $ClO_2^{-}(aq)$. It has been opined that the measured $E°$ values are less reliable than the value calculated from the NBS $\Delta_f G°$ values [7]; however, independent support for the potentiometric results comes from spectrophotometric determinations of the equilibrium constant for the reaction $[Fe(phen)_3]^{2+} + ClO_2^{\bullet} \rightleftharpoons [Fe(phen)_3]^{3+} + ClO_2^{-}$ [8].

One approach to resolving this discrepancy is to recalculate $\Delta_f G°$ for $ClO_2^{\bullet}(aq)$ from the well-established solubility of $ClO_2^{\bullet}$ and $\Delta_f G°$ for $ClO_2^{\bullet}(g)$. This is essentially the method that was used to obtain the NBS value for $\Delta_f G°$ for $ClO_2^{\bullet}(aq)$ [7]. The NIST Chemistry WebBook (March 2003 release) recommends a Henry's law constant (derived from direct solubility measurements) of 1.0 mol kg^{-1} bar^{-1} for $ClO_2^{\bullet}$, which corresponds to $\Delta G°$ = 0.0 kJ mol^{-1} for dissolution of $ClO_2^{\bullet}$. This solubility parameter is consistent with the 0.4 kJ mol^{-1} difference between the NBS data for $ClO_2(g)$ ($\Delta_f G°$ = +120.5 kJ mol^{-1}) and $ClO_2^{\bullet}(aq)$ ($\Delta_f G°$ = +120.1 kJ mol^{-1}), which implies that the Henry's law constant used in the NIST evaluation [6] is in agreement with more recent evaluations. The NIST value for $\Delta_f G°$ of $ClO_2^{\bullet}(g)$ is based on $\Delta_f H°$

= +102.5 kJ mol^{-1} for $ClO_2^{\bullet}(g)$, and several lines of evidence were cited in support of this enthalpy value [7]. On the other hand, the NIST-JANAF tables (prepared in 1992) cite a value of +115 ± 8 kJ mol^{-1} for $\Delta_f G°$ of $ClO_2^{\bullet}(g)$, which is based on a value of $\Delta_f H°$(298 K) of +99.7 ± 8 kJ mol^{-1} [9]. Gurvich *et al.* cite $\Delta_f H°$(298 K) = +105 ± 6 kJ mol^{-1} for $ClO_2^{\bullet}(g)$ [10]. More recently, the IUPAC Atmospheric Chemistry group has recommended a value of $\Delta_f H°$(298 K) = +95.6 ± 1.3 kJ mol^{-1} [11], based on reports of +96.7 ± 4 by Flesch *et al.* and +94.6 ± 1.3 kJ mol^{-1} by Nickolaisen *et al.* for this quantity [12, 13]. The latest NASA evaluation recommends a value of +94.6 ± 1.2 kJ mol^{-1} based on the kinetic result of Nickolaisen *et al.*, apparently electing to regard the result of Flesch *et al.* as merely supporting that of Nickolaisen *et al.* [14]. Most recently Xu and Lin report a value of +(100.8 ± 0.6) kJ mol^{-1} for $\Delta_f H°$ (at 0 K) as calculated from the dissociation energy of $ClO_2^{\bullet}$[15]; correction (assuming the same correction as reported in the NIST-JANAF Tables) to 298 K gives $\Delta_f H°$ ~ +(98.8 ± 0.6) kJ mol^{-1}. It is clear that a wide range of values has been reported for $\Delta_f H°$(298 K) of $ClO_2^{\bullet}(g)$, but the result of Nickolaisen *et al.* seems to be quite robust. If this result is accepted, then the NIST-JANAF recommendation is corrected to $\Delta_f G°$ = +(109.9 ± 1.2) kJ mol^{-1} for $ClO_2^{\bullet}(g)$. The NIST-recommended Henry's-law constant then leads to $\Delta_f G°$ = +(109.9 ± 1.2) kJ mol^{-1} for $ClO_2^{\bullet}(aq)$. Combination of this value with the NBS value for $ClO_2^-(aq)$ ($\Delta_f G°$ = +17.2 kJ mol^{-1}) leads to $E°$ = +(0.961 ± 0.013)V for the $ClO_2^{\bullet}(aq)/ClO_2^-(aq)$ standard potential. The agreement of this corrected derived result with the experimental standard potential is much improved. On the other hand, there is no published discussion of the reliability of the more recent determinations of $\Delta_f H°$ for $ClO_2^{\bullet}(g)$ vis-a-vis the older determinations mentioned by Gurvich *et al.*, so we view the uncertainty selected in the NASA evaluation to be overly optimistic. For example, early direct calorimetric measurements of the decomposition of $ClO_2^{\bullet}(g)$ appear to have been ignored. We thus favor a larger uncertainty, perhaps as much as ±10 kJ mol^{-1}. Within this uncertainty there is no need to question the NBS value of $\Delta_f G°$ for $ClO_2^-(aq)$.

Schmitz reviewed the thermodynamic chemistry of the aqueous $ClO_2^{\bullet}/ClO_2^-$ system in 1979 [16]. He concluded that the value of $\Delta_f G°$ for $ClO_2^{\bullet}(aq)$ is essentially as given by NBS but that the corresponding value for $ClO_2^-(aq)$ differs quite substantially from the NBS value. His results were obtained by deciding on the value for $ClO_2^{\bullet}(aq)$ and then using the measured $E°$ for the $ClO_2^{\bullet}(aq)/ClO_2^-(aq)$ couple to derive $\Delta_f G°$ for $ClO_2^-(aq)$. In view of the unsettled status of $\Delta_f G°$ for $ClO_2^{\bullet}(aq)$ as described above, Schmitz's conclusions should not be considered definitive. On the other hand, there is much in his discussion that merits attention.

At present we differ from the NIST tables [6] in recommending a value of $\Delta_f G°$ = +110 ± 10 kJ mol^{-1} for $ClO_2^{\bullet}(aq)$; we consider that the potentiometric determination of $E°$ for the ClO_2/ClO_2^- couple is substantially more reliable than the individual values for $\Delta_f G°$. This recommendation for $\Delta_f G°$ of $ClO_2^{\bullet}(aq)$ makes the NBS value $\Delta_f G°$ of $ClO_2^-(aq)$ reasonably consistent with our recommended value for $E°$ for $ClO_2^{\bullet}(aq)/ClO_2^{-}(aq)$. It leads to inconsistency between the measured Henry's law constant for $ClO_2^{\bullet}$ and the NBS value for $\Delta_f G°$ of $ClO_2^{\bullet}(g)$, but that is probably the only such issue raised by this alteration to the NIST data [6].

Recommended values:

$E°(ClO_2^{\bullet}(aq)/ClO_2^{-}) = +(0.935 \pm 0.003)$ V

$\Delta_f G°(ClO_2^{\bullet}\ aq) = +(110 \pm 10)$ kJ mol^{-1}

Nomenclature: $ClO_2^{\bullet}$, dioxidochlorine(•), or chlorinedioxide; ClO_2^{-}, dioxidochlorate(1) or *chlorite*.

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Data Sheet 25

Summary of the $ClO^{\bullet}$ System

Data relating to $ClO^{\bullet}$ are presently limited to one reason [1]:

$$CO_3^{\bullet-} + ClO^- \rightleftharpoons CO_3^{2-} + ClO^{\bullet}. \quad (25.1)$$

The equilibrium constant for this reaction, $(9.5 \pm 3.0) \times 10^2$ was determined at $\mu = 3.0$ M, pH= 12.2, at 22.2 °C. Because of the high ionic strength and charge asymmetry of the reaction, it is difficult to make a safe extrapolation to zero ionic strength. Given a recommended value for $E^{\circ\prime}(CO_3^{\bullet-}/ CO_3^{2-})$ of +(1.57 ± 0.03) V at 0.5 M to 3 M ionic strength (Data Sheet 99), we derive $E^{\circ\prime} = +(1.39 \pm 0.03)$ V for $ClO^{\bullet}/ClO^-$. Although the $CO_3^{\bullet-}/CO_3^{2-}$ formal potential should be strongly dependent on ionic strength, the $ClO^{\bullet}/ClO^-$ formal potential should be considerably less dependent.

A value for $\Delta_f G^\circ(ClO^{\bullet})$ can be derived from E° and $\Delta_f G^\circ(ClO^-)$. The NIST value for this latter quantity is $-(36.8 \pm 8)$ kJ mol^{-1} [2]. This seems like an unreasonably large uncertainty. NIST also gives $\Delta_f G^\circ = +(6.94 \pm 0.8)$ kJ mol^{-1} for $Cl_2(aq)$. The equilibrium constant for Cl_2 hydrolysis ($Cl_2(aq) + H_2O(l) = HOCl(aq) + Cl^- + H^+$) is well defined as $(5.1 \pm 0.1) \times 10^{-4}$ M^2 at 25 °C and $\mu = 0.0$ M [3]. HOCl has a $pK_a = (7.53 \pm 0.02)$ at $\mu = 0.0$ M and 25 °C [4]. These data, along with NIST data for H_2O and Cl^- lead to $\Delta_f G^\circ = -(37.16 \pm 0.8)$ kJ mol^{-1} for $ClO^-(aq)$, which is in excellent agreement with the NIST value. We thus derive $\Delta_f G^\circ = +(97 \pm 3)$ kJ mol^{-1} for $ClO^{\bullet}(aq)$.

Recommended values:

$E^{\circ\prime} = +(1.39 \pm 0.03)$ V at $\mu = 3$ M.
$\Delta_f G^\circ = +(97 \pm 3)$ kJ mol^{-1} for $ClO^{\bullet}(aq)$

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Data Sheet 26

Summary of the $Br^\bullet/Br_2^{\bullet-}/BrOH^-$ System

Tabulated below are the presently recommended equilibrium constants involving this related group of bromine radicals. The values are as given in the individual evaluations, keyed by reaction number. Uncertainties are expressed as $\pm$ 1 σ; in many cases the value of σ is merely a subjective guess.

rxn #	Reaction	K_{eq}	dim.	uncertainty	μ / M	Data Sheet #
27.1	$2Br^- + Mn^{3+} \rightleftharpoons Br_2^{\bullet-} + Mn^{2+}$	1.0×10^{-1}	M^{-1}	± factor of 2	2	27
28.1	$Br_2^{\bullet-} + ClO_2^\bullet \rightleftharpoons Br_2 + ClO_2^-$	7.4×10^{5}		± factor of 2	low	28
29.1	$Br_2^{\bullet-} + N_3^- \rightleftharpoons N_3^\bullet + 2Br^-$	5.5×10^{4}	M	± factor of 2	0	29
30.1	$Br_2^{\bullet-} + CO_3^{2-} \rightleftharpoons 2Br^- + CO_3^{\bullet-}$	3.2	M	± 22%	3	30
31.1	$Br^\bullet(aq) + H_2O \rightleftharpoons BrOH^{\bullet-} + H^+$	none				31
32.1	$BrOH^{\bullet-} \rightleftharpoons Br^\bullet(aq) + HO^-$	3.2×10^{-4}	M	± 15%	low	32
33.1	$Br^\bullet(aq) + Br^- \rightleftharpoons Br_2^{\bullet-}$	3.9×10^{5}	M^{-1}	± 30%	low	33
34.1	$HO^\bullet + Br^- \rightleftharpoons BrOH^{\bullet-}$	3.2×10^{2}	M^{-1}	± factor of 2	low	34
35.1	$BrOH^{\bullet-} + Br^- \rightleftharpoons Br_2^{\bullet-} + HO^-$	7×10^{1}		± 43%	low	35
36.1	$BrSCN^{\bullet-} + Br^- \rightleftharpoons Br_2^{\bullet-} + SCN^-$	1×10^{-3}		± factor of 3	low	36
37.1	$BrSCN^{\bullet-} + SCN^- \rightleftharpoons (SCN)_2^{\bullet-} + Br^-$	1.1×10^{2}		± 50%	low	37
38.1	$Br_2^{\bullet-} + DMS \rightleftharpoons DMS\text{–}Br^\bullet + Br^-$	1.1×10^{4}		± factor of 2	low	38
39.2	$DMS\text{–}Br^\bullet + DMS \rightleftharpoons (DMS)_2^+ + Br^-$	1.6		± factor of 2	low	39

DMS = dimethylsulfide.

Reactions 32.1, 33.1, and 35.1 form a closed thermodynamicchemical cycle, which requires the following:

$K(32.1) = K(35.1)/K(33.1)$. We obtain $3.2 \times 10^{-4} \approx 1.8 \times 10^{-4}$ which is quite satisfactory.

Derived $Br_2^{\bullet-}/2Br^-$ Standard Potentials:

Reaction 27.1 leads directly to $E^{\circ\prime}$ for $Br_2^{\bullet-} + e^- \rightleftharpoons 2Br^-$ at $\mu = 2$ M through combination with $E^{\circ\prime}$ for Mn^{3+}/Mn^{2+}. We use the value of +(1.535 ± 0.003) V given by Rosseinsky and Hill for $E^{\circ\prime}$of Mn^{3+}/Mn^{2+} at 3.31 M ionic strength [1]. Thus we obtain:

$E^{\circ\prime} = +1.594 \pm 0.018$ V for $Br_2^{\bullet-} + e^- \rightleftharpoons 2Br^-$ at $\mu = 2$ M.

Reaction 28.1 leads directly to $E°$ for $Br_2 + e^- \rightleftharpoons Br_2^{\bullet-}$ through use of $E°(ClO_2^\bullet/ClO_2^-)$. For $E°(ClO_2^\bullet/ClO_2^-)$ we use +(0.935 ± 0.003) V as evaluated in Data Sheet 24. This leads to $E°$ = +0.588 ± 0.017 for $Br_2 + e^- = Br_2^{\bullet-}$. Use of $E°$ = 1.0874 V for $E°(Br_2(aq)/2Br^-)$ [2] leads to

$E°$ = +(1.587 ± 0.017) V for $Br_2^{\bullet-} + e^- \rightleftharpoons 2Br^-$.

Reaction 29.1 in combination with a value of +(1.33 ± 0.010) V for $E°(N_3^\bullet/N_3^-)$ (Data sheet 80) yields

$E°$ = +(1.610 ± 0.020) V for $Br_2^{\bullet-} + e^- \rightleftharpoons 2Br^-$.

Reaction 35.1 combined with reaction 34.1 leads to ln K = (10.12 ± 0.78) for $HO^\bullet + 2Br^- \rightleftharpoons Br_2^{\bullet-} + HO^-$. Use of $E°$ = (1.902 ± 0.017) V for $HO^\bullet/HO^-$ (Data sheet 7) leads to

$E°$ = +(1.645 ± 0.021) V for $Br_2^{\bullet-} + e^- \rightleftharpoons 2Br^-$.

The agreement among the above derivations of $E°$ is not very satisfactory, spanning a range of 50 mV. The result based on reaction 28.1 is particularly suspect: it is based on a kinetic analysis of the $ClO_2^\bullet/ Br_2^{\bullet-}$ system that involves a complex mechanism; Toth and Fabian used a simulation that required simultaneous optimization of several rate constants. Thus, we exclude the result from reaction 28.1 from the final estimate. The Taube result (reaction 27.1) can also be excluded because of the mechanistic complexities and the high ionic strength employed. This leaves the results from reactions 29.1 and 35.1, which agree within their uncertainties; they yield an average of $E°$ = +1.624 V. An uncertainty of ± 0.020 V is inferred from the uncertainties in each the two component results and the difference between them.

Recommended value:

$E°(Br_2^{\bullet-}/2Br^-)$ = +(1.627 ± 0.020) V.

Other derived quantities

From the recommended $E°(Br_2^{\bullet-}/2Br^-)$ and the $E°(Br_2/2Br^-)$ cited above we derive $E°$ = +(0.55 ± 0.02) V for $Br_2 + e^- \rightleftharpoons Br_2^{\bullet-}$.

From the recommended $E°(Br_2^{\bullet-}/2Br^-)$ and K_{eq} for reaction 33.1 we derive

$E° = +(1.96 \pm 0.02)$ V for $Br^\bullet + e^- \rightleftharpoons Br^-$.

From the recommended $E°(Br_2^{\bullet-}/2Br^-)$ and the NIST value [3] for $\Delta_fG°$ of Br^- (–103.96 kJ mol^{-1}) we derive

$\Delta_fG° = -(51 \pm 2)$ kJ mol^{-1} for $Br_2^{\bullet-}$.

From the recommended $E°(Br^\bullet/Br^-)$ and the NIST value for $\Delta_fG°$ of Br^- we derive

$\Delta_fG° = (85 \pm 2)$ kJ mol^{-1} for $Br^\bullet$.

From K_{eq} for reaction 32.1, the derived $\Delta_fG°(Br^\bullet)$, and the NIST value [3] of $\Delta_fG°$ for HO^- (–157.244 kJ mol^{-1}) we obtain $\Delta_fG° = -(92.5 \pm 2)$ kJ mol^{-1} for $BrOH^{\bullet-}$. From reaction 34.1, NIST value for $\Delta_fG°$ of Br^-, and the Task Group recommendation for $\Delta_fG°(HO^\bullet)$ (= +26.3 ± 1.6 kJ mol^{-1}) we obtain $\Delta_fG° = -(92.0 \pm 1.8)$ kJ mol^{-1} for $BrOH^{\bullet-}$. From K_{eq} for reaction 35.1, the value for $\Delta_fG°(Br_2^{\bullet-})$ derived above, and the NIST values of $\Delta_fG°$ for Br^- and HO^- we obtain $\Delta_fG° = -(93.8 \pm 2.2)$ kJ mol^{-1} for $BrOH^{\bullet-}$. These three derivations are in excellent agreement and yield an average value of –(93 ± 2) kJ mol^{-1} for $\Delta_fG°$ of $BrOH^{\bullet-}$.

From K_{eq} for reaction 36.1, the derived value for $\Delta_fG°(Br_2^{\bullet-})$ and NIST values for $\Delta_fG°(Br^-)$ and $\Delta_fG°(SCN^-)$ (= +92.71 kJ mol^{-1}) we obtain

$\Delta_fG° = +(129 \pm 3)$ kJ mol^{-1} for $BrSCN^{\bullet-}$.

From K_{eq} for reaction 32.1 and a value of 1×10^{-14} M^2 for K_w we derive $pK_a = (10.50 \pm 0.07)$ for $Br^\bullet$ (reaction 31.1).

From $\Delta_fG°(Br^\bullet, aq)$ as derived above and the NIST value for $\Delta_fG°$ for $Br^\bullet(g)$ (= +82.396 kJ mol^{-1}) we derive $\Delta G_{hyd} = +(2.3 \pm 2)$ kJ mol^{-1} for $Br^\bullet$.

Nomenclature: $Br^\bullet$, bromine(•); Br^-, bromide; Br_2, dibromine; $Br_2^{\bullet-}$, dibromide (•1−); $BrOH^{\bullet-}$, hydroxidobromate(•1−); $BrSCN^{\bullet-}$, cyanidobromidosulfate(•1−)

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Data Sheet 27

Chemical equilibrium: $2Br^- + Mn^{3+} \rightleftharpoons Br_2^{\bullet-} + Mn^{2+}$ (27.1)

List of reports:

$K_{eq} = 1/(16\ M)$ (= $6.3 \times 10^{-2}\ M^{-1}$) at 25.2 °C and $\mu = (2 - 2.15)$ M [1]. Obtained from the kinetics of Mn(III) catalysis of the reaction of bromine with oxalic acid.

$K_{eq} = 4 \times 10^{-2}\ M^{-1}$ at 25 °C at a various ionic strengths [2], derived from flash photolysis determination of the reverse rate constant and a conventional kinetic determination of the forward rate constant.

Discussion

Taube's early (1948) determination [1] of this radical equilibrium constant is remarkably prescient. His data yield a value of 0.27 (time in minutes) for $2k_5/K_d^2$, where these parameters refer to the reactions

$2Br_2^{\bullet-} \rightleftharpoons Br^- + Br_3^-$ k_5
$Br_2^{\bullet-} + Mn^{2+} + H_2C_2O_4 \rightleftharpoons 2Br^- + 2H^+ + [Mn(C_2O_4)]^+$ K_d

His value for K_{eq} was derived from this result by use of an assumed rate constant for the self-reaction of $Br_2^{\bullet-}$ ($2k_5 = 8.3 \times 10^{10}\ M^{-1}\ s^{-1}$) and the measured equilibrium constant for association of oxalic acid with Mn^{3+}:

$Mn^{3+} + H_2C_2O_4 \rightleftharpoons [Mn(C_2O_4)]^+ + 2H^+$ $K_a = (1.0 \pm 0.3) \times 10^5$ M

Taube's assumption for the value of $2k_5$ seems somewhat high; although there are no direct determinations of $2k_5$ at such high ionic strengths, it is reported that $2k_5$ is $(4.8 \pm 0.6) \times 10^9\ M^{-1}\ s^{-1}$ at 1 M ionic strength [3]. With $2k_5$ taken as $(4.8 \pm 0.6) \times 10^9\ M^{-1}\ s^{-1}$ we obtain $K_d = (1.0 \pm 0.3) \times 10^6\ M^2$, which is quite close to the value reported by Taube; presumably he made a computational or typographical error that has been largely compensated for by our 20-fold adjustment to $2k_5$. This leads to a corrected value of $(0.10 \pm 0.3)\ M^{-1}$ for K_{eq} at $\mu = 2$ M.

Laurence and Thornton [2] based their equilibrium constant on the following reaction mechanism:

$Mn^{3+} + Br^- \rightleftharpoons MnBr^{2+}$ K_{22}

$$\mathrm{MnBr^{2+} + Br^- \rightleftharpoons Mn^{2+} + Br_2^{\bullet-}} \qquad k_{23}, k_{-23}$$

They used flash photolysis of solutions that contained Mn^{2+} and Br_3^- to generate $Br_2^{\bullet-}$ and measure k_{-23} (= 9.0×10^6 M^{-1} s^{-1} [2]. These flash photolysis experiments were performed at 25 °C and ionic strength ranging from 0.21 M to 0.25 M. They then used Wells and Mays' data for the value of $K_{22}k_{23}$ (= 3.6×10^5 M^{-2} s^{-1}) at 4 M ionic strength [4]. Combining these two values led to $K_{eq} = 4 \times 10^{-2}$ M^{-1}.

Given the high ionic strength dependence expected for the rate constants in Laurence and Thornton's determination [2], the result can only be approximate. We thus prefer Taube's determination [1]. Given the agreement between the two reports and the overall complexity of the determinations we assume an uncertainty in K_{eq} of a factor of 2.

Recommended value:

$K_{eq} = 1.0 \times 10^{-1}$ M^{-1} at 25.2 °C and $\mu = (2 - 2.15)$ M within a factor of two.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 26.

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Data Sheet 28

Chemical equilibrium: $ClO_2^\bullet + Br_2^{\bullet-} \rightleftharpoons ClO_2^- + Br_2$ (28.1)

List of reports:

$K_{eq} = (2.7 \pm 1.4) \times 10^6$. This value has not been published, but it can be calculated from published values for the forward and reverse rate constants. A value of $(3.56 \pm 0.06) \times 10^9$ M^{-1} s^{-1} at $\mu = 1.0$ M (and presumably at room temperature) for k_f was reported by Tóth *et al.* from a flash photolysis study [1]. Experiments at $\mu = 0.10$ and 0.05 M show the rate constant to be essentially independent of ionic strength. Tóth and Fábián reported $k_r = (1.3 \pm 0.2) \times 10^3$ M^{-1} s^{-1} at 25.0 °C and $\mu = 1.0$ M; this result was obtained from stopped-flow experiments, with the rate constants being evaluated by numerical fitting of a complex model [2]. The value obtained for k_r varied over a factor of ~3 depending on the details of the model, and the indicated uncertainty is merely a statistical result for one of the models. Thus, we assign a larger uncertainty of a factor of 2 in K_{eq}.

Discussion

The value of K_{eq} presented above is the only experimental result available. It seems to be fairly reliable, although there is a large uncertainty because of the complex mechanism used to derive it. Some degree of skepticism in the value of k_r arises from a recent report on the reaction of HOBr with Cl(III) [3]. This new paper gives a significantly revised value for the rate constant of the reaction of HOBr + $HClO_2$, which also figured in the mechanism of the reaction that led to the value for k_r. This paper provides no information as to how this new information affects the fits from which k_r is derived.

As described in Tóth's Ph.D. dissertation [4], the revised data on the HOBr/Cl(III) reaction lead to an adjustment in the value for k_r to $(4.84 \pm 0.02) \times 10^3$ M^{-1} s^{-1}. This latest adjustment leads to a substantial change in K_{eq}, the new value being 7.4×10^5. According to a personal communication from Fábián, a more formal publication of this adjustment is not anticipated unless further data should become available.

The value of K_{eq} should not be very sensitive to ionic strength. The value of k_f should be only weakly temperature dependent, and thus the value of K_{eq} should be appropriate for 25 °C. Given the above, we make a wild guess that the uncertainty in the derived equilibrium constant is a factor of two.

Recommended value:

$K_{eq} = 7.4 \times 10^5$ within a factor of 2.

List of auxiliary thermodynamic data: none

Nomenclature: See Data Sheet 26. $ClO_2^{\bullet}$, dioxidochlorine(•).

References

1. Z. Tóth, I. Fábián, A. Bakac. *Inorg. React. Mech.* **3,** 147-152 (2001).
2. Z. Tóth, I. Fabian. *Inorg. Chem.* **39,** 4608-4614 (2000).
3. Z. Tóth, I. Fábián. *Inorg. Chem.* **43,** 2717-2723 (2004).
4. Z. Tóth. (Ph. D. dissertation: The reactions of chlorine(III) with bromine and hypobromous acid: kinetics and mechanism); University of Debrecen: Debrecen, Hungary, 2003.

Data Sheet 29

Chemical equilibrium: $Br_2^{\bullet-} + N_3^- \rightleftharpoons N_3^\bullet + 2Br^-$ (29.1)

List of reports:

$K_{eq} = 5.5 \times 10^4$ M, presumably at room temperature, with $\mu = 2$ or 3 M [1]. Results were obtained by pulse radiolysis of Br^-/N_3^- mixtures, and by measuring k_{obs} for the above reaction; a plot of $k_{obs}/[Br^-]^2$ vs $[N_3^-]/[Br^-]^2$ yields k_f and k_r from the slope and intercept, and K_{eq} from the ratio of k_f/k_r. A "similar" equilibrium constant was obtained from the equilibrium concentration of $Br_2^{\bullet-}$ determined at 360 nm.

Discussion

While we have no reason to doubt the quality of this work, the very high ionic strength of the solutions makes the result of limited value in determining the equilibrium constant at $\mu = 0$. The reaction is electrostatically balanced, in that there are two product anions and two reactant anions, so the equilibrium constant should not vary too much with ionic strength. We tentatively assign an uncertainty of a factor of 2.

Recommended value:

$K_{eq}^0 = 5.5 \times 10^4$ M within a factor of 2.

List of auxiliary thermodynamic data: none

Nomenclature: See Data Sheet 26. $N_3^\bullet$, trinitrogen*(2N–N)*(•)

References

1. Z. B. Alfassi, A. Harriman, R. E. Huie, S. Mosseri, P. Neta. *J. Phys. Chem.* **91,** 2120-2122 (1987).

Data Sheet 30

Trioxidocarbonate(•1–)/trioxidocarbonate(2–)

List of reported equilibrium constants:

Chemical equilibrium $Br_2^{\bullet-} + CO_3^{2-} \rightleftharpoons 2Br^- + CO_3^{\bullet-}$ (30.1)

Huie *et al.* [1].

$K = 3.2 \pm 0.7$ (I = 3 M, pH 12.0), $\Delta E = (0.030 \pm 0.006)$ V.

Based on reaction 30.1 and $E°(Br_2^{\bullet-}/Br^-) = +1.625$ V [2], (see Data Sheet 26) $E°(CO_3^{\bullet-}/ CO_3^{2-}) = +(1.59 \pm 0.02)$ V.

Chemical equilibrium $CO_3^{\bullet-} + 2SCN^- \rightleftharpoons CO_3^{2-} + (SCN)_2^{\bullet-}$ (30.2)

Lymar *et al.*, 2000 [3].

$K = (1.5 \pm 0.3) \times 10^4\ M^{-1}$ and $(2.1 \pm 0.2) \times 10^4\ M^{-1}$ at 0.5 M and 1.5 M ionic strength, respectively. Based on these equilibrium constants $E°(CO_3^{\bullet-}/CO_3^{2-})$ is 0.25 V higher than $E°((SCN)_2^{\bullet-}/2SCN^-)$. The authors have noted that this difference can be somewhat smaller at low ionic strength, as the electrolyte would tend to stabilize CO_3^{2-} the most. Given $E°((SCN)_2^{\bullet-}/2SCN^-) = 1.30$ V (see Data Sheet 101), $E°(CO_3^{\bullet-}/CO_3^{2-}) = +1.55$ V.

Chemical equilibrium $CO_3^{\bullet-} + ClO^- \rightleftharpoons CO_3^{2-} + ClO^{\bullet}$ (30.3)

Huie *et al.* [1].

$K = (9.5 \pm 3.0) \times 10^2$ ($\mu = 3.0$ M, pH 12.2, 22.2 °C), $\Delta E = (0.176 \pm 0.010)$ V.

Discussion

The equilibrium constant for reaction 30.1 is the average of (3.3 ± 0.3), derived from the absorbance at 360 nm ($Br_2^{\bullet-}$) at equilibrium and of 3.1 ± 0.5 from the rate constants for the decay of $Br_2^{\bullet-}$ to its equilibrium value. The error in the preliminary assessment of the $Br_2^{\bullet-}/2Br^-$

electrode potential determines that in $E°(CO_3^{•-}/ CO_3^{2-})$. The difference of 0.04 V between two careful measurements may be due to medium effects.

The standard electrode potential of the $ClO^•/ClO^-$ couple is not known precisely enough to determine $E°(CO_3^{•-}/CO_3^{2-})$; in fact the value of +1.59 V is used to estimate $E°(ClO^•/ClO^-)$ [1].

Recommended values:

$E°(CO_3^{•-}/ CO_3^{2-}) = +(1.57 \pm 0.03)$ V

$\Delta_f G°(CO_3^{•-}) = -(89.1 \pm 0.8)$ kcal/mol, or $-(373 \pm 3)$ kJ mol^{-1};

List of auxiliary thermodynamic data

Based on a review of earlier literature, Stanbury proposed a value of 1.5 V [2]. In an *ab initio* study, Armstrong *et al.* [4] suggest a value of +(1.23 ± 0.15) V. While not as accurate as the two experimentally derived values, this result is impressive for an *ab initio* calculation.

Chemical equilibrium $HCO_3^• \rightleftharpoons H^+ + CO_3^{•-}$ (30.4)

Czapski *et al.* [5].

A pK_a smaller than 0 has been determined [5], as expected for a $HOXO_2$ acid.

Recommended value:

Except that pK_a is negative, no numerical recommendation can be made.

Auxiliary thermodynamic data: Earlier pK_a estimates of 9.6 and 7.0 – 8.2 are discussed by Czapski *et al.* [5]. A recent value of 9.5 [6] was shown to be in error [3]. The result of an *ab initio* calculation [4], –4.1, also does not support the $pK_a \geq 7$ values.

References

1. R. E. Huie, C. L. Clifton, P. Neta. *Radiat. Phys. Chem.* **38,** 477-481 (1991).

2. D. M. Stanbury. *Adv. Inorg. Chem.* **33,** 69-138 (1989).

3. S. V. Lymar, H. A. Schwarz, G. Czapski. *Rad. Phys. Chem.* **59,** 387-392 (2000).

4. D. A. Armstrong, W. L. Waltz, A. Rauk. *Can. J. Chem.* **84,** 1614-1619 (2006).

5. G. Czapski, S. V. Lymar, H. A. Schwarz. *J. Phys. Chem. A* **103,** 3447-3450 (1999).

6. Z. Zuo, Z. Cai, Y. Katsumura, N. Chitose, Y. Muroya. *Radiat. Phys. Chem.* **55,** 15-23 (1999).

Data Sheet 31

Chemical equilibrium: $Br^{\bullet}(aq) + H_2O \rightleftharpoons BrOH^{\bullet-} + H^+$ (31.1)

List of reports:

$K_{eq} = 3.09 \times 10^{-11}$ M. We derive this result from the forward rate constant ($k_f = 1.36\ s^{-1}$) reported by Kläning and Wolff and the reverse rate constant ($k_r = (4.4 \pm 0.8) \times 10^{10}\ M^{-1}\ s^{-1}$) reported by Zehavi and Rabani [1, 2].

Discussion

Note that Kläning and Wolff erroneously cite Mamou *et al.* for k_r. [3]. The Kläning and Wolff paper is really just a poster abstract and is too concise to state what was really measured. However, it appears that the method used was laser flash photolysis, which means that the value for k_f is too small to have been measured in this way. In fact, it was calculated from a thermodynamic cycle; the actual measurement by Kläning and Wolff must have been for the corresponding reaction in alkaline media: $Br^{\bullet} + HO^- \rightleftharpoons BrOH^{\bullet-}$.

Recommended value:

None. We can derive a value from the corresponding alkaline equilibrium, but there is no direct measurement.

List of auxiliary thermodynamic data: none.

References

1. U. K. Kläning, T. Wolff. *Ber. Bunsenges. Phys. Chem.* **89,** 243-245 (1985).
2. D. Zehavi, J. Rabani. *J. Phys. Chem.* **76,** 312-319 (1972).
3. A. Mamou, J. Rabani, D. Behar. *J. Phys. Chem.* **81,** 1447-1448 (1977).

Data Sheet 32

Chemical equilibrium: $\mathrm{BrOH^{\bullet-}} \rightleftharpoons \mathrm{Br^{\bullet}}(aq) + \mathrm{HO^{-}}$ (32.1)

List of reports:

$K_{\mathrm{eq}} = 3.2 \times 10^{-4}$ M. This value calculated from $k_{\mathrm{f}}/k_{\mathrm{r}}$. $k_{\mathrm{f}} = (4.2 \pm 0.6) \times 10^{6}\ \mathrm{s^{-1}}$ was reported by Zehavi and Rabani from pulse radiolysis measurements.at 25 ± 2 °C [1]. Zehavi and Rabani obtained k_{f} by combining various measured quantities as described below. The value for k_{r} ($k_{\mathrm{r}} = 1.3 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$) was measured by Kläning and Wolff with flash photolysis of HOBr [2]. Due to the preliminary nature of Kläning and Wolff's report [2], the actual conditions of the experiment are unknown, but we can assume they were at room temperature and at pH 12. Note that Kläning and Wolff [2] eroneously cited Mamou *et al.* [3] for the value of k_{f}.

Discussion

Zehavi and Rabani's [1] determination of k_{f} is complex and is described here in outline. They assumed that the mechanism includes the steps

$\mathrm{Br^{-} + HO^{\bullet} \rightleftharpoons Br^{\bullet} + HO^{-}}$ k_1

$\mathrm{Br^{-} + HO^{\bullet} \rightleftharpoons BrOH^{\bullet-}}$ k_2, k_{-2}

$\mathrm{BrOH^{\bullet-} \rightleftharpoons Br^{\bullet} + HO^{-}}$ k_3, k_{-3}

$\mathrm{RH_2 + HO^{\bullet} \rightleftharpoons RH^{\bullet} + H_2O}$ k_5 ($\mathrm{RH_2}$ = ethanol or methanol)

$\mathrm{Br^{\bullet} + Br^{-} \rightleftharpoons Br_2^{\bullet-}}$ K_4

Note that k_1 is a pseudo-second-order rate constant that varies at high $[\mathrm{Br^-}]$. Thus, the yield of $\mathrm{Br_2^{\bullet-}}$ depends on the alcohol concentration. By determining the $\mathrm{Br_2^{\bullet-}}$ yield as a function of alcohol they obtained $k_3/k_{-2} = (0.127 \pm 0.007)$ at neutral pH. In acidic ethanolic media, similar competition experiments yielded $k_5/k_2 = (0.172 \pm 0.013)$. Use of the literature value for k_5 (= $1.83 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$) then gave $k_2 = 1.06 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$. In a series of experiments they measured k_1 at various bromide concentrations up to 2 M, they plotted a graph of $((k_2)(k_3/k_{-2}) - k_1)/[\mathrm{Br^-}]$ vs. k_1, and obtained a value of $k_2/k_{-2} = 3.2 \times 10^{2}\ \mathrm{M^{-1}}$ from the slope. A value of $3.3 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$ was derived for k_{-2} from the values for k_2 and k_2/k_{-2}. Finally, combining the values for k_{-2} and k_3/k_{-2} led to $k_3 = 4.2 \times 10^{6}\ \mathrm{s^{-1}}$, which is k_{f}.

We thus see that the value for k_{f} was obtained from data at various ionic strengths, some as high as 2 M. On the other hand, the value for k_{r} was determined at low ionic strength. However, neither rate constant should be particularly sensitive to ionic strength, so the derived equilibrium constant can be reasonably described as an ideal one.

We estimate the uncertainty as ±15% by combining the published uncertainty in k_f and our estimated uncertainty for k_r.

A strongly conflicting value for K_{eq} of 2×10^{-5} was calculated by Mamou *et al.* [3] from prior literature data of Behar [4]. Mamou *et al.* [3] then performed experiments that demonstrated an error in the results of Behar [4].

Recommended value:

$$K_{eq} = (3.2 \pm 0.5) \times 10^{-4}\ \text{M}$$

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 26

References

1. D. Zehavi, J. Rabani. *J. Phys. Chem.* **76,** 312-319 (1972).
2. U. K. Kläning, T. Wolff. *Ber. Bunsenges. Phys. Chem.* **89,** 243-245 (1985).
3. A. Mamou, J. Rabani, D. Behar. *J. Phys. Chem.* **81,** 1447-1448 (1977).
4. D. Behar. *J. Phys. Chem.* **76,** 1815-1818 (1972).

Data Sheet 33

Chemical equilibrium: $Br^{\bullet}(aq) + Br^{-} \rightleftharpoons Br_2^{\bullet-}$ (33.1)

List of reports:

$K_{eq} = 3.3 \times 10^{3}$ M^{-1}, presumably at room temperature at ionic strength ranging from quite low to 0.1 M [1]. Obtained from flash photolysis of Br^{-} solutions by fitting the pseudo-second-order rate constant for decay of $Br_2^{\bullet-}$.

$K_{eq} = (1.7 \pm 0.7) \times 10^{4}$ M^{-1} at 25 °C and various ionic strengths [2], from the kinetics of formation of $Br_2^{\bullet-}$ as a function of $[Br^{-}]$ in the flash photolysis of solutions of Br_2 in 0.12 M $HClO_4$ and of 1.4 mM C_6H_5Br.

$K_{eq} = (1.1 \pm 0.3) \times 10^{5}$ M^{-1}, at (24 ± 2) °C and low ionic strength [3]. Result obtained by pulse radiolysis determination of the equilibrium absorbance of $Br_2^{\bullet-}$ as a function of $[Br^{-}]$.

$K_{eq} = 3.1 \times 10^{3}$ M^{-1}, at 288 K and low ionic strength [4]. Result obtained by a flash photolysis of Br^{-} with conductivity detection. They obtained the rate of dissociation of $Br_2^{\bullet-}$ by fitting the kinetic traces with a complex mechanism. We calculate the equilibrium constant here from the ratio of the forward and reverse rate constants given in the paper.

$K_{eq} = 2.2 \times 10^{5}$ M^{-1}, presumably at room temperature and low ionic strength [5]. Obtained by pulse radiolysis of *N*-bromosuccinimide [IUPAC PIN: 1-bromopyrrolidine-2,5-dione], from the ratio of k_f and k_r for formation of $Br_2^{\bullet-}$.

$K_{eq} = 6 \times 10^{5}$ M^{-1} at 25 °C and $\mu \sim 0.1$ M [6]. Obtained from by pulse radiolysis of Br^{-} solutions, measuring the equilibrium $Br_2^{\bullet-}$ concentration. Also obtained from steady-state gamma radiolysis of Br^{-}/oxalic acid solutions, by measuring the CO_2 yield. The equilibrium constant inferred here was obtained by interpolation of a graph of K_{eq} vs T.

$K_{eq} = 6 \times 10^{5}$ M^{-1} at room temperature [7]. Pulse radiolysis of 1,2-dibromoethane was used to generate $Br_2^{\bullet-}$ through the direct reaction of $e^{-}(aq)$ with $C_2Br_2H_4$; the decay of $Br_2^{\bullet-}$ in the presence of 1-2 M propan-2-ol yielded $k_r = 1.9 \times 10^{4}$ s^{-1}. A value for k_f of 1.2×10^{10} M^{-1} s^{-1} was then used to determine K_{eq} from k_f/k_r.

$K_{eq} = (3.9 \pm 1.2) \times 10^{5}$ M^{-1} at 298 K and low ionic strength [8]. Flash photolysis of aqueous 1,2-dibromoethane in Br^{-} solutions was used to generate $Br^{\bullet}$ atoms. The equilibrium constant was obtained from the ratio of k_f to k_r, the two rate constants being obtained from the kinetics of formation of $Br_2^{\bullet-}$ as a function of $[Br^{-}]$.

Discussion

A wide range of values has been reported for K_{eq}. In the earlier studies the results seemed to cluster with low values for the flash-photolysis experiments and high values for the pulse radiolysis experiments. However, the latest flash photolysis result is in the range of the pulse radiolysis results, which leads us to believe that the early low results of Wong *et al.* [1] and Treinin *et al.* [2] may be disregarded.

Wagner and Strehlow [4] have pointed out that the result of Wong *et al.* [1] is probably the consequence of neglecting reactions of the solvated electron [4]. On the other hand, the result from Wagner and Strehlow [4] is rather similar to that of Wong *et al.* [1] and is also likely incorrect. The lower temperature in this study is unlikely to be the source of the discrepancy, in view of the temperature dependence reported by Kosanic [6]. In a personal communication from John Barker to Stanbury (Jan. 2005) is was suggested that the results reported by Wagner and Strehlow [4] might be incorrect because Runga Kutta integration was used to fit the data, while a more robust integrator should have been used. He also mentions the greater complexity of the Wagner and Strehlow mechanism, which is a consequence of the solvated electrons generated by bromide photolysis. Also, the high radical concentrations generated (*ca.* $10^{-6} - 10^{-4}$ M) mean that second-order processes will affect the results more strongly.

Kosanic's result is notable in providing the temperature dependence of K_{eq}, from which $\Delta H°$ for the reaction was derived.

The most recent result, from Barker's group, appears to be the most carefully conducted and analyzed, and accordingly we select it for recommendation. Their stated uncertainty comes close to encoMPasing the other reports.

Recommended value:

$$K_{eq} = (3.9 \pm 1.2) \times 10^{5}\ \mathrm{M}^{-1}$$

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 26.

References

1. D. Wong, B. Di Bartolo. *J. Photochem.* **4,** 249-268 (1975).
2. A. Treinin, E. Hayon. *J. Am. Chem. Soc.* **97,** 1716-1721 (1975).
3. A. Mamou, J. Rabani, D. Behar. *J. Phys. Chem.* **81,** 1447-1448 (1977).
4. I. Wagner, H. Strehlow. *Ber. Bunsenges. Phys. Chem.* **91,** 1317-1321 (1987).

5. J. Lind, X. Sen, T. E. Eriksen, G. Merényi, L. Eberson. *J. Am. Chem. Soc.* **113,** 4629-4633 (1991).
6. M. M. Kosanic. *J. Serb. Chem. Soc.* **58,** 55-62 (1993).
7. G. Merényi, J. Lind. *J. Am. Chem. Soc.* **116,** 7872-7876 (1994).
8. Y. Liu, A. S. Pimentel, Y. Antoku, B. J. Giles, J. R. Barker. *J. Phys. Chem. A* **106,** 11075-11082 (2002).

Data Sheet 34

Chemical equilibrium: $HO^\bullet + Br^- \rightleftharpoons BrOH^{\bullet-}$ (34.1)

List of reports:

$K_{eq} = 320\ M^{-1}$ at (25 ± 2) °C and a range of ionic strengths up to 2 M [1]. Obtained by pulse radiolysis with a combination of competition yields and kinetics as described in the evaluation of reaction 5.02 ($BrOH^{\bullet-} \rightleftharpoons Br^\bullet$ (*aq*) + OH^-).

$K_{eq} = (2.9 \pm 1.4) \times 10^3\ M^{-1}$ and $2300\ M^{-1}$ presumably at room temperature and low ionic strength [2]. Obtained by pulse radiolysis of Br^- solutions from the absorbance of $Br_2^{\bullet-}$ as a function of $[Br^-]$ and $[HO^-]$.

Discussion

Given the major disagreement between the first two determinations of K_{eq}, Mamou *et al.* measured two related equilibrium constants to calculate a value for K_{eq} [3]; their results supports the original result of Zehavi *et al.*

The magnitude of K_{eq} is not expected to depend significantly on ionic strength. Although K_{eq} was measured by Zehavi and Rabani in solutions having a wide range of ionic strengths, this should not be a serious consideration.

Given the complex procedure used by Zehavi and Rabani to obtain K_{eq} we suggest an uncertainty of a factor of two.

Recommended value:

Log $K_{eq} = (2.5 \pm 0.3)$.

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 26.

References

1. D. Zehavi, J. Rabani. *J. Phys. Chem.* **76,** 312-319 (1972).
2. D. Behar. *J. Phys. Chem.* **76,** 1815-1818 (1972).

3. A. Mamou, J. Rabani, D. Behar. *J. Phys. Chem.* **81,** 1447-1448 (1977).

Data Sheet 35

Chemical equilibrium: $BrOH^{\bullet-} + Br^- \rightleftharpoons Br_2^{\bullet-} + OH^-$ (35.1)

List of reports:

K_{eq} = (3.7 ± 1.5) and 4.35, presumably at room temperature and low ionic strength [1]. Obtained by pulse radiolysis of Br^- solutions from the equilibrium absorbance of $Br_2^{\bullet-}$ as a function of $[Br^-]$ and $[HO^-]$.

K_{eq} = (70 ± 30), at (24 ± 2) °C and low ionic strength [2]. Obtained by pulse radiolysis of Br^- solutions from the equilibrium absorbance arising from $Br_2^{\bullet-}$ and $BrOH^{\bullet-}$.

Discussion

The wide discrepancy between the two determinations of K_{eq} is attributed by Mamou *et al.* [2] to neglect of the absorbance of $BrOH^{\bullet-}$ in the original study of Behar [1]. Thus, we recommend the result of Mamou *et al.* [2].

Recommended value:

$K_{eq} = (0.7 \pm 0.3) \times 10^2$

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 26.

References

1. D. Behar. *J. Phys. Chem.* **76,** 1815-1818 (1972).
2. A. Mamou, J. Rabani, D. Behar. *J. Phys. Chem.* **81,** 1447-1448 (1977).

Data Sheet 36

Chemical equilibrium: $BrSCN^{\bullet-} + Br^{-} \rightleftharpoons Br_2^{\bullet-} + SCN^{-}$ (36.1)

List of reports:

$K_{eq} = 1 \times 10^{-3}$, presumably at room temperature with ionic strength ranging from low up to 2 M [1]. Obtained by pulse radiolysis with optical detection, measuring the position of equilibrium.

Discussion

The experiments appear to be well performed, and we see no reason to object to the results. The authors do not specify any range of uncertainty, but we suggest a factor of three, given the nature of the data.

Recommended value:

$K_{eq} = 1 \times 10^{-3}$ within the range of 03 to 3.

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 26.

References

1. M. Schöneshöfer, A. Henglein. *Ber. Bunsen-Ges. Phys. Chem.* **73,** 289-293 (1969).

Data Sheet 37

Chemical equilibrium: $BrSCN^{\bullet-} + SCN^{-} \rightleftharpoons (SCN)_2^{\bullet-} + Br^{-}$ (37.1)

List of reports:

$K_{eq} = 1.1 \times 10^{2}$, presumably at room temperature with ionic strength ranging from low up to 2 M [1]. Obtained by pulse radiolysis with optical detection, measuring the position of equilibrium.

Discussion

The experiments appear to be well performed, and we see no reason to object to the results. The authors do not specify any range of uncertainty, but we suggest ± 50%, given the nature of the data.

Recommended value:

$K_{eq} = (1.1 \pm 0.6) \times 10^{2}$.

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 26. $(SCN)_2^{\bullet-}$, bis(nitridosulfidocarbonate)(*S*–*S*)(•1−).

References

1. M. Schöneshöfer, A. Henglein. *Ber. Bunsen-Ges. Phys. Chem.* **73,** 289-293 (1969).

Data Sheet 38

Subject: Bromidodimethylsulfur(•) (Dimethyl sulfide radical cation-bromide complex)
Couple type: $R_2S\text{-}Br/\ R_2S,Br^{-}$, ($R = \text{-}CH_3$).
Solvent: Water

Method: Calculation in reference [1] from pulse radiolysis data in reference [2] and $E^{o}(Br_2^{\bullet-}/2Br^{-})$:

Equilibria: *(i)* $R_2S + Br_2^{\bullet-} \rightleftharpoons R_2S{\bullet}^{\bullet}{\bullet}Br + Br^{-}$; (38.1)
$K = 1.1 \times 10^{4}$. Error limit in K stated $\leq 2\times$.
(ii) $Br_2^{\bullet-} + e^{-} \rightleftharpoons 2Br^{-}$; $E^{o} = +(1.63 \pm 0.02)$ V (38.2)
(ii) - (i) $R_2S{\bullet}^{\bullet}{\bullet}Br + e^{-} \rightleftharpoons R_2S + Br^{-}$; $E^{o} = +(1.39 \pm 0.03)$ V (38.3)

Reference: $E^{o}(Br_2^{\bullet-}/2Br^{-})$.
Temperature: (293 ± 2) K. **Ionic strength effects estimated:** No.
Corrected equilibrium constant given: No.
Reference standard potential assumed: $E^{o} = +(1.63 \pm 0.03)$ V

Discussion

No correction needed for ionic strength. Equilibrium *(i)* has charge symmetry and therefore the Debye-Hückel corrections will cancel. *(ii)* is a standard potential.
Recalculation under the assumption of a 100% error limit in K gives: (1.39 ± 0.03) V *vs* NHE.

Recommended value:

$E^{o}(R_2S\text{-}Br/R_2S,Br^{-})$, ($R = \text{-}CH_3$) = +(1.39 ± 0.03) V *vs* NHE.

Nomenclature: See Data Sheet 26.

References

1. Armstrong, D. A. In *S-Centered Radicals*, (Alfassi, Z. B., ed.), p. 27-61. John Wiley & Sons, New York (1999).
2. M. Bonifacic, K.-D. Asmus. *J. Chem. Soc., Perkin Trans. II* 758-762 (1980).

Data Sheet 39

Subject: Bromidodimethylsulfur(•) (Dimethyl sulfide dimer radical cation).

Couple type: $R_2S\therefore R_2S^+/\ 2R_2S$, ($R = -CH_3$)

Solvent: Water

Method 1: Pulse radiolysis

Measurements by displacement and electron transfer equilibria in reference [1]:

Equilibrium: (i) $R_2S + Br_2^{\bullet -} \rightleftharpoons R_2S\therefore Br + Br^-$; (39.1)

$K = 1.1 \times 10^4$

(ii) $R_2S\therefore Br + R_2S \rightleftharpoons R_2S\therefore R_2S^+ + Br^-$; (39.2)

$K = 1.64$

Error limit in Ks ≤ factor of 2.

Calculated in reference [2] *:*

(i) + *(ii)* $2R_2S + Br_2^{\bullet -} \rightleftharpoons R_2S\therefore R_2S^+ + 2Br^-$; (39.3)

$K = 1.8 \times 10^4$

Reference: $Br_2^{\bullet -} + e^- \rightleftharpoons 2Br^-$;

Other solutes: Bromide salt.

Gas: N_2O **Buffer:** Not stated in [1].

pH = Not stated. **Temperature:** 293 ± 2 K. **Ionic strength:** ?? M

Uncorrected equilibrium constant from concentrations: 1.8×10^4

Ionic strength effects estimated: No.

Observed equilibrium constant/measurement corresponds to ΔE = ($0.24_9 \pm 0.03$) V

Reference standard potential assumed: $E^o = +1.62$ V

Standard potential of couple indicated in reference [2]**:** **+**1.37 V vs NHE

Method 2: Pulse radiolysis **Solvent:** Water

Measurements by electron transfer equilibria in reference [2] :

Equilibrium: $R_2S\therefore R_2S^{\bullet +} + N_3^- \rightleftharpoons 2R_2S + N_3^\bullet$; (39.4)

$K = 16.4\ \text{mol dm}^{-3}$.

Reference: $N_3^\bullet + e^- \rightleftharpoons N_3^-$;

Other solutes: Azide salt.

Gas: N_2O **Buffer:** Not stated.

pH = Not stated **Temperature:** ~295 K. **Ionic strength:** 0.1 ??M

Ionic strength effects estimated: No.

Observed equilibrium constant/measurement corresponds to ΔE = ($0.07_1 \pm 0.03$) V

Reference standard potential assumed: $E^o = +(1.33 \pm 0.03)$ V

Standard potential of couple indicated in reference [2]**:** +1.40 V vs NHE

Discussion

There are sufficient experimental details available to evaluate the data.

Calculation from method 1: (1.37 V ± 0.04) (Error in *K*s taken as ±100%).

Calculation from method 2: (1.40 V ± 0.02) (Error in *K*s taken as ± 50%; probably generous as $K_{(\mathrm{Kin})} = 12.5$). Method 2 is more direct and therefore weighted more heavily.

Correction desirable for ionic strength effects: The magnitude of the errors should be checked for both methods, but exact corrections are probably impractical due to lack of data.

Recommended value:

$E°(R_2S\therefore R_2S^+/ 2R_2S)$, (R = $-CH_3$) = +1.39 V ± 0.03 V

Nomenclature: See Data Sheet 26.

References

1. M. Bonifacic, K.-D. Asmus. *J. Chem. Soc., Perkin Trans. II* 758-762 (1980).
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Data Sheet 40

Summary of the $BrO_2^\bullet$ System

Tabulated below are the presently recommended equilibrium constants involving the $BrO_2^\bullet$ radical. Uncertainties are expressed as ± 1 σ; in many cases the value of σ is merely a subjective guess.

reaction	K_{eq}	dim.	uncertainty	μ, M	Data Sheet #
$ClO_2^\bullet + BrO_2^- \rightleftharpoons ClO_2^- + BrO_2^\bullet$	1.0×10^{-6}		0.1×10^{-6}	0	41
$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2^\bullet + H_2O$	1×10^{-6}	M^{-1}	$(0.5\text{-}2) \times 10^{-6}$	0	42
$Br_2O_4 \rightleftharpoons 2BrO_2^\bullet$	5.3×10^{-5}	M	1.1×10^{-5}	0.01	43
$Ce(III) + BrO_2^\bullet(aq) + H^+ \rightleftharpoons Ce(IV) + HBrO_2(aq)$	7	M^{-1}	2	1	44

From reaction 41.1 (see below) and our recommended $E°$ for $ClO_2^\bullet$ we derive $E° = +(1.290 \pm 0.005)$ V for $BrO_2^\bullet/BrO_2^-$. From reaction 42.1 and other data we derive $E° = +(1.260 \pm 0.024)$ V for the $BrO_2^\bullet/BrO_2^-$ couple These two completely independent determinations of $E°$ agree within their uncertainties. Overall, we recommend the value derived from reaction 41.1 because of its smaller uncertainty and because the result from reaction 42.1 was derived with a large extrapolation from data at high (1.0 M) ionic strength. This result leads to $\Delta_f G° = +(152 \pm 4)$ kJ mol^{-1} for $BrO_2^\bullet(aq)$. Formal potentials at $\mu = 1$ M are derived from reaction 44.1 and are in good agreement with that derived from reaction 41.1.

Recommended values:

$BrO_2^\bullet(aq) + e^- \rightleftharpoons BrO_2^-(aq)$ $E° = +(1.290 \pm 0.005)$ V
$BrO_2^\bullet(aq) + H^+ + e^- \rightleftharpoons HBrO_2$ $E°' = +(1.49 \pm 0.01)$ V at 20 °C in 1 M H_2SO_4
$BrO_2^\bullet(aq) + e^- \rightleftharpoons BrO_2^-$ $E°' = +(1.29 \pm 0.01)$ V at 20 °C in 1 M H_2SO_4
$\Delta_f G°(BrO_2^\bullet(aq)) = +(152 \pm 4)$ kJ mol^{-1}

Nomenclature: $BrO_2^\bullet$, dioxidobromine(•), BrO_2^-, dioxidobromate(1−)

Data Sheet 41

Chemical equilibrium: $ClO_2^\bullet + BrO_2^- \rightleftharpoons ClO_2^- + BrO_2^\bullet$ (41.1)

List of reports:

$K_{eq} = 1.0 \times 10^{-6}$ [1]. Result obtained from the ratio of the forward and reverse rate constants. The forward rate constant was obtained from a stopped-flow study of the reaction of $ClO_2^\bullet$ with BrO_2^- at 25.0 °C and $\mu = 1.0$ M [1]. The reverse rate constant was obtained by pulse radiolysis, presumably at room temperature at an unspecified ionic strength [2].

Discussion

As the reverse rate constant is expected to be independent of ionic strength, the calculation of K_{eq} is not seriously compromised. K_{eq} should also be independent of ionic strength. The reverse rate constant is rather large (3.6×10^7 M^{-1} s^{-1}) and hence should not be very temperature dependent. A 6% uncertainty was assigned to the forward rate constant. We suggest a 10% uncertainty for the reverse rate constant. Thus, the uncertainty in K_{eq} is about 10%.

Given our recommended value of $E° = +(0.935 \pm 0.003)$ V for $ClO_2^\bullet/ClO_2^-$, we thus derive $E° = +(1.290 \pm 0.005)$ V for the couple $BrO_2^\bullet/BrO_2^-$. Prior estimates of this quantity are considered to be much less reliable.

Although not given in the NIST tables [3], the value for $\Delta_f G°$ (= +27.2 kJ mol^{-1}) for BrO_2^- given by Lee and Lister seems widely accepted [4, 5]. We suggest that the uncertainty in Lee and Lister's result is ± 4 kJ. Thus we derive $\Delta_f G° = +(152 \pm 4)$ kJ mol^{-1} for $BrO_2^\bullet$.

Recommended values:

$K_{eq} = (1.0 \pm 0.1) \times 10^{-6}$ at 25 °C and $\mu = 0.0$ M.
$E°(BrO_2^\bullet/BrO_2^-) = +(1.290 \pm 0.005)$ V
$\Delta_f G°(BrO_2^\bullet) = +(152 \pm 4)$ kJ mol^{-1}

Nomenclature: see Data Sheet 40.

List of auxiliary thermodynamic data: none.

References

1. L. Wang, J. S. Nicoson, K. E. H. Hartz, J. S. Francisco, D. W. Margerum. *Inorg. Chem.* **41,** 108-113 (2002).
2. R. E. Huie, P. Neta. *J. Phys. Chem.* **90,** 1193-1198 (1986).
3. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall. *J. Phys. Chem. Ref. Data* **11,** Suppl. No. 2 (1982).
4. C. L. Lee, M. W. Lister. *Can. J. Chem.* **49,** 2822-2826 (1971).
5. D. M. Stanbury. *Adv. Inorg. Chem.* **33,** 69-138 (1989).

Data Sheet 42

Chemical equilibrium: $HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2^{\bullet} + H_2O$ (42.1)

List of reports:

1) $K_{eq} = 5 \times 10^{-4}$ M^{-1} [1]. We calculate this from the forward and reverse rate constants selected by Field *et al.* (1972). The forward rate was assumed to be twice the rate of isotopic exchange between Br_2 and BrO_3^- as reported by Betts and MacKenzie (1951) [2], and the rate constant was calculated by assuming a mechanism with rate-limiting exchange between $HBrO_2$ and BrO_3^-; the concentration of $HBrO_2$ used in this calculation was based on a pK_a for $HBrO_2$ that is now known to be in error [3]. The reverse rate constant was from the pulse radiolysis study of Buxton and Dainton [4].

2) $K_{eq} = 1 \times 10^{-6}$ M^{-1}, in 1 M H_2SO_4 at 20.0 °C [5]. Calculated by Field and Försterling [5] from the data of Försterling *et al.* (1980), originally thought to refer to the dimerization equilibrium of $BrO_2^{\bullet}$ [6]. The experimental data were the equilibrium absorbances due to $BrO_2^{\bullet}$ in acidic mixtures of $HBrO_2$ and BrO_3^-.

3) $K_{eq} = 0.9 \times 10^{-6}$ M^{-1}, in 1 M H_2SO_4 at 20.0 °C [5]. Obtained from the kinetics of decay of $BrO_2^{\bullet}$ in an acidic $HBrO_2/BrO_3^-$ mixture; the calculation is directly dependent on the value for the k of $HBrO_2$ disproportionation, which was reported by other workers.

4) $K_{eq} = 8.0 \times 10^{-7}$ M^{-1} [7]. We calculate this equilibrium constant from the forward and reverse rate constants of the two component reactions as summarized by Gao and Försterling [7]:

$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons Br_2O_4 + H_2O$ $k_{5'}, k_{-5'}, K_{5'}$ (42.2)

$Br_2O_4 \rightleftharpoons 2BrO_2^{\bullet}$ $k_{5''}, k_{-5''}, K_{5''}$ (42.3)

We use here the authors' rate constant numbering scheme. Gao and Försterling [7] measured the value for $k_{5'}$ and used values for the other three rate constants as recommended by Field and Försterling (1986) [5]. These authors obtained their values for $k_{5''}$ and $k_{-5''}$ from the pulse radiolysis results of Buxton and Dainton (1968) [4]. They obtained the value for k_{-5} by combining their values for K_{eq}, $k_{5''}$, $k_{-5''}$ and $k_{5'}$. Their value for $k_{5'}$ was obtained from the kinetics of the oxidation of Ce(III) with BrO_3^- and from an assumed value for k_4 ($HBrO_2$ disproportionation). We conclude that this procedure leads to circularity in the argument, since there is no independent determination of $k_{-5'}$.

5) $K_{eq} = 2.2 \times 10^{-6}$ M^{-1}. We calculate this result from the value for $2k_{-5'}/K_{5''}$ (= 4.3×10^7 M^{-1} s^{-1} at room temperature and $\mu = 0.01$ M) reported by Buxton and Dainton [4] and the value for $k_{5'}$ (= 48 M^{-2} s^{-1} in 1 M H_2SO_4 at 20.0 °C) measured by Gao and Försterling [7].

Discussion

We exclude determinations #1 and #4 for the reasons mentioned above. The remaining three determinations of K_{eq} (#2, 3, and 5) are based on fundamentally different methods and yield essentially the same result. However, as many of the experiments were conducted in 1 M H_2SO_4 and at 20 °C, it is difficult to specify an accurate value for K_{eq} at 25 °C and $\mu = 0$ M. We tentatively recommend a value of $K_{eq} = 1 \times 10^{-6}$ M^{-1} with an uncertainty of a factor of 2 at 25 °C and $\mu = 0$ M.

NIST values [8] are lacking for $\Delta_f G°$ for $BrO_2^{\bullet}$, $HBrO_2$ and BrO_2^-, while the corresponding values are –(237.13 ± 0.08) for H_2O and +(18.6 ± 0.8) kJ mol^{-1} for BrO_3^- [8]. From the title reaction we derive

$$2\Delta_f G°(BrO_2^{\bullet}) - \Delta_f G°(HBrO_2) = -RT \ln K_{eq} - \Delta_f G°(H_2O) + \Delta_f G°(BrO_3^-)$$

and with our recomended value for K_{eq} we obtain

$$2\Delta_f G°(BrO_2^{\bullet}) - \Delta_f G°(HBrO_2) = (290.0 \pm 2.3) \text{ kJ mol}^{-1}$$

The value for $\Delta_f G°$ (= +27.2 kJ mol^{-1}) for BrO_2^- given by Lee and Lister [9] seems widely accepted, and we suggest that the uncertainty is ± 4 kJ [9, 10]. The K_a of $HBrO_2$ is now believed to be $(3.7 \pm 0.9) \times 10^{-4}$ M at 25.0 °C and $\mu = 0.06$ M [3], and thus we derive $\Delta_f G°(HBrO_2)$ = +(6.8 ± 4) kJ mol^{-1}. We then derive from the above that $\Delta_f G°(BrO_2^{\bullet})$ = +(148 ± 2) kJ mol^{-1}, $E°(BrO_2^{\bullet},H^+/HBrO_2)$ = +(1.468 ± 0.024) V, and $E°(BrO_2^{\bullet}/BrO_2^-)$ = +(1.260 ± 0.024) V.

Recommended values:

$K_{eq} = 1 \times 10^{-6}$ M^{-1} with an uncertainty of a factor of 2 at 25 °C and $\mu = 0$ M
$\Delta_f G°(BrO_2^{\bullet})$ = +(148 ± 2) kJ mol^{-1}
$BrO_2^{\bullet} + H^+ + e^- \rightleftharpoons HBrO_2$ $E°$ = +(1.47 ± 0.02) V
$BrO_2^{\bullet} + e^- \rightleftharpoons BrO_2^-$ $E°$ = +(1.26 ± 0.02) V

Nomenclature: see Data sheet 40; $HBrO_2$, hydroxidooxidobromine; BrO_3^-, trioxidobromate(1−); Br_2O_4, tetraoxidodibromine.

List of auxiliary thermodynamic data: none.

References

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2. R. H. Betts, A. N. MacKenzie. *Can. J. Chem.* **29,** 655-665 (1951).
3. R. B. Faria, I. R. Epstein, K. Kustin. *J. Phys. Chem.* **98,** 1363-1367 (1994).
4. G. V. Buxton, F. S. Dainton. *Proc. Roy. Soc. A (London)* **304,** 427-439 (1968).
5. R. J. Field, H.-D. Försterling. *J. Phys. Chem.* **90,** 5400-5407 (1986).
6. H.-D. Försterling, H. J. Lamberz, H. Schreiber. *Z. Naturforsch.* **35a,** 1354-1360 (1980).
7. Y. Gao, H.-D. Försterling. *J. Phys. Chem.* **99,** 8638-8644 (1995).
8. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall. *J. Phys. Chem. Ref. Data* **11,** Suppl. No. 2 (1982).
9. C. L. Lee, M. W. Lister. *Can. J. Chem.* **49,** 2822-2826 (1971).
10. D. M. Stanbury. *Adv. Inorg. Chem.* **33,** 69-138 (1989).

Data Sheet 43

Chemical equilibrium: $Br_2O_4 \rightleftharpoons 2BrO_2^{\bullet}$ (43.1)

List of reports:

$1/K_{eq} = (18.8 \pm 4.0)\ M^{-1}$ at room temperature and $\mu = 0.01$ M [1]. Buxton and Dainton obtained this result by pulse radiolysis of BrO_3^-, measuring the optical absorbance at equilibrium. This result was later shown to be inconsistent with the reported optical traces [2].

$K_{eq} = 1.5 \times 10^{-6}$ M at 20 °C and $\mu = 2$ M [2]. From the equilibrium absorbance of $BrO_2^{\bullet}$ in BrO_2^-/BrO_3^- mixtures. It was later shown that this result was mistakenly attributed to reaction 43.1 instead of reaction 42.1 [3].

$K_{eq} = 5.3 \times 10^{-5}$ M at room temperature and $\mu = 0.01$ M [4]. Obtained from the data of Buxton and Dainton by correcting for a computational error. This result was qualitatively confirmed in unpublished experiments Försterling *et al.* that were cited by Field and Försterling [3]; the experiments utilized flash photolysis in 1 M H_2SO_4.

Discussion

From this remarkable set of experiments and subsequent corrections we recommend the value of 5.3×10^{-5} M for K_{eq} at room temperature and $\mu = 0.01$ M. We also recommend the 21% uncertainty reported in the original work of Buxton and Dainton.

Recommended values:

$K_{eq} = (5.3 \pm 1.1) \times 10^{-5}$ M at room temperature and $\mu = 0.01$ M

Nomenclature: see Data sheet 42.

List of auxiliary thermodynamic data: none.

References

1. G. V. Buxton, F. S. Dainton. *Proc. Roy. Soc. A (London)* **304,** 427-439 (1968).
2. H.-D. Försterling, H. J. Lamberz, H. Schreiber. *Z. Naturforsch.* **35a,** 1354-1360 (1980).
3. R. J. Field, H.-D. Försterling. *J. Phys. Chem.* **90,** 5400-5407 (1986).
4. L. Kuhnert, H.-J. Krug, L. Pohlmann. *J. Phys. Chem.* **89,** 2022-2026 (1985).

Data Sheet 44

Chemical equilibrium: Ce(III) + $BrO_2^•(aq)$ + H^+ $\rightleftharpoons$ Ce(IV) + $HBrO_2(aq)$ (44.1)

List of reports:

$K_{eq} = 1.5\ M^{-1}$ at $\mu \sim 1$ M and ~25 °C. Calculated here from the ratio of the forward and reverse rate constants as summarized by Field and Försterling [1]. The forward reaction was investigated by Försterling *et al.* at 20 °C in 1 M H_2SO_4 by conventional spectrophotometry [2]; they obtained a rate constant of $(1.0 \pm 0.05) \times 10^5\ M^{-1}\ s^{-1}$. Note that the rate constant was reported as a second order one: the pH dependence was not investigated. Field and Forsterling subsequently converted the rate constant to third-order dimensions on the assumption of a first-order dependence on $[H^+]$, and they corrected for the effects of the reversibility of the reaction to obtain a forward rate constant of $8 \times 10^4\ M^{-2}\ s^{-1}$ [1]. The reverse reaction was studied by Sullivan and Thompson at 25 °C with 0.3 M $NaClO_4$ and 0.3 M H_2SO_4 by stopped-flow spectrophotometry; they obtained a reverse rate constant of $5.5 \times 10^4\ M^{-1}\ s^{-1}$ [3]. However, they [3] were unable to obtain meaningful kinetic results at higher acidities because the reaction did not proceed.

Discussion

Försterling and Varga [4] reinvestigated the reverse reaction, using a special reactor design that allowed meaningful data to be acquired at acidities higher than those attained by Sullivan and Thompson [3]. Försterling and Varga [4] noted a strong dependence of the rate constant on ionic strength, which was attributed to the medium dependence of the distribution between the various Ce(IV)/SO_4^{2-} species. At 20 °C and 1 M H_2SO_4 they obtained a reverse rate constant of $1.2 \times 10^4\ M^{-2}\ s^{-1}$. If we combine this rate constant with the forward rate constant recommended by Field and Försterling [1] ($8 \times 10^4\ M^{-2}\ s^{-1}$), we obtain an equilibrium constant of 6.7 for reaction 44.1 at 20 °C in 1 M H_2SO_4. Given the strong medium effects and other complications we suggest an uncertainty of ± 30% for this result.

Field and Försterling interpreted the Ce(III)/$BrO_2^•$ reaction by use of $E°' = 1.44$ V for Ce(IV)/Ce(III), but they did not cite a source for this potential [1]. A formal potential of 1.44 V in 1 M H_2SO_4 is recommended in *Standard Potentials in Aqueous Solution* [5]. We assume an uncertainty of ± 10 mV in this formal potential. This leads to $E°' = (1.49 \pm 0.01)$ V for the couple ($BrO_2^•(aq)$, H^+)/$HBrO_2$.

The pK_a of $HBrO_2$ is (3.43 ± 0.05) at 25 °C and $\mu = 0.06$ M [6]. No doubt this pK_a depends significantly on ionic strength, but procedures to extrapolate to $\mu = 1$ M are unreliable. However, by working in analogy with the pK_a of $HClO_2$, we suggest that the pK_a of $HBrO_2$ is (3.16 ± 0.10) at $\mu = 1.0$ M. This leads to $E^{\circ\prime} = (1.30 \pm 0.01)$ V for $BrO_2^{\bullet}/BrO_2^-$.

Recommended values:

$K_{eq} = (7 \pm 2)$ at 20 °C in 1 M H_2SO_4.

$BrO_2^{\bullet}(aq) + H^+ + e^- \rightleftharpoons HBrO_2$ $\quad E^{\circ\prime} = +(1.49 \pm 0.01)$ V at 20 °C in 1 M H_2SO_4

$BrO_2^{\bullet}(aq) + e^- \rightleftharpoons BrO_2^-$ $\quad E^{\circ\prime} = +(1.30 \pm 0.01)$ V at 20 °C in 1 M H_2SO_4

List of auxiliary thermodynamic data: $E^{\circ\prime}$ for Ce(IV)/Ce(III), pK_a for $HBrO_2$.

Nomenclature: see Data Sheet 43.

References

1. R. J. Field, H.-D. Försterling. *J. Phys. Chem.* **90,** 5400-5407 (1986).
2. H. D. Försterling, H. J. Lamberz, H. Schreiber. *Z. Naturforsch.* **40a,** 368-372 (1985).
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6. R. B. Faria, I. R. Epstein, K. Kustin. *J. Phys. Chem.* **98,** 1363-1367 (1994).

Data Sheet 45

Summary of the $I/I_2^{\bullet-}$ System

Tabulated below are the presently recommended equilibrium constants involving this related group of iodine radicals. Uncertainties are expressed as ± 1 σ; in many cases the value of σ is merely a subjective guess.

rxn #	reaction	K_{eq}	dim.	uncertainty	μ / M	Data Sheet #
46.1	$2I^- + [Os(bpy)_3]^{3+} \rightleftharpoons I_2^{\bullet-} + [Os(bpy)_3]^{2+}$	3×10^{-4}	M^{-1}	$\pm 1 \times 10^{-4}$	0.1	46
47.1	$I_2(aq) + HO_2^{\bullet} \rightleftharpoons I_2^{\bullet-} + H^+ + O_2(aq)$	30	M	± 15	1.0	47
48.1	$I_2^{\bullet-} + DMTD^{2-} \rightleftharpoons DMTD^{\bullet-} + 2I^-$	2.0×10^3	M	$\pm 0.5 \times 10^3$	0.2	48
49.1	$NO_2^{\bullet} + I^- \rightleftharpoons NO_2^- + I^{\bullet}(aq)$	none				49
50.1	$I_2^{\bullet-} + PZH^+ \rightleftharpoons PZH^{2+} + 2I^-$	90	M	45-180	~0.1	50
51.1	$I^{\bullet}(aq) + H_2O \rightleftharpoons IOH^{\bullet-} + H^+$	5×10^{-14}	M	$(1.5 - 15) \times 10^{-14}$	0.1	51
52.1	$I^{\bullet}(aq) + I^- \rightleftharpoons I_2^{\bullet-}$	1.35×10^5	M^{-1}	$\pm 0.11 \times 10^5$	Low	52
53.1	$HO^{\bullet} + I^- \rightleftharpoons IOH^{\bullet-}$	1.2×10^4	M^{-1}	$(0.6–2.4) \times 10^{-4}$	10	53
54.1	$IOH^{\bullet-} + I^- \rightleftharpoons I_2^{\bullet-} + HO^-$	2.5×10^4		$\pm 1.2 \times 10^4$	1.0	54
55.1	$ISCN^{\bullet-} + SCN^- \rightleftharpoons (SCN)_2^{\bullet-} + I^-$	2.5×10^{-3}		$\pm 0.4 \times 10^{-3}$	0.3 -1	55
56.1	$ISCN^{\bullet-} + I^- \rightleftharpoons I_2^{\bullet-} + SCN^-$	55		± 19	0.035	56
57.1	$(CH_3)_2S + I_2^{\bullet-} \rightleftharpoons (CH_3)_2S \therefore I + I^-$	2×10^{-1}		$(1 - 4) \times 10^{-1}$		57
58.1	$(CH_3CH_2)_2S + I_2^{\bullet-} \rightleftharpoons (CH_3CH_2)_2S \therefore I + I^-$	4.5×10^{-1}		$(2 - 9) \times 10^{-1}$		58

In reaction 48.1, DMTD is 2,5-dimercaptothiadiazole [IUPAC PIN: 1,3,4-thiadiazole-2,5-dithiol]. In reaction 50.1, PZH is promethazine (a phenothiazine); IUPAC PIN: *N,N*-dimethyl-1-(10*H*-phenazin-10-yl)propan-2-amine.

Internal consistency test.

A closed thermodynamicchemical cycle is formed from reactions 54.1, 51.1, and 52.1. Thus we expect to find that $K(54.1) = K(52.1)K_w/K(51.1)$. The above values give: $2.5 \times 10^4 = (1.35 \times 10^5\ M^{-1})(1 \times 10^{-14}\ M^2)/(10^{-13.3}\ M) = 2.7 \times 10^4$, in rather good agreement!

Derived $E°$ for $I_2^{\bullet -} + e^- \rightleftharpoons 2I^-$:

Reaction 46.1 leads directly to $E°$ for $I_2^{\bullet -} + e^- = 2I^-$. Nord *et al.* report that $E°' = +(0.857 \pm 0.004)$ V for Os(III)/Os(II) in 0.10 M NaCl, which thus gives $E°' = +(1.063 \pm 0.011)$ V for $I_2^{\bullet -}/2I^-$ [1].

Reaction 47.1 leads directly to $E°$ for $I_2(aq) + e^- \rightleftharpoons I_2^{\bullet -}$. Schwarz and Bielski used $E° = -0.33$ V for $O_2/O_2^{\bullet -}$, the NIST(68) value for $\Delta_f G°(O_2(aq)) = +16.4$ kJ (which is unchanged in the current NIST tabulation [2]), and $pK_a = 4.8$ to derive $E° = +0.21$ V for $I_2(aq)/I_2^{\bullet -}$ [3]. We now recommend $E° = -(0.35 \pm 0.01)$ V for $O_2(g)/O_2^{\bullet -}$, which leads to $E° = +(0.19 \pm 0.015)$ V for $I_2(aq)/I_2^{\bullet -}$. Use of the NIST values for $\Delta_f G°(I_2(aq)) = +16.40$ kJ and $\Delta_f G°(I^-) = -51.57$ kJ yields $E° = +(1.05 \pm 0.02)$ V for $I_2^{\bullet -}/2I^-$.

Reaction 48.1 leads to no recommendations because the $DMTD^{\bullet -}/DMTD^{2-}$ potential is presently not known independently.

Reaction 49.1 leads to no recommendation because no equilibrium constant is recommended.

Reaction 50.1 can be used to derive $E°(I_2^{\bullet -}/2I^-)$ from $E°$ for PZH^{2+}/PZH^+. Wardman recommends a value of +0.865 V for the latter [4], which leads to $E° = (0.981 \pm 0.021)$ V for $I_2^{\bullet -}/2I^-$. More recently, Madej and Wardman recommended $E° = +0.935$ V for PZH [5], which adjusts the derived $I_2^{\bullet -}/2I^-$ potential to +1.05 V.

The addition of reactions 53.1 and 54.1 gives $HO^\bullet + 2I^- \rightleftharpoons I_2^{\bullet -} + HO^-$, for which the recommended equilibrium constants give $K = 3 \times 10^8\ M^{-1}$ within a factor of 2.5. If we use the optimized potential (Data Sheet 7) for $HO^\bullet/HO^-$ ($E° = +1.902 \pm 0.017$ V), we derive $E° = +1.40$ V for $I_2^{\bullet -}/2I^-$, which is absurd in the context of the above results. We suggest that reaction 53.1 is far from correct, since the other reactions are part of the consistency cycle presented above. Equilibrium constant 53.1, taken from the ratio of the forward and reverse rate constants, makes use of a very low fitted reverse rate constant of $2 \times 10^6\ s^{-1}$, and a much lower value is required in order to obtain a reasonable $E°$. We suspect that this is the likely cause of the error.

By combining reactions 55.1 and 56.1 we obtain $I_2^{\bullet -} + 2SCN^- \rightleftharpoons (SCN)_2^{\bullet -} + 2I^-$, for which the equilibrium constant is calculated as $4.55 \times 10^{-5} \pm 50\%$. The presently recommended $E°((SCN)_2^{\bullet -}/2SCN^-)$ (Data Sheet 101) is $+(1.30 \pm 0.02)$ V, which leads to $E° = +(1.043 \pm 0.026)$ V for $I_2^{\bullet -}/2I^-$.

The two thioether reactions (57.1 and 58.1) given above do not lead to a derived $E°(I_2^{\bullet -}$

$/2I^-$) because there is no independent information regarding the product, iododimethylsulfur(•),

As reported by Stanbury *et al.* and summarized by Nord, a large group of one-electron oxidations of iodide have measured rate constants for the step $M_{ox} + I^- \rightleftharpoons M_{red} + I^\bullet$ [6, 7]. It was argued that the reverse process, in general, is diffusion controlled, with $k_r = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}$, which thus led to an assignment of $E° = +(1.33 \pm 0.03)$ V for $I^\bullet/I^-$. By combination with the above recommended value for reaction 52.1 we derive $E° = +(1.03 \pm 0.03)$ V for $I_2^{\bullet-}/2I^-$.

Summary and Evaluation of Derived $E°(I_2^{\bullet-}/2I^-)$

With the exclusion of the result derived from reaction 53.1, the five completely independent derived results given above are in agreement that $E°(I_2^{\bullet-}/2I^-)$ is within the range of +1.03 to 1.06 V, and the individual results are completely in agreement within their uncertainties. We thus recommend an average value of +(1.05 ± 0.02) V for $E°(I_2^{\bullet-}/2I^-)$. The other derived quantities given below are derived from this value with use of NIST thermodynamicchemical data [2] for the stable species and the recommended equilibrium constants given above.

Recommended values:

$I_2^{\bullet-} + e^- \rightleftharpoons 2I^-$	$E° = +(1.05 \pm 0.02)$ V
$I^\bullet + e^- \rightleftharpoons I^-$	$E° = +(1.35 \pm 0.02)$ V
$I_2(aq) + e^- \rightleftharpoons I_2^{\bullet-}$	$E° = +(0.19 \pm 0.02)$ V
$I_2^{\bullet-}$	$\Delta_f G° = -(2.1 \pm 1.9)$ kJ
$I^\bullet(aq)$	$\Delta_f G° = +(79 \pm 2)$ kJ
$IOH^{\bullet-}$	$\Delta_f G° = -(83 \pm 2)$ kJ
$ISCN^{\bullet-}$	$\Delta_f G° = +(152 \pm 2)$ kJ

Nomenclature: $I^\bullet$, iodine(•); I^-, iodide; I_2, diiodine; $I_2^{\bullet-}$, diiodide(•1−); $IOH^{\bullet-}$, hydroxidoiodate(•1−); $ISCN^{\bullet-}$, (iodosulfato)nitridocarbonate(•1−); $(CH_3)S\therefore I$, iododimethylsulfur(•).

References

1. G. Nord, B. Pedersen, E. Floryan-Løvborg, P. Pagsberg. *Inorg. Chem.* **21,** 2327-2330 (1982).
2. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall. *J. Phys. Chem. Ref. Data* **11,** Suppl. No. 2 (1982).
3. H. A. Schwarz, B. H. Bielski. *J. Phys. Chem.* **90,** 1445-1448 (1986).

4. P. Wardman. *J. Phys. Chem. Ref. Data* **18,** 1637-1755 (1989).
5. E. Madej, P. Wardman. *Rad. Phys. Chem.* **75,** 990-1000 (2006).
6. G. Nord. *Comments Inorg. Chem.* **13,** 221-239 (1992).
7. D. M. Stanbury, W. K. Wilmarth, S. Khalaf, H. N. Po, J. E. Byrd. *Inorg. Chem.* **19,** 2715-2722 (1980).

Data Sheet 46

Chemical equilibrium: $2I^- + [Os(bpy)_3]^{3+} \rightleftharpoons I_2^{\bullet -} + [Os(bpy)_3]^{2+}$ (46.1)

List of reports:

$K_{eq} = (3.1 \pm 0.9) \times 10^{-4}\ M^{-1}$, at 22 °C and $\mu = 0.1$ M [1]. We calculate this result from the ratio of the forward and reverse rate constants reported by Nord *et al.* The forward rate constant was obtained by stopped-flow kinetics, while the reverse was obtained by pulse radiolysis.

Discussion

This work appears to be reliable and is accepted as given.

Recommended value:

$K_{eq} = (3.1 \pm 0.9) \times 10^{-4}\ M^{-1}$, at 22 °C and $\mu = 0.1$ M.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 45

References

1. G. Nord, B. Pedersen, E. Floryan-Løvborg, P. Pagsberg. *Inorg. Chem.* **21,** 2327-2330 (1982).

Data Sheet 47

Chemical equilibrium: $I_2(aq) + HO_2 \rightleftharpoons I_2^{\bullet-} + H^+ + O_2(aq)$ (47.1)

List of reports:

K_{eq} = (30 ± 15) M at 25 °C and μ = 1.0 M ($LiClO_4$) [1]. From pulse radiolysis of $I^-/I_2/O_2$ solutions, measuring the equilibrium yield of $I_2^{\bullet-}$.

Discussion

As this is the sole report on this reaction, and it appears to have been conducted competently, we recommend the reported result. Note, however, that the result should depend significantly on ionic strength.

Recommended value:

K_{eq} = (30 ± 15) M at 25 °C and μ = 1.0 M

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 45.

References

1. H. A. Schwarz, B. H. Bielski. *J. Phys. Chem.* **90,** 1445-1448 (1986).

Data Sheet 48

Chemical equilibrium: $I_2^{\bullet-} + DMTD^{2-} \rightleftharpoons DMTD^{\bullet-} + 2I^{-}$ (48.1)

DMTD^{2-} is the dianion of 2.5-dimercaptothiadiazole.

DMTD IUPAC PIN: 1,3,4-thiadiazole-2,5-dithiol.

List of reports:

$K_{eq} = 2 \times 10^3$ M, at room temperature (presumably) and $\mu = 0.2$ M [1]. Kishore *et al.* obtained this result with pulse radiolysis, determining the equilibrium constant from the kinetics of approach to equilibrium.

Discussion

No uncertainty was specified in the original publication, but we suggest is should be ± 25%.

Recommended value:

$K_{eq} = (2.0 \pm 0.5) \times 10^3$ M at $\mu = 0.2$ M.

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 45.

References

1. K. Kishore, G. R. Dey, P. N. Moorthy. *J. Phys. Chem.* **99,** 13476-13479 (1995).

Data Sheet 49

Chemical equilibrium: $NO_2^\bullet(aq) + I^- \rightleftharpoons NO_2^- + I^\bullet(aq)$ (49.1)

List of reports:

$k_f = 1.1 \times 10^5\ M^{-1}\ s^{-1}$ was mentioned by Willson and co-workers, stating that it was determined by pulse radiolysis [1]. This number does not contradict the upper limit $k_f < 1 \times 10^7\ M^{-1}\ s^{-1}$ obtained earlier by Barkatt and Ottolenghi who also used pulse radiolysis [2].

$k_r = 8.8 \times 10^9\ M^{-1}\ s^{-1}$ was obtained using flash photolysis to generate the I atom; competition with the $I^\bullet + I^-$ reaction was measured [2]. An upper limit $K_{eq} < 1.1 \times 10^{-3}$ was suggested.

Discussion

$K_{eq} = 1.3 \times 10^{-5}$ can be derived from the reported $k_f = 1.1 \times 10^5\ M^{-1}\ s^{-1}$ and $k_r = 8.8 \times 10^9\ M^{-1}\ s^{-1}$. The reverse rate constant appears to be fairly reliable, as it is based on $k = 9.8 \times 10^9\ M^{-1}\ s^{-1}$ for the competing $I^\bullet + I^-$ reaction and this value agrees within some 20% with most of the other measurements that have been tabulated [3]. In contrast, the reliability of the forward rate constant is impossible to judge. Indeed, Willson and co-workers [1] refer to their own work, which has never been published, so no experimental details are available. However, the accurate measurement of such a low k_f by pulse radiolysis appears to be extremely challenging (if at all possible) experimentally due to the approximately equal rate constants of $HO^\bullet$ with NO_2^- and I^- (requiring $[NO_2^-] >> [I^-]$ for selective formation of $NO_2^\bullet$) and the self-recombination of $NO_2^\bullet$ at low $[I^-]$. At the same time, the very rapid reverse reaction requires $[NO_2^-] << [I^-]$ to help quickly remove the I atom via the $I^\bullet + I^-$ reaction.

In the absence of any experimental evidence for k_f, it is prudent to refrain from evaluating K_{eq}.

Recommended value:

None

List of auxiliary thermodynamic data: none

Nomenclature: see Data Sheet 45; $NO_2^\bullet$, nitrogen dioxide or dioxidonitrogen(•)

References

1. L. G. Forni, V. O. Mora-Arellano, J. E. Packer, R. L. Willson. *J. Chem. Soc., Perkin Trans. II* 1-6 (1986).
2. A. Barkatt, M. Ottolenghi. *Mol. Photochem.* **6,** 253-261 (1974).
3. P. Neta, R. E. Huie, A. B. Ross. *J. Phys. Chem. Ref. Data* **17,** 1027-1284 (1988).

Data Sheet 50

Chemical equilibrium: $I_2^{\bullet-} + PZH^+ \rightleftharpoons PZH^{\bullet 2+} + 2I^-$ (50.1)

PZH = promethazine (a phenothiazine)

IUPAC PIN: *N,N*-dimethyl-1-(10*H*-phenazin-10-yl)propan-2-amine

List of reports:

K_{eq} = (90 ± 5) M, at room temperature and variable ionic strength [1]. Bahnemann *et al.* obtained this result with pulse radiolysis, and the reported result is the average of the kinetic result (k_f/k_r) and the equilibrium result.

Discussion

As this equilibrium constant is expected to be sensitive to ionic strength and the ionic strength was not held constant in these studies, the reported uncertainty is an underestimate. We suggest a more reasonable estimate of the uncertainty is a factor of 2.

Recommended value:

K_{eq} = (45 − 180) M.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 45.

References

1. D. Bahnemann, K.-D. Asmus, R. L. Willson. *J. Chem. Soc., Perkin Trans. II* 1669-1673 (1983).

Data Sheet 51

Chemical equilibrium: $I^\bullet(aq) + H_2O \rightleftharpoons IOH^{\bullet-} + H^+$ (51.1)

List of reports:

$pK_a = (11.7 \pm 1)$, at 296 K and 10 M ionic strength [1]. Büchler and Bühler used pulse radiolysis of iodide in strongly alkaline solutions, and fitted the kinetics of $I_2^{\bullet-}$ growth and decay to a complex mechanism to obtain the equilibrium constant.

$pK_a = 13.3$, no specified uncertainty, at (22 ± 2) °C and $\mu = 10^{-4}$ to 0.1 M [2]. Mulazzani and Buxton used pulse radiolysis of iodide at pH 10 and 13, monitored the kinetics at 380 nm, and fit the complex kinetics to a complex mechanism to derive forward and reverse rate constants for the addition of HO^- to $I^\bullet$. This equilibrium constant was then converted to a pK_a by use of an unspecified value for K_w.

Discussion

The two reports differ quite substantially with regard to the value of pK_a. Both reports used essentially the same method and obtained rather similar results. The main difference between the two seems to be the absorption coefficients of $HOI^{\bullet-}$ and $I_2^{\bullet-}$ used in the fitting. Mullazani and Buxton argue that Büchler and Bühler erred in resolving the two spectra by neglecting the absorbance of $HOI^{\bullet-}$ at 360 nm. This seems to be a reasonable argument, and thus we accept the result of Mullazani and Buxton. Given the apparent sensitivity of the derived parameters to the model specifications, we infer that the derived pK_a has an uncertainty of at least 0.2 units. Further adding to the uncertainty are unknowns relating to the conversion between $[HO^-]$ and pH and ionic strength effects. Overall, an uncertainty of ± 0.5 pK_a units seems appropriate.

Recommended value:

$pK_a = (13.3 \pm 0.5)$ at 22 °C and $\mu = 0.1$ M.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 45.

References

1. H. Büchler, R. E. Bühler. *Chem. Phys.* **16,** 9-18 (1976).
2. Q. G. Mulazzani, G. V. Buxton. *Chem. Phys. Lett.* **421,** 261-265 (2006).

Data Sheet 52

Chemical equilibrium: $I^{\bullet}(aq) + I^{-} \rightleftharpoons I_2^{\bullet-}$ (52.1)

List of reports:

$K_{eq} > 1.2 \times 10^4$ M^{-1}. From flash photolysis of iodide solutions. A very early report (1957) from Grossweiner and Matheson [1].

$K_{eq} = 1.3 \times 10^5$ M^{-1} at 22 °C at pH 7 in phosphate buffer of unspecified ionic strength [2]. Baxendale *et al.* used pulse radiolysis of iodide solutions, monitoring the kinetics of decay.

$K_{eq} = 1.13 \times 10^5$ M^{-1} at 22 °C at pH 7 in phosphate buffer of unspecified ionic strength [2, 3]. Baxendale *et al.* used pulse radiolysis of iodide solutions, with spectrophotometric detection of the position of equilibrium.

$K_{eq} = 8.4 \times 10^4$ M^{-1} under unspecified conditions [4]. Thomas used pulse radiolysis of iodide solutions.

$K_{eq} = 1.4 \times 10^4$ M^{-1} at unspecified temperature and low ionic strength [5]. Fournier de Violet et al used flash photolysis of iodine solutions, monitoring the yield of $I_2^{\bullet-}$. No mention was made regarding the pH of the solutions or any measures to remove O_2.

$K_{eq} = 1.2 \times 10^4$ M^{-1} at unspecified temperature and low ionic strength [6]. Fournier de Violet et al used flash photolysis of HgI_2/I^- solutions, monitoring the kinetics of formation of $I_2^{\bullet-}$. No mention was made regarding the pH of the solutions or any measures to remove O_2.

$K_{eq} = (1.1 \pm 0.2) \times 10^4$ M^{-1} at (20 ± 2) °C and low ionic strength [7]. Barkatt and Ottolenghi used flash photolysis of I_3^- solutions, monitoring the yield of $I_2^{\bullet-}$ and also the kinetics of its formation. No mention was made regarding the pH of the solutions or any measures to remove O_2.

$K_{eq} = (3 \pm 2) \times 10^3$ M^{-1} at 25 °C and low ionic strength [8]. Treinin and Hayon used flash photolysis of I_3^- solutions, monitoring the yield of $I_2^{\bullet-}$ and also the kinetics of its formation.

$K_{eq} = 5.0 \times 10^4$ M^{-1} at 22 °C and low ionic strength [9]. Elliot and Sopchyshyn used pulse radiolysis of I^- solutions, monitoring the yield of $I_2^{\bullet-}$.

$K_{eq} = 1.1 \times 10^5$ M^{-1} (± 15%) at 25 °C and low ionic strength [10]. Schwarz and Bielski used pulse radiolysis of I^- solutions, monitoring the yield of $I_2^{\bullet-}$.

$K_{eq} = 1.28 \times 10^5$ M^{-1} at 25 °C and low ionic strength [11]. Elliot interpolated this result from the temperature-dependent data of Schwarz and Bielski [10].

$K_{eq} = 1.0 \times 10^5$ M^{-1} at 25 °C and low ionic strength [12]. Merény and Lind used pulse radiolysis of ICH_2CH_2I, measuring the rate of dissociation of $I_2^{\bullet-}$ produced, and obtained the equilibrium constant from the ratio of the formation and dissociation rate constants.

$K_{eq} = (1.35 \pm 0.10) \times 10^5\ M^{-1}$ at 21 °C and low ionic strength [13]. Barker's group used flash photolysis of I^-, measuring the rate of formation of $I_2^{\bullet-}$ to obtain the forward and reverse rate constants, from the ratio of which the equilibrium constant is derived.

Discussion

The reported equilibrium constants range from 3×10^3 M to $1.35 \times 10^5\ M^{-1}$, and in none of the reports is an explanation provided for disagreement with prior results. It was noted in 1989 that the flash-photolysis results clustered around the lower value while the pulse radiolysis results clustered around the higher value [14]; recently, however, the careful flash-photolysis study from Barker's group supports the highest value.

Another conceivable explanation for the diversity of reported values for K_{eq} is the failure to remove O_2 or control pH. O_2 could interfere in studies where the solvated electron was involved, or possibly through direct reaction with $I_2^{\bullet-}$, high pH could lead to the formation of IOH^- from $I^\bullet$ and HOI from I_2, and low pH could lead to formation of $HI^{\bullet-}$ through reaction of H atoms with I^- [15].This would exclude the results from Thomas [4], from Barkatt and Ottolenghi [7], and from Fornier de Violet [5, 6]. These exclusions would lead to values of K_{eq} clustering at the high end of the range, with the notable outlier from Treinin and Hayon [8]. Note, however, that Treinin and Hayon specifically state that O_2 had no effect and that I_2 is insignificantly hydrolyzed at pH 6 [8]. Treinin and Hayon found that the $I_2^{\bullet-}$ dissociation rate constant was the same at (25 and 75) °C, which seems quite unlikely. Apparently, the results of Treinin and Hayon are flawed, although for unknown reasons. Thus we support the results obtained with K_{eq} near $10^5\ M^{-1}$.

We presently recommend the most recent result from Barker's group on the basis of the care and in-depth character of the study although we would be more comfortable if the prior low values could be rationalized or tested.

Recommended value:

$$K_{eq} = (1.35 \pm 0.10) \times 10^5\ M^{-1}$$

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 45.

References

1. L. I. Grossweiner, M. S. Matheson. *J. Phys. Chem.* **61,** 1089-1095 (1957).
2. J. H. Baxendale, P. L. T. Bevan, D. A. Stott. *Trans. Faraday Soc.* **64,** 2389-2397 (1968).
3. J. H. Baxendale, P. L. T. Bevan. *J. Chem. Soc. (A)* 2240-2241 (1969).
4. J. K. Thomas. *Adv. Rad. Chem.* **1,** 103-198 (1969).
5. P. Fornier de Violet, R. Bonneau, J. Joussot-Dubien. *J. Chim. Phys.* **70,** 1404-1409 (1973).
6. P. Fornier de Violet, R. Bonneau, S. R. Logan. *J. Phys. Chem.* **78,** 1698-1701 (1974).
7. A. Barkatt, M. Ottolenghi. *Mol. Photochem.* **6,** 253-261 (1974).
8. A. Treinin, E. Hayon. *Int. J. Radiat. Phys. Chem.* **7,** 387-393 (1975).
9. A. J. Elliot, F. C. Sopchyshyn. *Int. J. Chem. Kinet.* **16,** 1247-1256 (1984).
10. H. A. Schwarz, B. H. Bielski. *J. Phys. Chem.* **90,** 1445-1448 (1986).
11. A. J. Elliot. *Can. J. Chem.* **70,** 1658-1661 (1992).
12. G. Merényi, J. Lind. *J. Am. Chem. Soc.* **116,** 7872-7876 (1994).
13. Y. Liu, R. L. Sheaffer, J. R. Barker. *J. Phys. Chem. A* **107,** 10296-10302 (2003).
14. D. M. Stanbury. *Adv. Inorg. Chem.* **33,** 69-138 (1989).
15. A. J. Elliot, S. Geertsen, G. V. Buxton. *J. Chem. Soc., Faraday Trans. 1* **84,** 1101-1112 (1988).

Data Sheet 53

Chemical equilibrium: $HO^{\bullet} + I^{-} \rightleftharpoons IOH^{\bullet-}$ (53.1)

List of reports:

$K_{eq} = 1.2 \times 10^{4}\ M^{-1}$, within a factor of 2 at 296 K and 10 M ionic strength [1]. We obtain this result from the ratio of forward and reverse rate constants reported by Büchler and Bühler. The estimated uncertainty is derived from the reported uncertainties in the individual rate constants. They obtained their rate constants by pulse radiolysis of iodide, fitting the kinetics with a complex procedure.

Discussion

As this is the sole report and seems to have been performed competently, we accept the result. Although the experiments were conducted at very high ionic strength, the equilibrium constant is not expected to be very sensitive to this parameter. However, this result leads to an unacceptable standard potential for $I_2^{\bullet-}/2I^{-}$, which implies that there is something fundamentally wrong with this result; see the iodine radical summary pages (Data Sheet 45) for an explanation.

Recommended value:

None, or $K_{eq} = 1.2 \times 10^{4}\ M^{-1}$, within a factor of 2.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 45.

References

1. H. Büchler, R. E. Bühler. *Chem. Phys.* **16,** 9-18 (1976).

Data Sheet 54

Chemical equilibrium: $IOH^{\bullet-} + I^- \rightleftharpoons I_2^{\bullet-} + HO^-$ (54.1)

List of reports:

$K_{eq} = (2.5 \pm 1.2) \times 10^4$, at 296 K and 1 - 10 M ionic strength [1]. Büchler and Bühler used pulse radiolysis of iodide in strongly alkaline solutions, determining the position of equilibrium spectrophotometrically.

Discussion

As this is the sole report on this reaction, and it appears to have been conducted competently, we recommend the reported result. Note, however, that the result should depend significantly on ionic strength.

Recommended value:

$K_{eq} = (2.5 \pm 1.2) \times 10^4$ at 25 °C and $\mu = 1.0$ M

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 54.

References

1. H. Büchler, R. E. Bühler. *Chem. Phys.* **16,** 9-18 (1976).

Data Sheet 55

Chemical equilibrium: $ISCN^{\bullet-} + SCN^- \rightleftharpoons (SCN)_2^{\bullet-} + I^-$ (55.1)

List of reports:

$K_{eq} = 2.5 \times 10^{-3}$, presumably at room temperature, ionic strength varying from 0.3 to 1 M, N_2O saturated, no pH control [1]. Shöneshofer and Henglein obtained this result by pulse radiolysis, monitoring the equilibrium absorbance at 550 nm.

Discussion

As this is the sole report on this reaction, and it appears to have been conducted competently, we recommend the reported result. The result should not depend significantly on ionic strength. Although no uncertainty was specified, we suggest ±15% based on the quality of the data.

Recommended value:

$K_{eq} = (2.5 \pm 0.4) \times 10^{-3}$.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 45.

References

1. M. Schöneshöfer, A. Henglein. *Ber. Bunsenges. Phys. Chem.* **74,** 393-398 (1970).

Data Sheet 56

Chemical equilibrium: $ISCN^{\bullet-} + I^- \rightleftharpoons I_2^{\bullet-} + SCN^-$ (56.1)

List of reports:

K_{eq} = 55, presumably at room temperature, ionic strength 0.03 M, N_2O saturated, no pH control [1]. Shöneshofer and Henglein obtained this result by pulse radiolysis, plotting a function of the difference in the equilibrium absorbances at 420 nm and 550 nm as a function of $[SCN^-]$, and deriving the equilibrium constant from the midpoint of the sigmoidal curve.

Discussion

As this is the sole report on this reaction, and it appears to have been conducted competently, we recommend the reported result. The result should not depend significantly on ionic strength. Although no uncertainty was specified, we suggest ±35% based on the graphical method of extracting the equilibrium constant from the data.

Recommended value:

$K_{eq} = 55 \pm 19$.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 45.

References

1. M. Schöneshöfer, A. Henglein. *Ber. Bunsenges. Phys. Chem.* **74,** 393-398 (1970).

Data Sheet 57

Subject: Dimethyl sulfide radical cation-iodide complex (iododimethylsulfur(•))

Couple type: $R_2S\text{-}I/\ R_2S,I^-$, (R = $-CH_3$).

Solvent: Water

Method: Calculation in reference [1] from pulse radiolysis data in reference [2] and $E^o(I_2^{\bullet -}/2I^-)$:

Equilibria: *(i)* $R_2S + I_2^{\bullet -} \rightleftharpoons R_2S{\therefore}I + I^-$ (57.1)

$K = 2.0 \times 10^{-1}$ Error limit in K stated ≤ 2 x.

(ii) $I_2^{\bullet -} + e^- \rightleftharpoons 2I^-$ (57.2)

$E^o = (1.03 \pm 0.02)$ V

(ii) - (i) $R_2S{\therefore}I + e^- \rightleftharpoons R_2S + I^-$ (57.3)

$E^o = (1.07 \pm 0.03)$ V

Reference: $E^o(I_2^{\bullet -}/2I^-)$.

Temperature: (293 ± 2) K. **Ionic strength effects estimated:** Not needed.

Reference potential assumed: $E^o = (1.03 \pm 0.02)$ V

Discussion

No correction needed for ionic strength. *(i)* is charge symmetrical and Debye-Hückel corrections will cancel. *(ii)* is a standard potential. Recalculation taking ±100% error limit in K gives: (1.07 ± 0.03) V vs NHE.

Correction desirable for reference potential used: no.

Recommended value:

$E°(R_2S\text{-}I/R_2S,I^-$, (R = $-CH_3$)) = (1.07 ± 0.03) V vs NHE.

Nomenclature: see Data Sheet 45.

References

1. Armstrong, D. A. In *S-Centered Radicals*, (Alfassi, Z. B., ed.), p. 27-61. John Wiley & Sons, New York (1999).
2. M. Bonifacic, K.-D. Asmus. *J. Chem. Soc., Perkin Trans. II* 758-762 (1980).

Data Sheet 58

Subject: Diethyl sulfide radical cation-iodide complex (iododiethylsulfur(•))

Couple type: $R_2S\text{-}I/\ R_2S,I^-$, ($R = \text{-}CH_2\text{-}CH_3$).

Solvent: Water.

Method: Calculation in reference [1] from pulse radiolysis data in reference [2] and $E^o(I_2^{\bullet-}/2I^-)$:

Equilibria: *(i)* $R_2S + I_2^{\bullet-} \rightleftharpoons R_2S{\therefore}I + I^-$ (58.1)

$K = 4.5 \times 10^{-1}$. Error in K stated ≤ 2 x.

(ii) $I_2^{\bullet-} + e^- \rightleftharpoons 2I^-$ (58.2)

$E^o = (1.03 \pm 0.02)$ V

(ii) - (i) $R_2S{\therefore}I + e^- \rightleftharpoons R_2S + I^-$ (58.3)

$E^o = (1.05 \pm 0.03)$ V

Reference: $E^o(I_2^{\bullet-}/2I^-)$.

Temperature: (293 ± 2) K. **Ionic strength effects estimated:** No.

Reference potential assumed: $E^o = (1.03 \pm 0.02)$ V

Discussion

No correction needed for ionic strength. Equilibrium *(i)* has charge symmetry and Debye-Hückel corrections will cancel. *(ii)* is a standard potential.

Recalculation with ± 100% error limit in K gives $E^o = +(1.05 \pm 0.03)$ V vs NHE.

Recommended value:

$E^\circ(R_2S\text{-}Cl/R_2S,I^-, (R = \text{-}CH_2\text{-}CH_3)) = +(1.05 \pm 0.03)$ V vs NHE

References

1. Armstrong, D. A. In *S-Centered Radicals*, (Alfassi, Z. B., ed.), p. 27-61. John Wiley & Sons, New York (1999).
2. M. Bonifacic, K.-D. Asmus. *J. Chem. Soc., Perkin Trans. II* 758-762 (1980).

Data Sheet 59

Summary of the $SO_3^{\bullet-}$ System

Tabulated below are the presently recommended equilibrium constants involving the trioxidosulfate(•1–) (sulfite) radical. Uncertainties are expressed as ± 1 sigma; in many cases the value of sigma is merely a subjective guess.

rxn #	reaction	K_{eq}	uncertainty	μ / M	Data Sheet #
60.1	$SO_3^{2-} + [Ru(phen)(NH_3)_4]^{3+} \rightleftharpoons SO_3^{\bullet-} + [Ru(phen)(NH_3)_4]^{2+}$	(1.8 – 7.4) × 10^{-4}	Factor of 2	0.1	60
61.1	$SO_3^{\bullet-}$ + chlorpromazine^{+} $\rightleftharpoons$ S(IV) + chlorpromazyl$^{\bullet 2+}$	11	± 2	0.1	61
62.1	$SO_3^{\bullet-} + ClO_2^{-} \rightleftharpoons SO_3^{2-} + ClO_2^{\bullet}$	4850	?	0	62
63.1	$SO_3^{\bullet-}$+ phenoxide^{-} $\rightleftharpoons$ SO_3^{2-} + phenoxyl(•)	0.056	± 0.008	0	63
64.1	$TyrO^{\bullet} + SO_3^{2-} \rightleftharpoons TyrO^{-} + SO_3^{\bullet-}$	0.61	± 0.04	0	64
65.1	$3\text{-}MeC_6H_4O^{\bullet} + SO_3^{2-} \rightleftharpoons 3\text{-}MeC_6H_4O^{-} + SO_3^{\bullet-}$	0.88	0.09	0	65

Reaction 60.1with $E°'[Ru(phen)(NH_3)_4]^{3+/2+}$ measured by cyclic voltammetry as +(0.516 ± 0.002) V, leads to $E°'$ = +(0.72 ± 0.02) V at 25 °C and μ = 0.1 M.

Reaction 61.1 leads to $E°'$ = +(0.71 ± 0.01) V for $SO_3^{\bullet-}/SO_3^{2-}$. Note that this result is drastically corrected from the original report.

Reaction 62.1 has K_{eq} extrapolated to zero ionic strength. With use of $E°$ = +0.934 V for $ClO_2^{\bullet}/ClO_2^{-}$, this leads to $E°$ = +(0.72 ± 0.01) V for $SO_3^{\bullet-}/SO_3^{2-}$. A recent paper by Horvath and Nagypal attempts to discredit the prior work on this reaction [1]. They claim that the prior report by Merényi, Lind and Shen [2] mistakenly observed the formation of a $ClO_2SO_3^{-}$ adduct rather than electron-transfer products. However, the experimental basis for this assertion is quite tenuous. On the other hand, it must be acknowleged that Merényi *et al.* performed their equilibrium measurements at only one ClO_2^{-} concentration, so their data do not rule out adduct formation. As is described in Data Sheet 62, the measurement of K_{eq} for this reaction was also compromised by neglect of the effects of $(ClO_2)_2^{\bullet-}$.

Reaction 63.1 leads to $E°$ = +(0.72 ± 0.01) V for $SO_3^{\bullet-}/SO_3^{2-}$ and appears quite reliable.

Reaction 64.1 leads to $E°$ = +(0.723 ± 0.01) V for $SO_3^{\bullet-}/SO_3^{2-}$ and appears quite reliable.

Reaction 65.1 leads to $E°$ = +(0.737 ± 0.01) V for $SO_3^{\bullet-}/SO_3^{2-}$ but was studied less extensively than reactions 63.1 and 64.1.

The broad agreement of the above determinations suggests that $E°$ is in the neighborhood of +0.72 V for $SO_3^{\bullet-}/SO_3^{2-}$. To obtain a more precise recommendation we disregard reaction 60.1 because of the difficulties in extrapolation to zero ionic strength for a reaction involving such high charges. We exclude reaction 61.1 because of the large corrections required to extrapolate from pH 3.3 to high pH. We also exclude reaction 62.1 because of the concerns raised by Horvath and Nagypal and because of the unknown effects of $(ClO_2)_2^{\bullet-}$. We also exclude reaction 65.1 because it was not studied in depth. We are then left with reactions 63.1 and 64.1. Taking the average of these two leads to $E°$ = +(0.72 ± 0.01) V.

Using the NBS value of –(486.5 ± 8) kJ mol^{-1} for $\Delta_f G°$ of $SO_3^{2-}(aq)$, the recommended value of $E°(SO_3^{\bullet-}/SO_3^{2-})$ leads to $\Delta_f G°$ = –(416 ± 8) kJ mol^{-1} for $SO_3^{\bullet-}$ (*aq*). Note that the NBS uncertainty in $\Delta_f G°(SO_3^{2-})$ seems unreasonably large. A more realistic assessment is based on $\Delta_f H°_{298}(SO_2,g)$ = –(296.84 ± 0.21) kJ mol^{-1} as reported in the NIST Webbook and in the JANAF tables, 4th ed. This then leads to $\Delta_f G°(SO_2,g)$ = –(300.125 ± 0.21) kJ mol^{-1}. We then use following equilibrium constants as recommended in the Smith, Martell, and Motekaitis NIST compendium of aqueous formation constants [3]: for the Henry's law constant (M/atm) of SO_2, $\log K$ = (0.09 ± 0.01), for the first K_a of "H_2SO_3" pK_a = (1.85 ± 0.01); for HSO_3^- pK_a = (7.19 ± 0.01). These data then lead to $\Delta G°$ = +(51.11 ± 0.11) kJ mol^{-1} for $SO_2(g) + H_2O(l) = SO_3^{2-}(aq) + 2H^+(aq)$. Finally, using the NBS $\Delta_f G°$ for $H_2O(l)$ we obtain $\Delta_f G°$ = –(486.1 ± 0.2) kJ mol^{-1}, which is in excellent agreement with the NBS value except for a much smaller uncertainty. This revised uncertainty then leads to an uncertainty of ± 2 kJ mol^{-1} for $\Delta_f G°(SO_3^{\bullet-})$.

Recommended values:

$SO_3^{\bullet-} + e^- \rightleftharpoons SO_3^{2-}$ $E°$ = +(0.72 ± 0.01) V.
$SO_3^{\bullet-}$ (*aq*) $\Delta_f G°$ = –(416 ± 2) kJ mol^{-1}

Nomenclature: $ClO_2^{\bullet}$, dioxidochlorine(•); $SO_3^{\bullet-}$, trioxidosulfate(•1−); chlorpromazine, IUPAC PIN 3-(2-chloro-10*H*-phenothiazin-10-yl)-*N*,*N*-dimethylpropan-1-amine

References

1. A. K. Horvath, I. Nagypal. *J. Phys. Chem. A* **110,** 4753-4758 (2006).
2. G. Merényi, J. Lind, X. Shen. *J. Phys. Chem.* **92,** 134-137 (1988).

3. A. E. Martell, R. M. Smith, R. J. Motekaitis. *NIST Critically Selected Stability Constants of Metal Complexes Database, 7.0*, U.S. Department of Commerce, Gaithersburg, MD (2003).

Data Sheet 60

Chemical equilibrium: $SO_3^{2-} + [Ru(phen)(NH_3)_4]^{3+} \rightleftharpoons SO_3^{\bullet-} + [Ru(phen)(NH_3)_4]^{2+}$ (60.1)

List of reports:

$K_{eq} = 3.7 \times 10^{-4}$ at ~25 °C and $\mu = 0.1$ M [1] obtained from the ratio of the forward and reverse rate constants. The forward rate constant was measured by stopped-flow kinetics of the reaction of SO_3^{2-} with $[Ru(phen)(NH_3)_4]^{3+}$ as a function of pH at 25.0 °C. The reverse was measured by pulse radiolysis at room temperature (~22 °C). Uncertainties in K_{eq} were not reported.

Discussion

An estimate of the uncertainty in K_{eq} can be derived from the uncertainties in the individual rate constants. An uncertainty of ± 7% was reported for k_f. The uncertainty in k_r was not reported but could be as large as a factor of 2, given the effects of the competing reaction

$SO_3^{\bullet-} + Ru^{3+} \rightarrow SO_3 + Ru^{2+}$

Thus we assign an uncertainty of a factor of 2 to K_{eq}.

Cyclic voltammetry was used to determine $E°' = +(0.516 \pm 0.002)$ V for $[Ru(phen)(NH_3)_4]^{3+/2+}$ at $\mu = 0.1$ M and 25 °C [1]. By combining this E_f with K_{eq}, a value of +0.72 V was derived for $E°'$ for $SO_3^{\bullet-}/SO_3^{2-}$. The factor-of-2 uncertainty in K_{eq} leads to a 20 mV uncertainty in $E°'$.

Recommended values:

$SO_3^{2-} + [Ru(phen)(NH_3)_4]^{3+} \rightleftharpoons SO_3^{\bullet-} + [Ru(phen)(NH_3)_4]^{2+}$

$K_{eq} = 3.7 \times 10^{-4}$ within a factor of 2 at ~25 °C and $\mu = 0.1$ M.

$SO_3^{\bullet-} + e^- \rightleftharpoons SO_3^{2-}$ $E°' = (0.72 \pm 0.02)$ V at 25 °C and $\mu = 0.1$ M.

List of auxiliary thermodynamic data: K_w

Nomenclature: See Data Sheet 59

References

1. R. Sarala, M. S. Islam, S. B. Rabin, D. M. Stanbury. *Inorg. Chem.* **29,** 1133-1142 (1990).

Data Sheet 61

Chemical equilibrium: $SO_3^{\bullet-}$ + chlorpromazine$^+$ $\rightleftharpoons$ S(IV) + chlorpromazyl$^{\bullet 2+}$ (61.1)
Chlorpromazine IUPAC PIN: 3-(2-chloro-10*H*-phenothiazin-10-yl)-*N*,*N*-dimethylpropan-1-amine

List of reports:

$K_{eq} = (11 \pm 2)$ at pH 3.6, $\mu = 0.1$ M, unspecified temperature [1]. Result obained by pulse radiolysis, by measurement of the equilibrium optical absorbance of the chlorpromazyl radical cation.

Discussion

We presume that the work was conducted at room temperature, 22 ± 2 °C.

Huie and Neta used $E = +0.78$ V for the chlorpromazine (ClPz) couple to derive $E = +0.84$ V for the $SO_3^{\bullet-}$/S(IV) couple at pH 3.6. The value for $E^{\circ\prime}(ClPz^{\bullet 2+}/ClPz^+)$ was originally reported by Pelizzetti and Mentasti [2]. The Pelizzetti and Mentasti result was obtained in 1 M $HClO_4$, and there is no indication as to whether it should be applicable at pH 3.6. Several of the phenothiazine potentials reported by Pelizzetti and Mentasti subsequently have been argued to be incorrect [3].

Huie and Neta then used their E value at pH 3.6, literature pK_a values for "H_2SO_3" and HSO_3^-, and the assumption that $HSO_3^\bullet$ is completely dissociated in the pH range considered, to derive $E^\circ = +0.63$ V for the couple $SO_3^{\bullet-}/SO_3^{2-}$.

Madej and Wardman have recently revised $E^{\circ\prime}(ClPz^{\bullet 2+}/ClPz^+)$, using both pulse radiolysis and cyclic voltammetry to confirm their result; they now recommend $E^\circ = +0.860 \pm 0.010$ V [4] (see Supplementary Data Sheet S-9). Use of this revised potential leads to $E^{\circ\prime} = +0.92 \pm 0.01$ V for the $SO_3^{\bullet-}$/S(IV) couple at pH 3.6. Adjustment for the pK_as as described above leads to $E^\circ = +(0.71 \pm 0.1)$ V for $SO_3^{\bullet-}/SO_3^{2-}$.

Recommended values:

$SO_3^{\bullet-}$ + chlorpromazine$^+$ $\rightleftharpoons$ S(IV) + chlorpromazyl$^{\bullet 2+}$
$K_{eq} = (11 \pm 2)$ at pH 3.6, $\mu = 0.1$ M, 22 °C
$SO_3^{\bullet-} + e^- \rightleftharpoons SO_3^{2-}$ $E^\circ = +(0.71 \pm 0.1)$ V

List of auxiliary thermodynamic data: *E*° for chlorpromazyl, pK_a1 and pK_a2 for SO_2(*aq*)

Nomenclature: See Data Sheet 59

References

1. R. E. Huie, P. Neta, *J. Phys. Chem.* **88,** 5665-5669 (1984).
2. E. Pelizzetti, E. Mentasti, *Inorg. Chem.* **18,** 583-588 (1979).
3. S. V. Jovanovic, S. Steenken, M. G. Simic, *J. Phys. Chem.* **94,** 3583-3588 (1990).
4. E. Madej, P. Wardman, *Rad. Phys. Chem.* **75,** 990-1000 (2006).

Data Sheet 62

Chemical equilibrium: $ClO_2^{\bullet} + SO_3^{2-} \rightleftharpoons ClO_2^{-} + SO_3^{\bullet-}$ (62.1)

List of reported equilibrium constants:

$K_c = 2100$ from absorbance at 360 nm at $\mu = ca.$ 1 M [1].
At $\mu = 1$ M, the extended Debye-Huckel treatment yields the activity coefficient ratio,
$K_\gamma = \gamma_{ClO2-}\gamma_{SO3.-}/\gamma_{ClO2.}\gamma_{SO32-} = 2.31$. The thermodynamic equilibrium constant
$K = K_c \times K\gamma = 2100 \times 2.31 = 4850$.
Taking $E^o(ClO_2^{\bullet}/ClO_2^{-}) =+ 0.934$ V (Data Sheet 24)
$E^o(SO_3^{\bullet-}/SO_3^{2-}) = +(0.72 \pm 0.02)$ V.

Discussion

In ref. [1] an erroneous calculation was made, in that K_c was divided rather than multiplied by the otherwise correctly evaluated factor $K_\gamma = 2.31$.

Some uncertainty is introduced into the value of $K_{62.1}$ because its determination neglected the association of $ClO_2^{\bullet}$ with ClO_2^{-} as in eq 62.2 [2, 3]:

$$ClO_2^{\bullet} + ClO_2^{-} \rightleftharpoons (ClO_2)_2^{\bullet-} \qquad (62.2)$$

A value of 5.01 M^{-1} has been reported for $K_{62.2}$, which means that at the high (1 M) ClO_2^{-} concentrations used in measuring $K_{62.1}$ approximately 80% of the $ClO_2^{\bullet}$ will be bound as $(ClO_2)_2^{\bullet-}$. This species contributes significantly to the absorbance at the wavelength where ClO_2 was monitored, which introduces an additional complication to the interpretation of the results. While it seems likely that $K_{62.1}$ is in the neighborhood of 5×10^3, further analysis of the experimental results is required.

Recommended value:

None

Nomenclature: See Data Sheet 59

References

1. G. Merényi, J. Lind, X. Shen, *J. Phys. Chem.* **92,** 134-137 (1988).
2. Z. Körtvelyesi, G. Gordon, *J. Am. Wat. Works. Assoc.* **96,** 81-87 (2004).
3. G. Gordon, F. Emmenegger, *Inorg. Nucl. Chem. Lett.* **2,** 395-398 (1966).

Data Sheet 63

Chemical equilibrium: $SO_3^{\bullet -}$+ phenoxide$^-$ $\rightleftharpoons$ SO_3^{2-} + phenoxyl$^\bullet$ (63.1)

List of reports:

$1/K_{eq} = (17 \pm 5)$ at pH 11.1, $\mu = 0.15$ M, at an unspecified temperature [1]. This result was obtained by pulse radiolysis, by measuring the equilibrium optical absorbance of the phenoxyl radical.

$1/K_{eq} = (9 - 16)$ at pH 11.6; this value was obtained at (21 ± 2) °C [2] and depends on μ, Result obtained by pulse radiolysis, measuring the equilibrium optical absorbance of the phenoxyl radical.

Discussion

Huie and Neta (1984) used this equilibrium constant plus their (now) questionable $E°(SO_3^{\bullet -}/SO_3^{2-})$ to derive $E°$(phenoxyl/phenoxide) = +0.70 V [1].

In their reinvestigation, Das, Huie, and Neta (1999) confirmed their prior determination of the equilibrium constant, and they measured the equilibrium constant as a function of ionic strength. Das *et al.* then used $E°$(phenoxyl/phenoxide) = (0.80 ± 0.01) V to derive $E° = +0.720$ V for $SO_3^{\bullet -}/SO_3^{2-}$.

Extrapolation of the data in Table 2 of Das *et al.*'s report to zero ionic strength is a challenge, because the value of $1/K$ at lowest ionic strength ($\mu = 0.067$ M) is rather divergent. Inspection of their Figure 3 reveals that this is probably a typo. Recalculation of the data in Das *et al.*'s Figure 3 and extrapolation to $\mu = 0$ yields $1/K° = (18 \pm 1)$. Based on our current recommendation (Data Sheet S-2) for $E°(PhO^\bullet/PhO^-) = +(0.793 \pm 0.008)$ V we derive $E°(SO_3^{\bullet -}/SO_3^{2-}) = +(0.72 \pm 0.01)$ V.

Recommended values:

$SO_3^{\bullet -}$ + phenoxide$^-$ $\rightleftharpoons$ SO_3^{2-} + phenoxyl$^\bullet$ $K_{eq} = (0.056 \pm 0.003)$
$SO_3^{\bullet -} + e^- \rightleftharpoons SO_3^{2-}$ $E° = +(0.72 \pm 0.01)$ V

Nomenclature; See Data Sheet 59.

List of auxiliary thermodynamic data: none

References

1. R. E. Huie, P. Neta. *J. Phys. Chem.* **88,** 5665-5669 (1984).
2. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103,** 3581-3588 (1999).

Data Sheet 64

Chemical equilibrium: $\mathrm{TyrO^{\bullet} + SO_3^{2-} \rightleftharpoons TyrO^{-} + SO_3^{\bullet-}}$ (64.1)

$\mathrm{TyrO^{\bullet}}$ is the phenoxyl radical from tyrosine; $\mathrm{TyrO^{-}}$ is the phenoxide form of tyrosine.

List of reports:

$K_{\mathrm{eq}} = 0.5 - 0.6$ at pH 11.6 and 21 ± 2°C, a value that depends on μ [1]. This result was obtained by pulse radiolysis, by measurement of the equilibrium optical absorbance of the tyrosyl radical.

Discussion

Das, Huie, and Neta (1999) found only a small dependence of K_{eq} on μ, $\mu = (0.1 - 0.3)$ M). We infer a value for $K°$ of (0.61 ± 0.04). Das *et al.* also determined $E° = +0.736$ V for the tyrosyl radical at pH 11.3 (relative to phenoxyl), and they used this result to derive $E° = +0.736$ V for $\mathrm{SO_3^{\bullet-}/SO_3^{2-}}$. Given that they assigned an uncertainty of ± 0.01 V to $E°$(phenoxyl), we propagate this to give an uncertainty of ± 0.01 V for $E°(\mathrm{SO_3^{\bullet-}/SO_3^{2-}})$. We note that they assign an uncertainty of only 0.003 V to $E°$, but this clearly does not take the uncertainty of the reference potential into account.

We currently recommend $E°(\mathrm{TyrO^{\bullet}/TyrO^{-}}) = +(0.723 \pm 0.010)$ V (Supplementary Data Sheet S4). This leads to an adjustment of the derived value to $E°(\mathrm{SO_3^{\bullet-}/SO_3^{2-}}) = +(0.723 \pm 0.010)$ V.

Recommended values:

$\mathrm{TyrO^{\bullet} + SO_3^{2-} \rightleftharpoons TyrO^{-} + SO_3^{\bullet-}}$ $K_{\mathrm{eq}} = K_{\mathrm{eq}}° = (0.61 \pm 0.04)$

$\mathrm{SO_3^{\bullet-} + e^{-} \rightleftharpoons SO_3^{2-}}$ $E° = +(0.723 \pm 0.01)$ V

List of auxiliary thermodynamic data: none

Nomenclature: See Data Sheet 59

References

1. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103**, 3581-3588 (1999).

Data Sheet 65

Chemical equilibrium: $3\text{-MeC}_6\text{H}_4\text{O}^\bullet + \text{SO}_3^{2-} \rightleftharpoons 3\text{-MeC}_6\text{H}_4\text{O}^- + \text{SO}_3^{\bullet-}$ (65.1)

$3\text{-MeC}_6\text{H}_4\text{OH}$ = 3-cresol; IUPAC PIN: 3-methylphenol

List of reports:

K_{eq} = (0.88 ± 0.09) at pH 11.6, μ = 0.080 M, and (21 ± 2) °C [1]. This result was obtained by pulse radiolysis, by the measurement of the equilibrium optical absorbance of the cresyl radical.

Discussion

It is unclear how Das *et al.* extrapolated to zero ionic strength, given that they have data only at μ = 0.80 M. We assume they made no correction and that $K°$ = (0.88 ± 0.09). Das *et al.* derive $E°$ = +(0.737 ± 0.004) V for $\text{SO}_3^{\bullet-}/\text{SO}_3^{2-}$ based on $E°$ = +(0.736 ± 0.003) V for the cresyl radical. The later, however, was measured relative to the phenoxyl radical, so full propagation of error gives an uncertainty of ± 0.01 V for $E°'(\text{SO}_3^{\bullet-}/\text{SO}_3^{2-})$.

Recommended values:

$3\text{-MeC}_6\text{H}_4\text{O}^\bullet + \text{SO}_3^{2-} \rightleftharpoons 3\text{-MeC}_6\text{H}_4\text{O}^- + \text{SO}_3^{\bullet-}$ $K_{eq}°$ = (0.88 ± 0.09)

$\text{SO}_3^{\bullet-} + e^- \rightleftharpoons \text{SO}_3^{2-}$ $E°'$ = +(0.737 ± 0.01) V

Nomenclature: See Data Sheet 59.

List of auxiliary thermodynamic data: none

References

1. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103,** 3581-3588 (1999).

Data Sheet 66

Summary of the $SO_5^{\bullet-}$ System

Tabulated below are the recommended equilibrium constants involving the $SO_5^{\bullet-}$ radical. Uncertainties are expressed as ± 1 σ; in many cases the value of σ is merely a subjective guess.

rxn #	Reaction	K_{eq}	Uncertainty	μ / M	Data Sheet #
67.1	$C_6H_4O^\bullet + SO_5^{2-} \rightleftharpoons C_6H_4O^- + SO_5^{\bullet-}$	0.28	± 0.03	0.06	67
68.1	$\text{3-Me-}C_6H_4O^\bullet + SO_5^{2-} \rightleftharpoons \text{3-Me-}C_6H_4O^- + SO_5^{\bullet-}$	3.7×10^{-2}	$\pm 0.4 \times 10^{-2}$	0.382	68
69.1	$TyrO^\bullet + SO_5^{2-} \rightleftharpoons TyrO^- + SO_5^{\bullet-}$	2.1×10^{-2}	$\pm 0.2 \times 10^{-2}$	0.4	69
70.1	$DMA^{\bullet+} + SO_5^{2-} \rightleftharpoons DMA + SO_5^{\bullet-}$	3.7×10^{-3}	$\pm 0.4 \times 10^{-3}$	~0.1	70

(DMA = *N,N*-dimethylaniline)

Reactions 67.1, 68.1, 69.1, and 70.1 lead to $E°$ = +(0.813 ± 0.008) V, +(0.81 ± 0.01) V, +(0.804 ± 0.01) V, and $E°$ = +(0.84 ± 0.01) V, respectively, for the $SO_5^{\bullet-}/SO_5^{2-}$ couple. Das *et al.* suggest that the last value (from DMA) should be excluded because of the possibility that the DMA was incompletely dissolved [1]. Exclusion of reaction 70.1 leads to excellent agreement between the three other determinations, with an average value of $E°$ = +(0.81 ± 0.01) V for $SO_5^{\bullet-}/SO_5^{2-}$.

Balej reports $\Delta_f G°$ = –(637.5 ± 2.0) kJ mol^{-1} for HSO_5^-(*aq*) [2]. The pK_a of HSO_4^- is 9.3 ± 0.2 [3], and thus $\Delta_f G°(SO_5^{2-})$ = –(584 ± 3) kJ mol^{-1}. In combination with the $E°$ recommended above we then derive $\Delta_f G°$ = –(506 ± 3) kJ mol^{-1} for $SO_5^{\bullet-}$.

Recommended values:

$E°$ = +(0.81 ± 0.01) V for $SO_5^{\bullet-}/SO_5^{2-}$

$\Delta_f G°$ = –(506 ± 3) kJ mol^{-1} for $SO_5^{\bullet-}$

Nomenclature: $SO_5^{\bullet-}$, (dioxido)trioxidosulfate(•–)

References

1. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103,** 3581-3588 (1999).

2. J. Balej. *J. Electroanal. Chem.* **214,** 481-483 (1986).
3. H. Elias, U. Götz, K. J. Wannowius. *Atmos. Envir.* **28,** 439-448 (1994).

Data Sheet 67

Chemical equilibrium: $C_6H_4O^\bullet + SO_5^{2-} \rightleftharpoons C_6H_4O^- + SO_5^{\bullet-}$ (67.1)

List of reports:

$K_{eq} = (0.28 \pm 0.03)$ at $\mu = 0.06$ M, pH 11.3, and (21 ± 2) °C [1]. Das *et al.* obtained this result by pulse radiolysis, measuring the position of equilibrium optically.

Discussion

Das *et al.* extrapolated K_{eq} to zero ionic strength and then used $E° = +0.800 \pm 0.005$ V for the phenoxyl radical to derive $E° = +(0.820 \pm 0.005)$ V for $SO_5^{\bullet-}/SO_5^{2-}$. Use of our presently recommended reference potential; (+0.793 ± 0.008) V for phenoxyl, Data Sheet S-2, leads to $E° = +(0.813 \pm 0.008)$ V for $SO_5^{\bullet-}/SO_5^{2-}$.

Recommended values:

$K_{eq} = (0.28 \pm 0.03)$ at $\mu = 0.06$ M, pH 11.3, and (21 ± 2) °C
$E° = +(0.813 \pm 0.008)$ V for $SO_5^{\bullet-}/SO_5^{2-}$

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 66.

References

1. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103,** 3581-3588 (1999).

DataSheet 68

Chemical equilibrium: $3\text{-Me-C}_6\text{H}_4\text{O}^\bullet + \text{SO}_5^{2-} \rightleftharpoons 3\text{-Me-C}_6\text{H}_4\text{O}^- + \text{SO}_5^{\bullet-}$ (68.1)

List of reports:

$K_{\text{eq}} = (3.7 \pm 0.4) \times 10^{-2}$ at $\mu = 0.382$ M, pH 11.4, and (21 ± 2) °C [1]. Das *et al.* obtained this result by pulse radiolysis, measuring the position of equilibrium optically.

Discussion

Das *et al.* extrapolated K_{eq} to zero ionic strength and then used $E° = +(0.736 \pm 0.003)$ V for the 3-methylphenoxyl radical to derive $E° = +(0.806 \pm 0.005)$ V for the $\text{SO}_5^{\bullet-}/\text{SO}_5^{2-}$ couple Use of our presently recommended reference potential (+0.74 ± 0.01 V for 3-methylphenoxyl, Data Sheet S-3) leads to $E° = +(0.81 \pm 0.01)$ V for $\text{SO}_5^{\bullet-}/\text{SO}_5^{2-}$.

Recommended values:

$K_{\text{eq}} = (3.7 \pm 0.4) \times 10^{-2}$ at $\mu = 0.382$ M, pH 11.4, and 21 ± 2 °C
$E° = +(0.81 \pm 0.01)$ V for $\text{SO}_5^{\bullet-}/\text{SO}_5^{2-}$

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 66.

References

1. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103,** 3581-3588 (1999).

Data Sheet 69

Chemical equilibrium: $\mathrm{TyrO^{\bullet} + SO_5^{2-} \rightleftharpoons TyrO^{-} + SO_5^{\bullet -}}$ (69.1)

$\mathrm{TyrO^{\bullet}}$ is the phenoxyl radical from tyrosine; $\mathrm{TyrO^{-}}$ is the phenoxide form of tyrosine.

List of reports:

$K_{\mathrm{eq}} = (2.1 \pm 0.2) \times 10^{-2}$ at $\mu = 0.40$ M, pH 11.4, and (21 ± 2) °C [1]. Das *et al.* obtained this result by pulse radiolysis, measuring the position of equilibrium optically.

Discussion

Das *et al.* extrapolated K_{eq} to zero ionic strength and then used $E° = +(0.737 \pm 0.004)$ V for the tyrosyl radical to derive $E° = +(0.818 \pm 0.005)$ V for $\mathrm{SO_5^{\bullet -}/SO_5^{2-}}$. Use of our presently recommended reference potential (+0.723 ± 0.01 V for the tyrosyl/tyrosine couple, Data Sheet S-4) leads to $E° = +(0.804 \pm 0.01)$ V for $\mathrm{SO_5^{\bullet -}/SO_5^{2-}}$.

Recommended values:

$K_{\mathrm{eq}} = (2.1 \pm 0.2) \times 10^{-2}$ at $\mu = 0.40$ M, pH 11.4, and (21 ± 2) °C
$E° = +(0.804 \pm 0.01)$ V for $\mathrm{SO_5^{\bullet -}/SO_5^{2-}}$

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 66.

References

1. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103**, 3581-3588 (1999).

Data Sheet 70

Chemical equilibrium: $DMA^{\bullet+} + SO_5^{2-} \rightleftharpoons DMA + SO_5^{\bullet-}$ (70.1)
(DMA = *N,N*-dimethylaniline)

List of reports:

$K_{eq} = (3.7 \pm 0.4) \times 10^{-3}$ at $\mu = (0.090 - 0.141)$ M, pH 11, and (21 ± 2) °C [1]. Das *et al.* obtained this result by pulse radiolysis, measuring the position of equilibrium optically.

Discussion

Das *et al.* extrapolated K_{eq} to zero ionic strength and then used $E° = +(0.692 \pm 0.003)$ V for the $DMA^{\bullet+}$ radical to derive $E° = +(0.836 \pm 0.005)$ V for $SO_5^{\bullet-}/SO_5^{2-}$. Use of our presently recommended reference potential (+0.69 ± 0.01) V for DMA, Data Sheet S-5 leads to $E°$ = +(0.84 ± 0.01) V for SO_5/SO_5^{2-}. Das *et al.* suggest that the equilibrium constant may not be very accurate because in incomplete dissolution of DMA.

Recommended values:

$K_{eq} = (3.7 \pm 0.4) \times 10^{-3}$ at $\mu = (0.0.090 - 0.141)$ M, pH 11, and (21 ± 2) °C
$E° = +(0.84 \pm 0.01)$ V for $SO_5^{\bullet-}/SO_5^{2-}$

List of auxiliary thermodynamic data: none.

References

1. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103,** 3581-3588 (1999).

Data Sheet 71

Summary of the $S_2O_3^{-}/S_4O_6^{\bullet 3-}$ System

Tabulated below are the presently recommended equilibrium constants involving this related group of hexaoxidodisulfate(•3−) (thiosulfate and tetrathionate-derived) radicals. Uncertainties are expressed as ± 1 σ; in many cases the value of σ is merely a subjective guess.

rxn #	reaction	K_{eq}	dim.	uncertainty	μ / M	Data Sheet #
72.1	$N_3^{\bullet} + 2S_2O_3^{2-} \rightleftharpoons N_3^{-} + (S_2O_3)_2^{\bullet 3-}$	1.9×10^4	M^{-1}	$\pm 0.2 \times 10^4$	0.44	72
73.1	$4\text{-}CNC_6H_4O^{\bullet} + 2S_2O_3^{2-} \rightleftharpoons 4\text{-}CNC_6H_4O^{-} + (S_2O_3)_2^{\bullet 3-}$	2.2	M^{-1}	± 0.2	0.28	73
74.1	$HS_4O_6^{\bullet 2-} \rightleftharpoons S_4O_6^{\bullet 3-} + H^+$	$pK_a = 6.2$				74
75.1	$S_2O_3^{\bullet -} + SCN^{-} \rightleftharpoons SCNS_2O_3^{\bullet 2-}$	1.2×10^3	M^{-1}	$(2.4 - 0.6) \times 10^3$	?	75
76.1	$(SCN)_2^{\bullet -} + S_2O_3^{2-} \rightleftharpoons SCNS_2O_3^{\bullet 2-} + SCN^{-}$	1.6×10^2		$\pm 0.4 \times 10^2$	0.0	76

The equilibrium constant for the reaction

$$S_2O_3^{\bullet -} + 2SCN^{-} \rightleftharpoons S_2O_3^{2-} + (SCN)_2^{\bullet -} \qquad (71.1)$$

is obtained as the ratio of $K_{75.1}/K_{76.1}$: $K = 7.5\ M^{-1}$ within a factor of 2.1. Given our recommended $E° = +1.30 \pm 0.02$ V for $(SCN)_2^{\bullet -}/2SCN^{-}$, we derive $E° = +(1.35 \pm 0.03)$ V for $S_2O_3^{\bullet -}/S_2O_3^{2-}$.

An independent derivation of $E°' = +1.30$ V for $S_2O_3^{\bullet -}/S_2O_3^{2-}$ at $\mu = 0.1$ M was obtained from the rate constants for oxidation of $S_2O_3^{2-}$ by several outer-sphere metal-complex oxidants, making the assumption that the reverse reactions had diffusion-controlled rates [1].

In view of the ionic strength issues, the agreement between the two above determinations is good. We recommend the value derived from the thiocyanate equilibria because an assumed (not measured) reverse rate constant was used for the derivation from the reactions with metal complexes.The NBS Tables [2] give $\Delta_f G° = -(522.5 \pm 8)$ kJ mol^{-1} for $S_2O_3^{2-}$(*aq*). Thus, we derive $\Delta_f G° = -(392 \pm 8)$ kJ mol^{-1} for $S_2O_3^{\bullet -}$(*aq*). Note that Cobble *et al.* [2a] recommend a value of $-(544.3 \pm 7.5)$ kJ mol^{-1} for $\Delta_f G°(S_2O_3^{2-})$, which differs substantially from the NBS value; however, to maintain consistency we retain the NBS value in calculating our recommended values.

Reaction 72.1 leads to $E° = +(1.10 \pm 0.01)$ V for $S_4O_6^{\bullet 3-}/2S_2O_3^{2-}$, while reaction 73.1 leads to $+(1.09 \pm 0.03)$ V for this potential. The two results are equivalent within the specified uncertainties, and thus we recommend the more precise value derived from reaction 72.1. The corresponding $\Delta_f G°$ is $-(939 \pm 8)$ kJ mol^{-1} for $S_4O_6^{\bullet 3-}$.

Das *et al.* [3] combined $E°(S_4O_6^{\bullet 3-}/2S_2O_3^{2-}) = +1.07$ V and $E°(S_2O_3^{\bullet -}/S_2O_3^{2-}) = +1.30$ V to derive the equilibrium constant for reaction 71.2:

$$(S_2O_3)_2^{\bullet 3-} \rightleftharpoons S_2O_3^{\bullet -} + S_2O_3^{2-} \qquad (71.2)$$

Their result, $K_{71.2} = 1.3 \times 10^{-4}$ M, is based on $E°$ values that differ slightly from our recommended values; however, the differing $E°$ values lead to an approximate cancellation of errors, so the final result is not much affected. Given the uncertainties in the component $E°$ values, we assign an uncertainty of a factor of 3 for $K_{71.2}$. Thus, the reverse of reaction 71.2 (which is a hemicolligation reaction) has $\log K_{eq} = (4.1 \pm 0.5)$.

Recommended values:

$E° = +(1.35 \pm 0.03)$ V for $S_2O_3^{\bullet -}/S_2O_3^{2-}$ at 25 °C and $\mu = 0$ M.
$\Delta_f G° = -(392 \pm 8)$ kJ mol^{-1} for $S_2O_3^{-}$
p$K_a = 6.2$ for $HS_4O_6^{\bullet 2-}$
$E° = +(1.10 \pm 0.01)$ V for $S_4O_6^{\bullet 3-}/2S_2O_3^{2-}$
$\Delta_f G°$ is $-(939 \pm 8)$ kJ mol^{-1} for $S_4O_6^{\bullet 3-}$
$\log K_{eq} = (4.1 \pm 0.5)$ for $S_2O_3^{\bullet -} + S_2O_3^{2-} = S_4O_6^{\bullet 3-}$

Nomenclature: $N_3^{\bullet}$, trinitrogen*(2N–N)*(•); N_3^{-}, trinitride(1−); SCN^{-}, nitridosulfidocarbonate(1−), thiocyanate is allowed; $(SCN)_2^{\bullet -}$, bis(nitridosulfidocarbonate)(*S–S*)(•1−); $S_2O_3^{\bullet -}$, trioxidosulfidosulfate*(S–S)*(•−); $S_2O_3^{2-}$, trioxidosulfidosulfate*(S–S)*(2−), thiosulfate is allowed; $S_4O_6^{\bullet 3-}$, bis[(trioxidosulfate)sulfate](•3−), and $SCNS_2O_3^{\bullet 2-}$, (nitridosulfidocarbonato)trioxidosulfidosulfate(•2−)

References

1. R. Sarala, D. M. Stanbury. *Inorg. Chem.* **31,** 2771-2777 (1992).

2. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall. *J. Phys. Chem. Ref. Data* **11,** Suppl. No. 2 (1982).

2a. J. W. Cobble, H. P. Stephens, I. R. McKinnon, E. F. Westrum. *Inorg. Chem.* **11**, 1669-1674 (1972).

3. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103,** 3581-3588 (1999).

Data Sheet 72

Chemical equilibrium: $N_3^\bullet + 2S_2O_3^{2-} \rightleftharpoons N_3^- + (S_2O_3)_2^{\bullet 3-}$ (72.1)

List of reports:

$K_{eq} = (2.0 \pm 0.2) \times 10^4$ M^{-1} at $\mu = 0.85$ M and (21 ± 2) °C [1]. Result obtained by pulse radiolysis with optical detection of the position of equilibrium.

$K_{eq} = (1.9 \pm 0.2) \times 10^4$ M^{-1} at $\mu = 0.44$ M and (21 ± 2) °C [1]. Result obtained by pulse radiolysis with optical detection of the position of equilibrium.

Discussion

Das *et al.*[1] argue that the species $(S_2O_3)_2^{\bullet 3-}$ (or $S_4O_6^{\bullet 3-}$) on the time scale of the above measurements is not $(O_3SSSSO_3)^{\bullet 3-}$ but rather an isomer, such as $(O_3SSOSO_2S)^{\bullet 3-}$.

This equilibrium constant should be sensitive to ionic strength. Das *et al.* [1] corrected the equilibrium constant to zero ionic strength by use of an incorrect equation (their eq. 27) for activity coefficients. The equation used may be appropriate when all reactants are uncharged as in their eq 26, but this is not the case for reaction 72.1.

A more correct equation can be derived as follows: first,

$$\log K^\circ = \log K + \log (\gamma(N_3^-)\gamma(S_4O_6^{\bullet 3-})/\gamma(S_2O_3^{2-})^2)$$
$$= \log K + \log \gamma(N_3^-) + \log \gamma(S_4O_6^{\bullet 3-}) - 2\log \gamma(S_2O_3^{2-})$$

Then, we use the Guggenheim eq. for single-ion activity coefficients:
$\log \gamma = -Az_i^2\mu^{1/2}/(1 + \mu^{1/2}) + \beta\mu$.

This leads to $\log K^\circ = \log K - A\mu^{1/2}/(1 + \mu^{1/2})(z(N_3^-)^2 + z(S_4O_6^{\bullet 3-})^2 - 2z(S_2O_3^{2-})^2)$
(the β terms cancel out for this reaction, so long as β is the same for all ions).

Thus, $\log K^\circ = \log K - A\mu^{1/2}/(1 + \mu^{1/2})((-1)^2 + (-3)^2 - 2(-2)^2) = \log K - A\mu^{1/2}/(1 + \mu^{1/2})(2)$
or, $\log K = \log K^\circ + 2A\mu^{1/2}/(1 + \mu^{1/2})$. $A = 0.509$ for water at 25 °C.

From the data at $\mu = 0.44$ M we thus calculate $\log K^\circ = 3.87$, and $\Delta E = 0.229$ V. With our recommended $E^\circ = +(1.33 \pm 0.01)$ V for $N_3^\bullet/N_3^-$ we then obtain $E^\circ = +(1.10 \pm 0.01)$ V.

Recommended values:

$K_{\mathrm{eq}} = (1.9 \pm 0.2) \times 10^4$ M^{-1} at $\mu = 0.44$ M and (21 ± 2) °C
log $K° = (3.87 \pm 0.04)$ at $\mu = 0.0$ M
$E° = +(1.10 \pm 0.01)$ V for $S_4O_6^{\bullet 3-}/2S_2O_3^{2-}$

Nomenclature: see Data Sheet 71.

List of auxiliary thermodynamic data: none.

References

1. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103,** 3581-3588 (1999).

Data Sheet 73

Chemical equilibrium: $4\text{-CNC}_6\text{H}_4\text{O}^{\bullet} + 2\text{S}_2\text{O}_3^{2-} \rightleftharpoons 4\text{-CNC}_6\text{H}_4\text{O}^{-} + (\text{S}_2\text{O}_3)_2^{\bullet 3-}$ (73.1)

$4\text{-CNC}_6\text{H}_4\text{O}^{-}$ = 4-cyanophenoxide

List of reports:

$K_{\text{eq}} = (2.2 \pm 0.2)\ \text{M}^{-1}$ at $\mu = 0.28$ M and (21 ± 2) °C [1]. Result obtained by pulse radiolysis with optical detection of the position of equilibrium.

Discussion

This equilibrium constant should be sensitive to ionic strength. Das *et al.* [1] corrected the equilibrium constant to zero ionic strength by use of an incorrect equation (their eq 27) for activity coefficients. The equation used may be appropriate when all reactants are uncharged as in their eq 26, but this is not the case for reaction 73.1.

A more correct eq can be derived as follows: first,

$$\log K^{\circ} = \log K + \log (\gamma(4\text{-CNC}_6\text{H}_4\text{O}^{-})\gamma(\text{S}_4\text{O}_6^{\bullet 3-})/\gamma(\text{S}_2\text{O}_3^{2-})^2)$$
$$= \log K + \log \gamma(4\text{-CNC}_6\text{H}_4\text{O}^{-}) + \log \gamma(\text{S}_4\text{O}_6^{\bullet 3-}) - 2\log \gamma(\text{S}_2\text{O}_3^{2-})$$

Then, we use the Guggenheim eq. for single-ion activity coefficients:
$\log \gamma = -Az_i^2\mu^{1/2}/(1 + \mu^{1/2}) + \beta I$.

This leads to $\log K^{\circ} = \log K - AI^{1/2}/(1 + \mu^{1/2})(z(4\text{-CNC}_6\text{H}_4\text{O}^{-})^2 + z(\text{S}_4\text{O}_6^{\bullet 3-})^2 - 2z(\text{S}_2\text{O}_3^{2-})^2)$
(the β terms cancel out for this reaction, so long as β is the same for all ions).

So, $\log K^{\circ} = \log K - A\mu^{1/2}/(1 + \mu^{1/2})((-1)^2 + (-3)^2 - 2(-2)^2) = \log K - A\mu^{1/2}/(1 + \mu^{1/2})(2)$
or, $\log K = \log K^{\circ} + 2A\mu^{1/2}/(1 + \mu^{1/2})$. $A = 0.509$ for water at 25 °C.

From the data at $\mu = 0.28$ M we thus calculate $\log K^{\circ} = -(0.010 \pm 0.020)$, and $\Delta E = -(0.001 \pm 0.002)$ V. With our recommended $E^{\circ} = +(1.09 \pm 0.03)$ V $4\text{-CNC}_6\text{H}_4\text{O}^{\bullet}/4\text{-CNC}_6\text{H}_4\text{O}^{-}$ (Data Sheet S-6) we then obtain $E^{\circ} = +(1.09 \pm 0.03)$ V for $\text{S}_4\text{O}_6^{\bullet 3-}/2\text{S}_2\text{O}_3^{2-}$.

Recommended values:

K_{eq} = (2.2 ± 0.2) M^{-1} at μ = 0.28 M and (21 ± 2) °C
log $K°$ = –(0.01 ± 0.02) at μ = 0.0 M
$E°$ = +(1.09 ± 0.03) V for $S_4O_6^{\bullet 3-}/2S_2O_3^{2-}$

Nomenclature: see Data Sheet 71.

List of auxiliary thermodynamic data: none.

References

1. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103,** 3581-3588 (1999).

Data Sheet 74

Chemical equilibrium: $HS_4O_6^{\bullet 2-} \rightleftharpoons S_4O_6^{\bullet 3-} + H^+$ (74.1)

List of reports:

$pK_a = 6.2$ [1]. Determined by pulse radiolysis of $S_2O_3^{2-}$ solutions, with conductivity measured 25 μs after the pulse.

Discussion

Das *et al.* argue that the species $S_4O_6^{\bullet 3-}$ produced on this time scale is not $(O_3SSSSO_3)^{\bullet 3-}$ but an isomer such as $(O_3SSOSO_2S)^{\bullet 3-}$ [2].Their measurements on reactions 72.1 and 73.1 were performed at pH 8.8 and 12, and thus do not disagree with the reported pK_a.

Recommended value:

$pK_a = 6.2$

List of auxiliary thermodynamic data: none.

References

1. M. Schöneshöfer. *Int. J. Radiat. Phys. Chem.* **5,** 375-386 (1973).
2. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103,** 3581-3588 (1999).

Data Sheet 75

Chemical equilibrium: $S_2O_3^{\bullet-} + SCN^- \rightleftharpoons SCNS_2O_3^{\bullet 2-}$ (75.1)

List of reports:

$1/K_{eq} = (8.3 \pm 2.5) \times 10^{-4}$ M, presumably at room temperature, with μ varying from 0.01 M to 0.12 M [1]. Obtained by pulse radiolysis of $SCN^-/S_2O_3^{2-}$ mixtures, deriving the equilibrium constant from the thiocyanate dependence of the kinetics.

Discussion

The equilibrium constant is not expected to differ significantly between room temperature and 25 °C. On the other hand, K_{eq} is expected to be sensitive to ionic strength, which varied drastically in these experiments. Given this concern, we expand the uncertainty to ± a factor of 2.

Recommended value:

$K_{eq} = 1.2 \times 10^3\ M^{-1}$ within a factor of 2.

List of auxiliary thermodynamic data: none.

References

1. M. Schöneshöfer. *Ber. Bunsen-Ges. Phys. Chem.* **77,** 257-262 (1973).

Data Sheet 76

Chemical equilibrium: $(SCN)_2^{\bullet-} + S_2O_3^{2-} \rightleftharpoons SCNS_2O_3^{\bullet 2-} + SCN^-$ (76.1)

List of reports:

$K_{eq} = (1.6 \pm 0.4) \times 10^2$, presumably at room temperature, with μ ranging from 0.01 M to 0.1 M [1]. Obtained by pulse radiolysis of $SCN^-/S_2O_3^{2-}$ mixtures, and derivation of the equilibrium constant from the thiocyanate dependence of the kinetics.

Discussion

This equilibrium constant is expected to be insensitive to ionic strength; thus, the variable ionic strength in the experiments is not a concern. The equilibrium constant is not expected to differ significantly between room temperature and 25 °C.

Recommended value:

$K_{eq} = (1.6 \pm 0.4) \times 10^2$ at $\mu = 0.0$ M and 25 °C.

List of auxiliary thermodynamic data: none.

References

1. M. Schöneshöfer. *Ber. Bunsen-Ges. Phys. Chem.* **77,** 257-262 (1973).

Data Sheet 77

Chemical equilibrium:

$$\text{4-OCH}_3\text{-C}_6\text{H}_4\text{-NH}_2^{\bullet+} + \text{HS}^-/\text{H}_2\text{S} \rightleftharpoons \text{4-OCH}_3\text{-C}_6\text{H}_4\text{-NH}_2 + \text{S}^{\bullet-} \text{ at pH} = 7 \qquad (77.1)$$

List of reports:

Only one study has been made of this system. Das *et al.* [1] used pulse radiolysis to measure the equilibrium quotient as (68 ± 10) M^{-1} for reaction 77.2 at pH 7 and $\mu = 0.1$ M:

$$\text{4-OCH}_3\text{-C}_6\text{H}_4\text{-NH}_2^{\bullet+} + 2\text{HS}^-/\text{H}_2\text{S} \rightleftharpoons \text{4-OCH}_3\text{-C}_6\text{H}_4\text{-NH}_2 + \text{HSS}^{\bullet 2-} + \text{H}^+ \text{ at pH} = 7 \quad (77.2)$$

$$\text{S}^{\bullet-} + \text{SH}^- \rightleftharpoons \text{HSS}^{\bullet 2-} \qquad (77.3)$$

By combining the equilibrium quotients for reactions 77.2 and 77.3 (taken as 9×10^3 M^{-1}, see Data Sheet 117) we calculate the equilibrium constant for reaction 77.1 to be 7.55×10^{-3} at pH = 7. Using +0.79 V reported for the anilinium couple [2], Das *et al.* calculated $E°'(\text{S}^{\bullet-}/(\text{HS}^-/\text{H}_2\text{S}))$ = +(0.92 ± 0.03) V at pH = 7.

Discussion

The equilibrium "constant" calculated above for reaction 77.1 is obtained by combining equilibrium quotients at different ionic strengths, and hence is not well defined. Further complicating matters, the $E°'(\text{S}^{\bullet-}/(\text{HS}^-/\text{H}_2\text{S}))$ value is derived by using the aniline $E°$ value, leading to a further mixing of conditions. In what follows we make the approximation that results are obtained at zero ionic strength.

The newly revised $E°$-value for promethazine [3] raises the $E°$ of the anilinium couple to +(0.80 ± 0.02) V (see Supplementry Data Sheet S-11). Hence $E°'(\text{S}^{\bullet-}/(\text{HS}^-/\text{H}_2\text{S}))$ = +(0.93 ± 0.03) V at pH = 7 and $\mu = 0$. Utilizing that $\text{p}K_a(\text{H}_2\text{S}) = 6.97$ and noting that $\text{p}K_a(\text{HS}^\bullet) << 7$, we can calculate from these data the following potentials at pH = 0:

$$\text{S}^{\bullet-} + \text{e}^- + \text{H}^+ \rightleftharpoons \text{HS}^- \qquad E°(\text{S}^{\bullet-},\text{H}^+/\text{HS}^-) = +(1.33 \pm 0.03)\text{ V and} \qquad (77.4)$$

$$\text{S}^{\bullet-} + \text{e}^- + 2\,\text{H}^+ \rightleftharpoons \text{H}_2\text{S} \qquad E°(\text{S}^{\bullet-},2\text{H}^+/\text{H}_2\text{S}) = +(1.74 \pm 0.03)\text{ V} \qquad (77.5)$$

From recently revised and apparently rather accurate gas phase data [4], we calculate $\Delta_f G°(\text{HS}^\bullet(\text{g})) = 113.6$ kJ mol^{-1}. As is well-known, $\Delta_f G°(\text{H}_2\text{S}(\text{g})) = -35.56$ kJ mol^{-1}. The Henry's law constants, K_H, of sulfides increase monotonously with increasing alkylation [5]. Thus, they vary from 1.07 M MPa^{-1} (0.107 M/bar) for H_2S to 3.9 M MPa^{-1} (0.39 M/bar) for CH_3SH to 5.4 M

$\mathrm{MPa^{-1}}$ (0.54 M/bar) for $(CH_3)_2S$. This trend reveals that hydrogen bonding between S-H bonds and water oxygens are of no consequence. Rather it is the hydrogen bonding between the lone pair on S and the water protons that matter. This suggests that $K_\mathrm{H}(\mathrm{H_2S})/K_\mathrm{H}(\mathrm{HS^\bullet}) \leq K_\mathrm{H}(\mathrm{HSCH_3})/K_\mathrm{H}(\mathrm{H_2S})$. In fact, we assume $K_\mathrm{H}(\mathrm{H_2S})/K_\mathrm{H}(\mathrm{HS^\bullet}) \approx (K_\mathrm{H}(\mathrm{HSCH_3})/ K_\mathrm{H}(\mathrm{H_2S}))^{1/2} = 1.9$. Hence, we calculate the following aqueous potential:

$$\mathrm{HS^\bullet + e^- + H^+ \rightleftharpoons H_2S} \qquad E^\circ(\mathrm{HS^\bullet,H^+/H_2S}) = +(1.54 \pm 0.03)\ \mathrm{V} \tag{77.6}$$

The error margin assumes a maximum uncertainty factor of 3 in the Henry's constant ratios of the two species. This yields $E^\circ(\mathrm{HS^\bullet/HS^-}) = +(1.13 \pm 0.03)$ V and $\mathrm{p}K_\mathrm{a}(\mathrm{HS^\bullet}) = (3.4 \pm 0.7)$. When combined with NBS data for $\mathrm{HS^-}$ and $\mathrm{H_2S(aq)}$ the above $E^{\circ\prime}$ values yield $\Delta_\mathrm{f}G^\circ = +(140 \pm 3)\ \mathrm{kJ\ mol^{-1}}$ for $\mathrm{S^{\bullet-}}$ and $\Delta_\mathrm{f}G^\circ = +(121 \pm 3)\ \mathrm{kJ\ mol^{-1}}$ for $\mathrm{HS^\bullet}$.

Das *et al.* [1] also determined the equilibrium constant for reaction 77.7:

$$\mathrm{[Mo(CN)_8]^{3-} + 2\ SH^- \rightleftharpoons [Mo(CN)_8]^{4-} + HSS^{\bullet 2-} + H^+} \tag{77.7}$$

The result provides good support for the result obtained from the methoxyaniline reaction (eq 77.1). However, this measurement was performed at $\mu = 0.1$ M, and given the high ionic charges involved in this reaction we prefer to base our recommendations on eq 77.1.

Given our recommended equilibrium constant for eq 77.3 ($K = (9 \pm 2) \times 10^3\ \mathrm{M^{-1}}$, see Data Sheet 117), the NBS value of $+(12.08 \pm 0.8)\ \mathrm{kJ\ mol^{-1}}$ for $\Delta_\mathrm{f}G^\circ(\mathrm{HS^-})$ [6], and our derived value for $\Delta_\mathrm{f}G^\circ(\mathrm{S^{\bullet-}})$, we obtain $\Delta_\mathrm{f}G^\circ(\mathrm{HSS^{\bullet 2-}}) = +(129 \pm 4)\ \mathrm{kJ\ mol^{-1}}$. Kamyshny *et al.* have reported a value of $+(20.2 \pm 1.3)\ \mathrm{kJ\ mol^{-1}}$ for $\Delta_\mathrm{f}G^\circ(\mathrm{HS_2^-})$ [7], which thus leads to a value of $-(1.13 \pm 0.05)$ V for $E^\circ(\mathrm{HS_2^-/HSS^{\bullet 2-}})$.

Recommended values:

$E^\circ(\mathrm{S^{\bullet-},H^+/HS^-}) = +(1.33 \pm 0.03)$ V
$E^\circ(\mathrm{S^{\bullet-},2H^+/H_2S}) = +(1.74 \pm 0.03)$V
$E^\circ(\mathrm{HS^\bullet,H^+/H_2S}) = +(1.54 \pm 0.03)$ V
$E^\circ(\mathrm{HS^\bullet/HS^-}) = +(1.13 \pm 0.03)$ V
$E^\circ(\mathrm{HS_2^-/HSS^{\bullet 2-}}) = -(1.13 \pm 0.05)$ V
$\mathrm{p}K_\mathrm{a}(\mathrm{HS^\bullet}) = (3.4 \pm 0.7)$
$\Delta_\mathrm{f}G^\circ = +(140 \pm 3)\ \mathrm{kJ\ mol^{-1}}$ for $\mathrm{S^{\bullet-}}$
$\Delta_\mathrm{f}G^\circ = +(121 \pm 3)\ \mathrm{kJ\ mol^{-1}}$ for $\mathrm{HS^\bullet}$

$\Delta_f G^\circ(\mathrm{HSS}^{\bullet 2-})$ = (129 ± 4) kJ mol^{-1}
$\Delta_f G^\circ(\mathrm{HS_2}^-)$ = +(20.2 ± 1.3) kJ mol^{-1}

List of auxiliary thermodynamic data: none

Nomenclature: $\mathrm{S}^{\bullet -}$, sulfide(•−) or sulfanidyl, $\mathrm{HS}^{\bullet}$, hydridosulfur(•) or sulfanyl; $\mathrm{H_2S}$, dihydridosulfur or sulfane (hydrogen sulfide or, better, dihydrogen sulfide is acceptable); $\mathrm{HS_2}^-$, hydridodisulfide(*S*-*S*)(1−) or disulfanide; $\mathrm{HSS}^{\bullet 2-}$, hydridodisulfide(*S*-*S*)(•2−) or disulfanudi-idyl; $\mathrm{HSSH}^{\bullet -}$, dihydridodisulfide(*S*-*S*)(•1−) or disulfanuidyl.

References

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4. K. Lodders. *J. Phys. Chem. Ref. Data* **33**, 357-367 (2004).
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7. A. Kamyshny, A. Goifman, J. Gun, D. Rizkov, O. Lev. *Environ. Sci. Technol.* **38**, 6633-6644 (2004).

Data Sheet 78

Chemical equilibria:

$$SeO_3^{2-} + HO^{\bullet} \rightleftharpoons HSeO_4^{\bullet 2-} \quad (78.1)$$

$$SeO_3^{2-} + O^{\bullet -} + H_2O \rightleftharpoons HSeO_4^{\bullet 2-} + HO^{-} \quad (78.2)$$

$$SeO_3^{\bullet -} + HO^{-} \rightleftharpoons HSeO_4^{\bullet 2-} \quad (78.3)$$

List of reports:

There is only one report [1]. Kläning and Sehested have determined by pulse radiolysis the equilibrium constants $K_{78.1} = 4.8 \times 10^3$ M^{-1}; $K_{78.2} = 37$; $K_{78.3} = 0.78$ M^{-1}, all corrected to zero ionic strength.

Discussion

Although the above constants are extracted from a somewhat complex scheme, they appear to be very carefully and professionally done. Experimentally, rate constants for forward and reverse reactions are measured separately with due allowance for ionic strength effects. As for equilibrium 78.3, the hydrolysis of the $SeO_3^{\bullet -}$ radical, the authors analyze the spectral change with varying [HO^-] at constant dose, while making the appropriate corrections. From the finding of a distinct isosbestic point, the simultaneous presence of only two species, $SeO_3^{\bullet -}$ and $HSeO_4^{\bullet 2-}$, is deduced. At high pH the radical(s) disappear in a first order process, the rate increasing with increasing [HO^-]. When O_2 is present in such solutions, the authors observe a first order build-up of $O_3^{\bullet -}$, at a rate that exactly matches the decay of the $HSeO_4^{\bullet 2-}$ radicals. Hence the occurrence of reactions −78.1 and −78.2 is inferred. From measurements of the rate of radical disappearance at varying [HO^-] both $k_{-78.1}$ and $k_{-78.2}$ are obtained, while $k_{78.1}$ and $k_{78.2}$ are derived directly from the build-up of radical absorbance during SeO_3^{2-} consumption by $HO^{\bullet}/O^{\bullet -}$. From the above equilibrium constants the authors derive a number of electrode potentials as well as Gibbs energies of formation for selenium radical species. These hinge, of course, on the correctly assumed values for the references $HO^{\bullet}$ and $O^{\bullet -}$. Fortunately, the authors use the same electrode potential for ($HO^{\bullet}$,H^+/H_2O) = +2.73 V, as we have agreed upon. Hence we can use their published values, which they believe to be correct within 10 mV, a value that should be doubled to include all error sources.

The qualitatively interesting part in this study is the finding that Se(V) can exist in four-coordinate form, something S(V) cannot. This is no doubt mainly due to the size difference of the central atoms. Of further interest is the finding that both the four- and three-coordinate Se(V)-species can rapidly be produced by reduction of tetraoxidoselenate(2−), Se(VI), by the hydrated electron. This is in sharp contrast to SO_4^{2-}, which is inert against one-electron reduction. It is also intuitively non-trivial to understand how the electrode potential of $SeO_3^{\bullet-}$ and the H-O bond strength in $H\text{-}O\text{-}SeO_2^-$ can exceed by *ca.* 1 eV the corresponding values for $SO_3^{\bullet-}$and $H\text{-}O\text{-}SO_2^-$. Be it as it may, the finding that $SeO_3^{\bullet-}$ oxidizes CO_3^{2-} rather fast (with $E°(CO_3^{\bullet-}/CO_3^{2-}) = +1.59$ V), while $SO_3^{\bullet-}$ is completely unreactive towards CO_3^{2-}, firmly proves this ranking.

Recommended values:

$E°(SeO_3^{\bullet-}/SeO_3^{2-}) = +(1.68 \pm 0.03)$ V
$E°(SeO_3^{\bullet-},H^+/HSeO_3^-) = +(2.18 \pm 0.03)$ V
$\Delta_f G^o(SeO_3^{\bullet-}) = -(202 \pm 3)$ kJ mol^{-1}
$\Delta_f G^o(HSeO_4^{\bullet 2-}) = -(358 \pm 3)$ kJ mol^{-1}

Nomenclature: $SeO_3^{\bullet-}$, trioxidoselenate(•−); SeO_3^{2-}, trioxidoselenate(2−); $HSeO_3^-$, hydroxidodioxidoselenate(−), and $HSeO_4^{\bullet 2-}$, hydroxidotrioxidoselenate(•2−)

List of auxiliary thermodynamic data: none

References

1. U. K. Kläning, K. Sehested. *J. Phys. Chem.* **90,** 5460-5464 (1986).

Data Sheet 79

Chemical equilibria:

$TeO_3^{2-} + HO^\bullet \rightleftharpoons HTeO_4^{\bullet 2-}$ (79.1)

$TeO_3^{2-} + O^{\bullet -} \rightleftharpoons TeO_4^{\bullet 3-}$ (79.2)

$TeO_3^{\bullet -} + H_2O \rightleftharpoons HTeO_4^{\bullet 2-} + H^+$ (79.3)

$HTeO_4^{\bullet 2-} \rightleftharpoons TeO_4^{\bullet 3-} + H^+$ (79.4)

List of reports:

There is only one report [1]. From the pulse radiolytic data of Kläning and Sehested the following values for the above equilibrium constants are obtained:

$K_{79.1} = (3.7 \pm 1.3) \times 10^6$ M^{-1}; $K_{79.2} = (2.7 \pm 0.5) \times 10^5$ M^{-1}; p$K_{79.3}$ = (9.96 ± 0.15); p$K_{79.4}$ = (13.2 ± 0.2). $K_{79.1}$ should be independent of ionic strength. $K_{79.2}$ at μ = 0.1 M, $K_{79.3}$ at μ = (0.01- 0.03) M; $K_{79.4}$ at μ = (0.01 - 0.3) M.

Discussion

Qualitatively, tellurium behaves similarly to selenium. Thus Te(V) species are facilely obtained either by way of one-electron oxidation of Te(IV) by $HO^\bullet/O^{\bullet -}$ or by one-electron reduction of Te(VI) by the hydrated electron. Just as in the case of selenium, and in contrast to S, the four-coordinate Te(V) can exist in equilibrium with the corresponding three-coordinate Te(V) species. In the case of tellurium, the four-coordinate species is stable in a considerably larger pH-interval than the Se(V) species. This is in agreement with the larger size of Te as coMPared to Se. Hence, the authors can observe four Te(V) species: to wit $TeO_3^{\bullet -}$, $H_2TeO_4^{\bullet -}$, $HTeO_4^{\bullet 2-}$ and $TeO_4^{\bullet 3-}$. By spectral and kinetic analysis some acid –base dissociation constants can be evaluated. From the kinetics of decay at different pH-values of the four-coordinate species the rate constants of expulsion of $HO^\bullet/O^{\bullet -}$ were determined, which in combination with the forward rates yielded the pertinent equilibrium constants. Hence, just as in the case of Se(V), the electrode potentials and Gibbs energies of formation of the Te(V) species hinge on the reference values for $HO^\bullet$ and $O^{\bullet -}$. The authors happen to employ the same electrode potential for these species as was recommended by our task group. Hence their reported values can be recommended. The error margins in the potentials are probably ± 20 mV. Note that the Gibbs energies of formation are dependent on a non-NBS value for $\Delta_f G°(TeO_3^{2-})$ as is described in the cited publication. Although the derived $E°$ and $\Delta_f G°$ values are based, in part, on equiibrium constants that have not been corrected to zero ionic strength, we consider that the errors introduced are small enough relative to the stated uncertainties.

Recommended values:

$E°(\mathrm{TeO_3}^{\bullet-}/\mathrm{TeO_3}^{2-}) = +(1.74 \pm 0.03)$ V
$E°(\mathrm{TeO_3}^{\bullet-},\mathrm{H}^{+}/\mathrm{HTeO_3}^{-}) = +(2.31 \pm 0.03)$ V
$\Delta_f G^o(\mathrm{TeO_3}^{\bullet-}) = -(214 \pm 3)$ kJ mol^{-1}
$\Delta_f G^o(\mathrm{HTeO_4}^{\bullet 2-}) = -(394 \pm 3)$ kJ mol^{-1}
$\Delta_f G^o(\mathrm{TeO_4}^{\bullet 3-}) = -(319 \pm 3)$ kJ mol^{-1}

Nomenclature: $\mathrm{TeO_3}^{\bullet-}$, trioxidotellurate(•−); $\mathrm{TeO_3}^{2-}$, trioxidotelurate(2−); $\mathrm{HTeO_3}^{-}$, hydroxidodioxidotellurate(1−); $\mathrm{TeO_4}^{\bullet 3-}$ tetraoxidotellurate(•3−), and $\mathrm{HTeO_4}^{\bullet 2-}$, hydroxidotrioxidotellurate(•2−)

List of auxiliary thermodynamic data: none

References

1. U. K. Kläning, K. Sehested. *J. Phys. Chem. A.* **105,** 6637-6645 (2001).

Data Sheet 80

Summary of the $N_3^{\bullet}$ System

Tabulated below are the presently recommended equilibrium constants involving the trinitrogen*(2N–N)*(•) ($N_3^{\bullet}$) radical. Uncertainties are expressed as ± 1 σ; in many cases the value of σ is merely a subjective guess.

rxn #	Reaction	K_{eq}	dim.	uncertainty	μ / M	Data Sheet #
81.1	$N_3^- + [Ru(bpy)_3]^{3+} \rightleftharpoons N_3^{\bullet} + [Ru(bpy)_3]^{2+}$	14		±4	0	81
82.1	$N_3^- + [IrCl_6]^{2-} \rightleftharpoons N_3^{\bullet} + [IrCl_6]^{3-}$	1.7×10^{-7}		± 0.2	1.0	82
83.1	$ClO_2^{\bullet} + N_3^- \rightleftharpoons ClO_2^- + N_3^{\bullet}$	4×10^{-7}		$\pm 1 \times 10^{-7}$	0	83
29.1	$Br_2^{\bullet-} + N_3^- \rightleftharpoons N_3^{\bullet} + 2Br^-$	5.5×10^4	M	factor of 2	0	29
84.1	$(DMS)_2^{\bullet+} + N_3^- \rightleftharpoons 2DMS + N_3^{\bullet}$	16.4	M	± 1.0	?	84
72.1	$N_3^{\bullet} + 2S_2O_3^{2-} \rightleftharpoons N_3^- + (S_2O_3)_2^{\bullet 3-}$	1.9×10^4	M^{-1}	$\pm 2 \times 10^3$	0.44	72
85.1	$N_3^{\bullet} + N_3^- \rightleftharpoons N_6^{\bullet-}$	0.24	M^{-1}	± 30%	0	85
86.1	$N_3^{\bullet} + e^- \rightleftharpoons N_3^-$	1.32	V	± 0.03	0.2	86

DMS is dimethylsulfide, CH_3SCH_3

Reaction 81.1, in combination with the measured electrode potential of the Ru(III/II) couple leads to $E^{\circ\prime} = +(1.33 \pm 0.01)$ V for $N_3^{\bullet}/N_3^-$ at 25 °C and $\mu = 0.01$ M.

Reaction 82.1, in combination with the electrode potential of the Ir(IV/III) couple leads to $E^{\circ\prime} = +(1.33 \pm 0.02)$ V at 25 °C and $\mu = 1.0$ M.

Reaction 83.1, in combination with the standard potential of the $ClO_2^{\bullet}/ClO_2^-$ couple leads to $E^{\circ} = +(1.313 \pm 0.006)$ V at 25 °C and $\mu = 0.0$ M. The uncertainty here may be overly optimistic, given the wide range of reports for k_r.

Reaction 29.1, in combination with the standard potential of the $Br_2^-/2Br^-$ couple (+1.625 ± 0.020) V leads to $E^{\circ} = +(1.34 \pm 0.03)$ V at 25 °C.

Reaction 84.1 is unsuitable for deriving $E°(N_3^•/N_3^-)$ because it is used to derive the potential of the $(DMS)_2^{•+}/2DMS$ system.

Reaction 72.1 is unsuitable for deriving $E°(N_3^•/N_3^-)$ because it is used to derive the potential of the thiosulfate system.

Reaction 86.1 (from irreversible cyclic voltammetry) yields an electrode potential at $\mu = 0.2$ M.

The various routes to $E°$ given above are essentially all in agreement within their specified uncertainties. We assign relatively low weight to the result from reaction 83.1 because of concerns about the scatter in k_r. Given the consistency of the remaining results despite their varying ionic strengths, we recommend $E° = +(1.33 \pm 0.02)$ V at 25 °C.

NBS gives $\Delta_f G° = +(348 \pm 8)$ kJ for $N_3^-(aq)$. The $E°$ recommended above yields $\Delta_f G°(N_3^-,aq) - \Delta_f G°(N_3^•,aq) = -(128 \pm 1)$ kJ mol^{-1}. Thus, we obtain $\Delta_f G° = (476 \pm 8)$ kJ mol^{-1} for $N_3^•(aq)$, where most of the uncertainty reflects the uncertainty in N_3^-.

Recommended values:

$E°(N_3^•/N_3^-) = +(1.33 \pm 0.02)$ V at 25 °C
$\Delta_f G° = +(476 \pm 8$ kJ) mol^{-1} for $N_3^•(aq)$

Nomenclature: $Br_2^{•-}$, dibromide(•1−);Br^-, bromide(1−) or bromide; $ClO_2^•$, dioxidochlorine(•) or chlorine dioxide; $[IrCl_6]^{2-}$, hexachloridoiridate(2−); $N_3^•$, trinitrogen*(2N–N)*(•); N_3^-, trinitride(1−), azide is acceptable; $N_6^{•-}$, hexanitride(•1−); $S_2O_3^{2-}$, trioxidosulfidosulfate*(S–S)*(2−); $(S_2O_3)_2^{•3-}$, bis[(trioxidosulfidosulfate)]*(S–S)*(•3−); $[Ru(bpy)_3]^{2+}$, tris(bipyridine)ruthenium(2+).

Data Sheet 81

Chemical equilibrium: $N_3^- + [Ru(bpy)_3]^{3+} \rightleftharpoons N_3^\bullet + [Ru(bpy)_3]^{2+}$ (81.1)

List of reports:

$K_{eq} = (10 \pm 5)$ at $\mu = 0.01$ M and 25 °C [1]. Determined from the ratio of forward and reverse rate constants for approach to equilibrium, by pulse radiolysis experiments. The value of K_{eq} was not actually reported and the value given here is derived from the reported $E°'$ values for the $N_3^\bullet/N_3^-$ and $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couples.

$K_{eq} = (4.8 \pm 2.4)$ at $\mu = 0.01$ M and 25 °C [1]. Determined from absorbance measurements at equilibrium, during pulse radiolysis experiments. The value of K_{eq} was not actually reported and the value given here is derived from the reported $E°'$ values for the $N_3^\bullet/N_3^-$ and $Ru(bpy)_3]^{3+}$/ $Ru(bpy)_3]^{2+}$couples.

Discussion

The two determinations of the equilibrium constant are in good agreement and yield an average value of (7.4 ± 3.7) at 25 °C and $\mu = 0.01$ M. Given the low ionic strength of the measurements, it is reasonable to correct for activity coefficients by the eq $\log \gamma = -Az^2\mu^{1/2}/(1 + \mu^{1/2})$. This procedure yields $K_{eq} = (14 \pm 4)$ at 25 °C and $\mu = 0$ M.

As reported by the original authors, the equilibrium constant plus the measured potential for the Ru(III/II) couple $E°' = +(1.28 \pm 0.01)$ V at $\mu = 0.1$ M leads to $E°' = +(1.33 \pm 0.01)$ V for $N_3^\bullet/N_3^-$. The estimated uncertainty is probably too small, given the varying ionic strengths in the component measurements.

Recommended values:

$K_{eq} = (14 \pm 4)$ at 25 °C and $\mu = 0$ M
$E°' = +(1.33 \pm 0.01)$ V for the $N_3^\bullet/N_3^-$ couple at 25 °C and $\mu = 0.01$ M.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 80.

References

1. M. R. DeFelippis, M. Faraggi, M. H. Klapper. *J. Phys. Chem.* **94,** 2420-2424 (1990).

Data Sheet 82

Chemical equilibrium: $N_3^- + [IrCl_6]^{2-} \rightleftharpoons N_3^\bullet + [IrCl_6]^{3-}$ (82.1)

List of reports:

$K_{eq} = (1.45 \pm 0.23) \times 10^{-7}$ at unspecified ionic strength and temperature [1]. Result obtained from the ratio of the forward and reverse rate constants. The forward rate constant was obtained by stopped-flow measurements at 25 °C and $\mu = 1.0$ M. The reverse rate constant was obtained by pulse radiolysis at 22 °C and $\mu = (0.01 - 0.1)$ M.

$K_{eq} = 1.7 \times 10^{-7}$ at 25 °C and $\mu = 1.0$ M [2]. Result obtained from the ratio of the forward and reverse rate constants. The forward rate constant was obtained by stopped-flow measurements at 25 °C and $\mu = 1.0$ M. The reverse rate constant was obtained by pulse radiolysis at 22 °C and $\mu = (0.01 - 0.1)$ M.

Discussion

The two reports of K_{eq} differ because of slightly different values used for the forward rate constant; the reverse rate constant was identical in the two reports. The first report was a preliminary version of the second, and so we recommend the second with uncertainties as given in the first: $K_{eq} = (1.7 \pm 0.2) \times 10^{-7}$ at 25 °C and $\mu = 1.0$ M. Although the reverse rate constant was obtained under various ionic strengths, it is expected to be independent of ionic strength, and thus the derived value of K_{eq} pertains to the ionic strength at which the forward rate constant was determined.

By use of $E°' = +0.93$ for Ir(IV/III) at $\mu = 1.0$ M, Ram and Stanbury derived $E°' = +(1.33 \pm 0.02)$ V for N_3/N_3^-.

Recommended values:

$K_{eq} = (1.7 \pm 0.2) \times 10^{-7}$ at 25 °C and $\mu = 1.0$ M
$E°' = +(1.33 \pm 0.02)$ V for $N_3^\bullet/N_3^-$ at 25 °C and $\mu = 1.0$ M

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 80.

References

1. M. S. Ram, D. M. Stanbury. *Inorg. Chem.* **24,** 4233-4234 (1985).
2. M. S. Ram, D. M. Stanbury. *J. Phys. Chem.* **90,** 3691-3696 (1986).

Data Sheet 83

Chemical equilibrium: $ClO_2^\bullet + N_3^- \rightleftharpoons ClO_2^- + N_3^\bullet$ (83.1)

List of reports:

$K_{eq} = (4.0 \pm 1) \times 10^{-7}$ at 25 °C and $\mu = 0.1$ M. Calculated herein from the ratio of the forward and reverse rate constants. Awad and Stanbury determined $k_f = (809 \pm 9)$ M^{-1} s^{-1} at 25 °C and $\mu = 0.1$ M from stopped-flow experiments [1]. The reverse rate constant was reported by DeFelippis *et al.* from pulse radiolysis as 7.8×10^7 M^{-1} s^{-1} at an unspecified temperature and $\mu = 0.1$ M [2]. Shoute *et al.* reported k_r from pulse radiolysis as 1.9×10^9 M^{-1} s^{-1} at 17 °C and 3.2×10^9 M^{-1} s^{-1} at 33 °C, both at $\mu = 0.1$ M [3]. These workers noted the discrepancy between their rate constant and that reported by DeFelippis *et al.* [2] (their ref. 25), and they also noted some other issues that undermine the credibility of ClO_2^- rate constants (with $(SCN)_2^{\bullet -}$ and $Br_2^{\bullet -}$) reported by DeFelippis *et al.* Difficulties in the $(SCN)_2^{\bullet -}$ and $Br_2^{\bullet -}$ reactions can be understood because ClO_2^- reacts with SCN^- and Br^- [4, 5]; a coMParable explanation for the N_3^- discrepancy is presently lacking. Merényi *et al.* used pulse radiolysis to obtain $k_r = 1.9 \times 10^9$ M^{-1} s^{-1} at an unspecified temperature and ionic strength [6]. We reject the report on k_r from DeFelippis *et al.* [2] on the grounds that it disagrees seriously with the two other reports, which are quite consistent with each other. The value of k_r should be rather insensitive to μ and T; combining the results of Shoute *et al.* and Merényi *et al.* we recommend $k_r = (2.0 \pm 0.5) \times 10^9$ M^{-1} s^{-1} at 25 °C and arbitrary ionic strength. The ratio of k_f and k_r is thus $(4 \pm 1) \times 10^{-7}$ at 25 °C and $\mu = 0.1$ M. Note that this specified uncertainty is perhaps too optimistic, as it is based on a somewhat arbitrary rejection of the results of DeFelippis *et al.* [2].

Discussion

As the values of k_f, k_r, and K_{eq} should be insensitive to μ, we recommend $K_{eq} = (4 \pm 1) \times 10^{-7}$ at 25 °C and $\mu = 0.0$ M.

With $E° = +0.935 \pm 0.003$ V for $ClO_2^\bullet/ClO_2^-$ as we have recommended elsewhere in this compendium, we derive $E° = +(1.313 \pm 0.006)$ V for $N_3^\bullet/N_3^-$ at 25 °C. The uncertainty here may be overly optimistic.

Recommended values:

$K_{eq} = (4 \pm 1) \times 10^{-7}$ at 25 °C and $\mu = 0.0$ M

$E°$ = +(1.313 ± 0.006) V for $N_3^•/N_3^−$ at 25 °C

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 80.

References

1. H. H. Awad, D. M. Stanbury. *J. Am. Chem. Soc.* **115,** 3636-3642 (1993).
2. M. R. DeFelippis, C. P. Murthy, M. Faraggi, M. H. Klapper. *Biochemistry* **28,** 4847-4853 (1989).
3. L. C. T. Shoute, Z. B. Alfassi, P. Neta, R. E. Huie. *J. Phys. Chem.* **95,** 3238-3242 (1991).
4. M. Alamgir, I. R. Epstein. *J. Phys. Chem.* **89,** 3611-3614 (1985).
5. O. Valdes-Aguilera, D. W. Boyd, I. R. Epstein, K. Kustin. *J. Phys. Chem.* **1986,** 6702-6708 (1986).
6. G. Merényi, J. Lind, X. Shen, T. E. Eriksen. *J. Phys. Chem.* **94,** 748-752 (1990).

Data Sheet 84

Chemical equilibrium:

$(DMS)_2^{\bullet +} + N_3^- \rightleftharpoons 2DMS + N_3^\bullet$ (84.1)

DMS is CH_3SCH_3

List of reports:

K_{eq} = 16.4 M at room temperature and an unspecified ionic strength [1]. Obtained from pulse radiolysis measuring the absorbance at equilibrium.

Discussion

We assume room temperature is 22 °C. An uncertainty of ± 1 seems appropriate, given the number of significant figures specified.

This reaction was used by Merényi *et al.* [1] to determine $E°'$ for the $(DMS)_2^{\bullet +}$/2DMS couple, and hence is not of much value in determining $E°$ for the $N_3^\bullet/N_3^-$ couple.

Recommended value:

K_{eq} = (16.4 ± 1.0) M at 22 °C and unspecified ionic strength.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 80.

References

1. G. Merényi, J. Lind, L. Engman. *J. Phys. Chem.* **100,** 8875-8881 (1996).

Data Sheet 85

Chemical equilibrium: $N_3^\bullet + N_3^- \rightleftharpoons N_6^{\bullet-}$ (85.1)

List of reports:

$K_{eq} = 0.33$ M^{-1} at an unspecified temperature with $\mu = (0.1 – 1)$ M [1]. Result obtained by pulse radiolysis, with optical measurement of the position of equilibrium. Data were probably acquired at room temperature: 22 °C.

$K_{eq} = (0.16 - 0.22)$ M^{-1} at an unspecified temperature with $\mu = (0.5 – 4)$ M [2]. This result was obtained by pulse radiolysis, by measuring the equilibrium absorbance of $N_6^{\bullet-}$. Data were probably acquired at room temperature: 22 °C.

Discussion

There is good agreement between the two reports on K_{eq}. Ionic strength considerations should not be important for this reaction. We recommend an average value of 0.24 M^{-1} to K_{eq} and assign an uncertainty of ± 30%. The temperature effect is not likely to make K_{eq} significantly different at 25 °C than at 22 °C.

Recommended value:

$K_{eq} = (0.24 \pm 0.08)$ M^{-1} at 25 °C and $\mu = 0$ M.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 80.

References

1. J. Butler, E. J. Land, A. J. Swallow, W. Prutz. *Radiat. Phys. Chem.* **23,** 265-270 (1984).
2. Z. B. Alfassi, W. A. Prütz, R. H. Schuler. *J. Phys. Chem.* **90,** 1198-1203 (1986).

Data Sheet 86

Chemical equilibrium: $N_3^{\bullet} + e^- \rightleftharpoons N_3^-$ (86.1)

List of reports:

$E_{1/2} = +(1.32 \pm 0.03)$ V at $\mu = 0.2$ M and an unspecified temperature. This result was obtained by cyclic voltammetry, based on the scan-rate dependence of the irreversible peak potential [1].

Discussion

We assume the experiments were performed at room temperature, *i.e.,* 22 °C. Although obtained from an unconventional method for determining electrode potentials, the result seems reliable. The conversion from $E_{1/2}$ to $E^{\circ\prime}$ is a function of the diffusion constants, but the difference is expected to be negligible relative to the specified uncertainty.

Recommended value:

$E^{\circ\prime} = +(1.32 \pm 0.03)$ V at $\mu = 0.2$ M and 22 °C.

List of auxiliary thermodynamic data: none.

Nomenclature: see Data Sheet 80.

References

1. Z. B. Alfassi, A. Harriman, R. E. Huie, S. Mosseri, P. Neta. *J. Phys. Chem.* **91,** 2120-2122 (1987).

Data Sheet 87

H_2NOH and $H_2NO^{\bullet}$

Simple 1-electron oxidation of hydroxylamine can yield the corresponding radical cation, $H_2NOH^{\bullet +}$; this cation is a strong acid as noted in Table 3. Thus, we begin with a discussion of the oxidation to the more accessible species $H_2NO^{\bullet}$ as in

$$H_2NO^{\bullet} + H^+ + e^- \rightleftharpoons H_2NOH \qquad (87.1)$$

$E°'$ values involving the $H_2NO^{\bullet}$ radical are derived from the kinetics of oxidation of hydroxylamine, as described by Lind and Merényi [1].

The oxidation of H_2NOH by Pu(IV) under conditions of a large excess of hydroxylamine in nitric acid media $[H^+] = (1.28 - 2.5)$ M has the rate law as presented by Barney [2]:

$$-\frac{d[\mathrm{Pu(IV)}]}{dt} = \frac{k[\mathrm{Pu(IV)}]^2[\mathrm{H_3NOH^+}]^2}{[\mathrm{Pu(III)}]^2[\mathrm{H^+}]^4(K_\mathrm{d} + [\mathrm{NO_3}^-])^2} \qquad (87.2)$$

Values for k of (0.029 ± 0.008) $M^5\ s^{-1}$ and $K_\mathrm{d} = (0.33 \pm 0.15)$ M were determined at 30 °C and 2.4 M ionic strength [2].

As discussed by Lind and Merényi, this rate law implies the following mechanism:

$$PuNO_3^{3+} \rightleftharpoons Pu^{4+} + NO_3^- \qquad K_\mathrm{d} \qquad (87.3)$$
$$Pu^{4+} + H_3NOH^+ \rightleftharpoons Pu^{3+} + H_2NO^{\bullet} + 2H^+ \qquad K_\mathrm{et} \qquad (87.4)$$
$$2\ H_2NO^{\bullet} \rightarrow H_4N_2O_2\ (\rightarrow N_2 + 2H_2O) \qquad k_\mathrm{dim} \qquad (87.5)$$

Thus, $k/K_\mathrm{d}^2 = K_\mathrm{et}^2(2k_\mathrm{dim}) = (0.27 \pm 0.16)\ M^3\ s^{-1}$.

The reaction of Fe(III) with hydroxylamine studied in perchlorate media has a similar rate law but lacking the nitrate dependence [3]. Bengtsson *et al.* interpreted the reaction as occurring via $Fe(OH)^{2+}$ and H_2NOH, but for the present purposes the alternative formulation ($Fe^{3+} + H_3NOH^+$) is equivalent. In terms of the above mechanism, the measured rate constant, $K_\mathrm{et}^2(2k_\mathrm{dim})$, is $(1.5 \pm 0.4) \times 10^{-9}\ M^3\ s^{-1}$ at 25 °C and $\mu = 1.0$ M [3]. This result is the average of measurements made both by initial rates and from the integrated rate law.

Lind and Merényi used pulse radiolysis to determine k_dim, obtaining $2k_\mathrm{dim} = (2.8 \pm 0.5) \times 10^8\ M^{-1}\ s^{-1}$ (presumably at room temperature) [1]. This rate constant is expected to be rather independent of ionic strength.

The above results lead to values for K_{et} of (3.1 ± 1.7) × 10^{-5} M^2 for Pu and (2.3 ± 0.8) × 10^{-9} M^2 for Fe.

In the calculation of $E°'(H_2NO^\bullet)$ from the plutonium reaction, Lind and Merényi used +(0.982 ± 0.001) V as the electrode potential of the Pu^{4+}/Pu^{3+} couple at 25 °C in 1 M $HClO_4$, which was measured by Connick and McVey [4]. A 1999 IUPAC recommendation seems to support a lower value of (0.954 ± 0.005) V in 1 M $HClO_4$ [5], but a more recent evaluation supports the older data [6]. According to Lemire's evaluation, the electrode potential is essentially unchanged between 1.0 and 2.0 M ionic strength. Use of this electrode potential with the measured value of K_{et} leads to $E°'(H_2NO^\bullet,2H^+/H_3NOH^+) = +(1.249 \pm 0.012)$ V.

An electrode potential of +(0.738 ± 0.001) V for the $Fe^{3+/2+}$ redox couple in 1 M $HClO_4$ at 25 °C was selected for analysis of the Fe^{3+}/H_2NOH reaction [7]. The derived electrode potential for the $H_2NO^\bullet,2H^+/H_3NOH$ couple is +(1.249 ± 0.010) V at $\mu = 1$ M.

In view of the excellent agreement between the potentials calculated from both the Pu^{4+} and Fe^{3+} reactions we have considerable confidence in the average result: $E°'((H_2NO^\bullet,2H^+/H_3NOH^+) = +(1.249 \pm 0.010)$ V at $\mu = 1$ M.

Following Lind and Merényi [1], we apply a correction of 4 mV for the activity coefficient of the proton in 1 M perchlorate media, as described by Schwarz and Dodson [8]. We make the assumption that activity coefficients for H_3NOH^+ and H^+ are equal, which is supported by the weak ionic-strength dependence of the pK_a of H_3NOH^+ [9]. The 4 mV correction leads to $E°((H_2NO^\bullet,2H^+/H_3NOH^+) = +(1.253 \pm 0.010)$ V.

The conjugate acid of hydroxylamine has a $pK_a = 5.96$ at 25 °C and $\mu = 0$ [9]. Thus, $E°(H_2NO^\bullet,H^+/H_2NOH) = +(0.900 \pm 0.010)$ V.

No value for $\Delta_fG°(H_2NOH(aq))$ is given in the NBS tables [10]. A value for this quantity is given in Bard, Parsons and Jordan's compilation [11], but it suffers from a sign error and is essentially just Latimer's estimate. In view of the uncertainties in Latimer's estimate we refrain from deriving further results from it. On the other hand, the NBS tables do provide a value of $\Delta_fH° = -98.3$ kJ mol^{-1} for $H_2NOH(aq)$ [10]. We derive the entropy of aqueous H_2NOH from its gas-phase entropy and its entropy of hydration. According to Gurvich *et al.* (Table 171), $S°(H_2NOH, g) = 236$ J K^{-1} mol^{-1} [12]. We estimate the entropy of hydration ($\Delta_{hyd}S°$) to be –100 ± 5 J K^{-1} mol^{-1} on the basis of coMParison with a variety of monohydroxy compounds [13] and N_2H_4 ($\Delta_{hyd}S° = -100$ J K^{-1} mol^{-1}, NBS [10]). This leads to $S°(H_2NOH, aq) = (136 \pm 5)$ J K^{-1} mol^{-1}. By combining this aqueous entropy with the value of $\Delta_fH°$ given above and the requisite standard NBS entropies [10] we obtain $\Delta_fG° = -(21 \pm 2)$ kJ mol^{-1} for aqueous hydroxylamine. This quantity, in combination with $E°(H_2NO^\bullet,H^+/H_2NOH) = +(0.900 \pm 0.010)$ V, leads to $\Delta_fG° = +(66 \pm 3)$ kJ mol^{-1} for $H_2NO^\bullet$ (*aq*).

This value for $\Delta_f G^\circ$ for $H_2NO^\bullet$ can be combined with $\Delta_f G^\circ$(HNO,aq) = +(116 ± 2) kJ mol^{-1} from Data Sheet 22 to derive a value for $E^\circ(HNO,H^+/H_2NO^\bullet)$ = +(0.52 ± 0.04) V.

Recommended values:

$H_2NO^\bullet + 2H^+ + e^- \rightleftharpoons H_3NOH^+$ E° = +(1.253 ± 0.010) V at 25 °C
$H_2NO^\bullet + H^+ + e^- \rightleftharpoons H_2NOH$ E° = +(0.900 ± 0.010) V at 25 °C
$HNO^\bullet + H^+ + e^- \rightleftharpoons H_2NO^\bullet$ E° = +(0.52 ± 0.04) V at 25 °C
$\Delta_f G^\circ$ = +66 ± 3 kJ mol^{-1} for $H_2NO^\bullet$ (*aq*)

Supplementary thermodynamic data: as indicated in the discussion above.

Nomenclature: ClO_4^-, tetraoxidochlorate, perchlorate is allowed; H_2NOH, dihydridohydroxidonitrogen, azanol; hydroxylamine is acceptable. $H_2NOH^{\bullet+}$, dihydridohydroxidonitrogen(•+); $H_2NO^\bullet$, dihydridooxidonitrogen(•), aminoxidanyl or hydroxyazanyl, aminoxyl is acceptable.

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Data Sheet 88

Summary of the $NO_2^{\bullet}$ System

Tabulated below are the presently recommended equilibrium constants involving the nitrogen dioxide radical. Uncertainties are expressed as ± 1 σ; in many cases the value of σ is merely a subjective guess.

rxn #	reaction	K_{eq}	dim.	uncertainty	μ / M	Data Sheet #
89.1	$N_2O_4 \rightleftharpoons 2NO_2^{\bullet}$	1.5×10^{-5}	M	± 20%	?	89
91.1	$NO_2^- + [Fe(TMP)_3]^{3+} \rightleftharpoons NO_2^{\bullet} + [Fe(TMP)_3]^{2+}$	3.9×10^{-4}		± 31%	0.3	91
92.1	$NO_2^- + RNO^+ \rightleftharpoons NO_2^{\bullet} + RNO^{\bullet}$ ($RNO^{\bullet}$ = TEMPO)	1.5×10^{-5}		± 33%	0	92
49.1	$NO_2^{\bullet} + I^- \rightleftharpoons NO_2^- + I^{\bullet}(aq)$	none				49
93.1	$NO_2^{\bullet}(g) \rightleftharpoons NO_2^{\bullet}(aq)$	1.2×10^{-2}	M bar^{-1}	± 17%	0	93
94.1	$2HNO_2(aq) \rightleftharpoons NO^{\bullet}(aq) + NO_2^{\bullet}(aq) + H_2O$	1.1×10^{-7}		± 10%	0	94
95.1	$2NO_2^{\bullet}(aq) \rightleftharpoons HNO_2 + H^+ + NO_3^-$	3.8×10^{9}	M	± 39%	0	95

TMP = tetramethylphenanthroline; TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl

Reaction 91.1, when combined with $E^{\circ\prime}$ (Fe(III)/Fe(II)), leads to $E^{\circ\prime} = +(1.04 \pm 0.01)$ V at $\mu = 0.3$ M for $NO_2^{\bullet}(aq)/NO_2^-$.

Reaction 92.1, in combination with $E^{\circ} = +(0.750 \pm 0.005)$ V for $TEMPO^{+/0}$ as reviewed in Data Sheet S-7, yields $E^{\circ} = +(1.04 \pm 0.02)$ V for $NO_2^{\bullet}(aq)/NO_2^-$.

Reaction 94.1 can be combined with the equilibrium constant for the corresponding mixed-phase reaction ($2HNO_2(aq) = NO^{\bullet}(g) + NO_2^{\bullet}(g) + H_2O(l)$) and the Henry's law constant for $NO^{\bullet}$ to obtain the Henry's law constant for $NO_2^{\bullet}$. An assumed value for H_{NO2} was used in the determination of K_{eq} for reaction 94.1, but the two quantities are not completely correlated because of an additional "*C*" parameter. This mixed-phase equilibrium constant ($1/K_{M2'}$ in the parlance of Schwartz and White (1981)) has a value of $1/(1.26 \times 10^2)$ $atm^2\ M^{-2}$ {*i.e.* $1/(1.23 \times 10^4)$ $MPa^2\ M^{-2}$} as reported by Schwartz and White [1]. Schwartz and White derived this value from the equilibrium constant for the corresponding gas-phase reaction and H_{HNO2}. The latter has been confirmed by Park and Lee [2].We use $H_{NO} = (1.93 \pm 0.06) \times 10^{-3}$ M bar^{-1} {*i.e.* 1.93×10^{-2} M MPa^{-1}} as recommended in Data Sheet 90. Thus, $H_{NO2} = K_{10.01}K_{M2'}/H_{NO} = 7.2 \times 10^{-3}$ M bar^{-1} ± 12% {*i.e.* 7.2 x 10^{-2} M MPa^{-1}}. The discrepancy between this result and the value tabulated above is likely due to the number of quantities used in the calculation and correlation issue noted above.

Reaction 95.1 can be combined with the equilibrium constant for the corresponding mixed-phase reaction ($2NO_2^{\bullet}(g) = HNO_2(aq) + H^+(aq) + NO_3^-(aq)$ to obtain the Henry's law constant for $NO_2^{\bullet}$. This latter reaction (M 1' in the parlance of Schwartz and White (1981)) has $K_{eq} = 4.78 \times 10^5$ M^3 atm^{-2} [1] {*i.e.* 4.66×10^7 M^3 MPa^{-2}}. Schwartz and White obtained this value by combining $K_{M2'}$and K_{M3}, and these, respectively were obtained by combining (K_{G2} and H_{HNO2}) and (K_{G3} and K_{V2}). We do not question the gas-phase equilibrium constants K_{G2} and K_{G3}, and the values selected for H_{HNO2} and K_{V2} were subsequently confirmed by Park and Lee [2]. Following Schwartz and White (1981) we thus obtain $H_{NO2} = 1.1 \times 10^{-2}$ M atm^{-1} {*i.e.* 10.9×10^{-2} M MPa^{-1} with a 39% uncertainty. In short, the tabulated equilibrium constants for reactions 94.1 and 95.1 are in acceptable agreement with the tabulated value for H_{NO2}.

The tabulated value for H_{NO2}, in combination with the NBS value for $\Delta_f G°(NO_2^{\bullet}(g))$ (= +51.31 ± 0.8 kJ mol^{-1}) [3] yields $\Delta_f G°(NO_2^{\bullet}(aq))$ = +62.3 ± 1.0 kJ mol^{-1}. The JANAF-NIST tables give a very similar value and uncertainty for $\Delta_f G°(NO_2^{\bullet}(g))$ [4]. With use of the 1982 NBS value for $\Delta_f G°(NO_2^-(aq))$ (= –32.2 ± 8.0 kJ mol^{-1}) [3] we derive $E°(NO_2^{\bullet}(aq)/NO_2^-(aq))$ = +0.98 ± 0.08 V. Ram and Stanbury have commented that the 1982 NBS value for $\Delta_f G°$ of $HNO_2(aq)$ or $NO_2^-(aq)$ may be incorrect [5, 6]. Further discussion of this issue appears in Park and Lee's discussion of their measurement of the solubility of HNO_2 [2]; there seems to be good evidence that the NBS values for $\Delta_f G°$ of $HNO_2(aq)$ and $HNO_2(g)$ are inconsistent with the solubility of HNO_2 by about 4.6 kJ mol^{-1}. At this time, it is unclear whether these considerations imply an error in $\Delta_f G°(NO_2^-(aq))$, but the potential magnitude of the error is less than the 8 kJ uncertainty for $\Delta_f G°(NO_2^-(aq))$ indicated above. Overall, we conclude that the $E°(NO_2^{\bullet}(aq)/NO_2^-(aq))$ value derived from the NBS data is consistent with the value derived from the equilibrium constant for reaction 92.1.

In summary, the various routes to determining $E°(NO_2^{\bullet}(aq)/NO_2^-(aq))$ discussed above are all reasonably consistent with a value of +1.04 V. The result derived from reaction 91.1 is not used in the final recommendation because of the difficulties in making accurate corrections for activity coefficients in 0.3 M ionic strength. The final recommendation is the one derived from reaction 92.1: $E°(NO_2^{\bullet}(aq)/NO_2^-(aq)) = +(1.04 \pm 0.02)$ V.

Recommended value:

$E°(NO_2^•(aq)/NO_2^-(aq)) = +(1.04 \pm 0.02)$ V

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Data Sheet 89

Chemical equilibrium: $N_2O_4(aq) \rightleftharpoons 2NO_2^{\bullet}(aq)$ (89.1)

List of reports:

$K_{eq} = 1.53 \times 10^{-5}$ M presumably at room temperature, obtained by Grätzel and co-workers using pulse radiolysis to generate $NO_2^{\bullet}$ from NO_2^{-} and spectrophotometric $NO_2^{\bullet}$ detection [1].

$K_{eq} = (1.3 \pm 0.4) \times 10^{-5}$ M presumably at room temperature, derived from pulse radiolysis experiment with spectrophotometric $NO_2^{\bullet}$ detection by Treinin and Hayon [2].

$K_{eq} = (0.75 \pm 0.06) \times 10^{-5}$ M at pH 8.8 and $K_{eq} = 1.8 \times 10^{-5}$ M at pH 3.3, both at 25 °C, derived from experiments on flash photolysis of nitrate with conductivity detection by Strehlow and co-workers [3].

Discussion

The first two measurements agree well, with the value by Grätzel and co-workers [1] being preferred, as the significant amount of primary data showing little scatter is reported. Treinin and Hayon [2] have performed essentially the same experiment with similar results, but show no primary data for determining K_{eq}. Both determinations rely on knowing $\varepsilon_{400}(NO_2^{\bullet})$, to which K_{eq} is inversely proportional; both have used $\varepsilon_{400}(NO_2^{\bullet}) = 200$ M^{-1} cm^{-1}. Recently, some 10% lower $\varepsilon_{400}(NO_2^{\bullet})$ value have been reported [4]; the difference is mainly due to the different G values used. Additional uncertainty (possibly another 10%) comes from the $H^{\bullet} + NO_2^{-}$ reaction [4] leading to $NO^{\bullet}$ that scavenges $NO_2^{\bullet}$.

The latest reported K_{eq} has been obtained by fitting to a complex mechanism suggested by Strehlow and co-workers for flash photolysis of nitrate [3]. However, this mechanism has been recently completely revised [5]. It is also difficult to see how K_{eq} can be pH-dependent.

Recommended value:

$K_{eq} = (1.5 \pm 0.3) \times 10^{-5}$ M, at room temperature

List of auxiliary thermodynamic data: none

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Data Sheet 90

Chemical equilibrium: $NO^\bullet(g) \rightleftharpoons NO^\bullet(aq)$ (90.1)

List of reports:

$K_H = (1.95 \pm 0.06) \times 10^{-3}$ M/atm (1.93×10^{-2} M MPa^{-1}) at 25 °C, obtained from the equilibrium NO solubility near atmospheric pressure with the chemical analysis of dissolved $NO^\bullet$ [1].

$K_H = 1.92 \times 10^{-2}$ M MPa^{-1} at 25 °C, obtained from the volumetric determination of equilibrium $NO^\bullet$ solubility near atmospheric pressure [2]. The uncertainty appears to be less than 1%.

$K_H = (1.3 \pm 0.3) \times 10^{-2}$ M MPa^{-1} at 24 °C, obtained from the chemiluminescent evaluation of dissolved $NO^\bullet$ at low $NO^\bullet$ partial pressures in mixtures with other gases [3].

Discussion

The first two reported values are in excellent agreement. Quite possibly, even earlier original determinations not listed above exist in the literature. There are also several critical reviews that agree on the K_H value of $(1.93 \pm 0.06) \times 10^{-3}$ M/bar {*i.e.* 1.9×10^{-2} M MPa^{-1}} at 25 °C (see, *e.g.*, comprehensive tables and discussions in Wilhelm *et al.* [4], Schwartz and White [5], and Battino [6]). The last listed reported value is most likely less accurate, due to the less straight forward technique and the large scatter in the results, as admitted by the authors.

We thus adopt $K_H = (1.93 \pm 0.06) \times 10^{-3}$ M bar^{-1} {*i.e.* (1.93×10^{-2} M MPa^{-1}} at 25 °C. Because there is no more accurately determined equilibrium involving $NO^\bullet$, we use this K_H and the NBS $\Delta_f G° = +86.55$ kJ mol^{-1} for NO(g) to calculate $\Delta_f G°$ for $NO^\bullet(aq)$; the ± 0.20 kJ mol^{-1} standard error is that what has been assumed for the NBS number.

Recommended values:

$K_H = (1.93 \pm 0.06) \times 10^{-2}$ M MPa^{-1} at 25 °C.
$\Delta_f G° = +102.0 \pm 0.2$ kJ mol^{-1} for $NO^\bullet(aq)$.

List of auxiliary thermodynamic data: $\Delta_f G° = +86.55$ kJ/mol for $NO^\bullet(g)$ from the NBS tables [7].

Nomenclature: $NO^\bullet$, oxidonitrogen(•) or nitrogen monoxide; nitric oxide is outdated.

References

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Data Sheet 91

Chemical equilibrium: $NO_2^- + [Fe(TMP)_3]^{3+} \rightleftharpoons NO_2^\bullet + [Fe(TMP)_3]^{2+}$ (91.1)
(TMP = 3,4,7,8-tetramethyl-1,10-phenanthroline)

List of reports:

$1/K_{eq} = 2.6 \times 10^3$ (or $K_{eq} = 3.85 \times 10^{-4}$), at ~25 °C and unstated ionic strength [1]. This result was obtained from the ratio of the forward and reverse rate constants. The forward rate constant was measured by stopped-flow spectrophotometry [2], and the reverse by pulse radiolysis [1].

Discussion

The forward rate constant was determined at 25.0 °C and 0.3 M ionic strength and reported as $(3.94 \pm 0.09) \times 10^3$ M^{-1} s^{-1}. The reverse rate constant was obtained at room temperature (23 °C) and 0.005 M ionic strength, with k_r reported as $(1.0 \pm 0.3) \times 10^7$ M^{-1} s^{-1}. It is reasonable to anticipate that, within its error margins, k_r is insensitive to ionic strength, so the value of K_{eq} is $(3.9 \pm 1.2) \times 10^{-4}$ at 25 °C and $\mu = 0.3$ M. This uncertainty is determined largely by the uncertainty in k_r. Note that the value for K_{eq} derived from the published value of $1/K_{eq}$ deviates somewhat (but insignificantly) from the result given here because of some incorrect handling of significant figures in the original publication.

Potentiometric titration of $[Fe(TMP)_3]^{2+}$ with Ce(IV) in 0.3 M H_2SO_4 led to $E°' = +0.84$ V vs NHE for the Fe(III/II) couple [2]. This result leads to $E°' = +1.04$ V for $NO_2^\bullet(aq)/NO_2^-$ at $\mu = 0.3$ M. The presumed uncertainty is ± 0.01 V.

Recommended values:

$K_{eq} = (3.94 \pm 1.2) \times 10^{-4}$ at 25 °C and $\mu = 0.3$ M.
$E°'(NO_2^\bullet(aq)/NO_2^-) = +1.04 \pm 0.01$ V at 25 °C and $\mu = 0.3$ M.

List of auxiliary thermodynamic data: none.

Nomenclature: $NO_2^\bullet$, dioxidionitrogen(•), NO_2^-, dioxidonitrate(1−)

References

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Data Sheet 92

Chemical equilibrium: $NO_2^- + RNO^+ \rightleftharpoons NO_2^\bullet + RNO^\bullet$ (92.1)
($RNO^\bullet$ = TEMPO)

List of reports:

$1/K_{eq} = 8.8 \times 10^4$ at $\mu = 0.1$ M and 25 °C [1]. Result obtained from the rate constant for reduction of RNO^+ by NO_2^-, which is taken as $2(K_{eq})^2 k_{disp}$ and k_{disp} refers to the disproportionation of $NO_2^\bullet$. A literature value of 7.6×10^7 M^{-1} s^{-1} was used for k_{disp}.

$1/K_{eq} = 7 \times 10^4$ at $\mu = 0.02$ M and 25 °C [1]. Obtained from the kinetics of reduction of $C(NO_2)_4$ by $RNO^\bullet$ with $RNO^\bullet$ as the limiting reagent. In these reactions, NO_2^- inhibits the rates and causes the $RNO^\bullet$ concentration to attain a steady state. Analysis of the steady-state concentration leads directly to a value for $(k_1/k_{disp})^{1/2}/K_{eq}$. Use of literature values for k_{disp} and k_1 then lead to the reported value for K_{eq}. Here, k_1 is the second-order rate constant for oxidation of NO_2^- by $C(NO_2)_4$.

Discussion

Goldstein *et al.* mention that the forward and reverse rate constants obtained in the above-mentioned studies are incorrect, but the equilibrium constant is not compromised by these errors [2]. A more significant potential source of error is the uncertainty in k_{disp}. Reported values of k_{disp} range from 2.7×10^7 M^{-1} s^{-1} [3] to 1.0×10^8 M^{-1} s^{-1} [4]. Much of the range in k_{disp} arises from the various values used for the Henry's law constant for $NO_2^\bullet$, as is discussed in Data Sheet 93. Accordingly, we assign an uncertainty of a factor of 2 to K_{eq}. Given the small difference between the two determinations of K_{eq} at $\mu = 0.1$ M and 0.02 M, we make the approximation that the result also applies at $\mu = 0$ M.

Given our recommended $E°'$ for $TEMPO^{+/0}$ of +0.750 ± 0.005 V (Data Sheet S-7), the value of $E°$ given below is derived.

Recommended values:

$K_{eq} = 1.3 \times 10^{-5}$ within a factor of ± 2 at 25 °C and $\mu = 0.0$ M.
$E° = +(1.04 \pm 0.02)$ V for $NO_2^\bullet(aq) + e^- = NO_2^-$

List of auxiliary thermodynamic data: none

Nomenclature: See Data Sheet 91.

References

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2. S. Goldstein, A. Samuni, A. Russo. *J. Am. Chem. Soc.* **125,** 8364-8370 (2003).
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4. Y.-N. Lee, S. E. Schwartz. *J. Phys. Chem.* **85,** 840-848 (1981).

Data Sheet 93

Chemical equilibrium: $NO_2^{\bullet}(g) \rightleftharpoons NO_2^{\bullet}(aq)$ (93.1)

List of reports:

$K_H = (7.0 \pm 0.5) \times 10^{-3}$ M atm^{-1} {*i.e.* 6.9×10^{-2} M MPa^{-1} at 22 °C, obtained from the absorption kinetics of $NO_2^{\bullet}$ bubbled into a water column [1].

$K_H = 2.0 \times 10^{-2}$ M bar^{-1} {*i.e.* 2.0×10^{-1} M MPa^{-1} at 20 °C, obtained from the $NO_2^{\bullet}$ gas uptake measurement at 15 °C by Komiyama and Inoue [2] and later temperature-adjusted by Cheung and co-workers [3].

$K_H = (1.4 \pm 0.2) \times 10^{-2}$ M bar^{-1} {*i.e.* (1.4×10^{-1} M MPa^{-1} at 20 °C, obtained from the measurement of gas-phase $NO_2^{\bullet}$ uptake by water in a bubble train flow reactor [3].

$K_H = (5.5 \pm 0.6) \times 10^{-2}$ M atm^{-1} {*i.e.* (5.4×10^{-1} M MPa^{-1}} at 10 °C [4]. Obtained by bubbling $NO_2^{\bullet}$ into water.

$K_H = 1.2 \times 10^{-2}$ M atm^{-1} {*i.e.* 1.18×10^{-1} M MPa^{-1}}at 25 °C [5]. Obtained with a formula published by Chameides [6].

Discussion

The Henry's constant measurements for $NO_2^{\bullet}$ are complicated by the $NO_2^{\bullet}$ dimerization in both gas and aqueous phases and by its second-order hydrolysis

$$2\ NO_2^{\bullet} + H_2O \rightarrow HNO_2 + HNO_3 \quad (93.2)$$

that occurs with a bimolecular rate constant k, which is subject to significant uncertainty. As a result, most measurements could only provide a product $K_H k^{1/2}$. These products are fairly consistent across 4 studies and range from {(70 ± 9) to (106 ± 20) M$^{1/2}$ bar^{-1} s$^{-1/2}$} {*i.e* (700 to 1060) M$^{1/2}$ MPa^{-1} s$^{-1/2}$), as has been summarized by Cheung and co-workers [3]. Three of these measurements are within their experimental uncertainties. The Henry's law constant of Lee and Schwartz was obtained under relatively high $NO_2^{\bullet}$ concentrations, where dissolution and disproportionation are competitive. The other two measurements (of Cheung and coworkers and of Komiyama and Inoue) were obtained under conditions where the disproportionation could be neglected.

In 1983 Schwartz and White published a very thorough review on the dissolution on nitrogen oxides, including $NO_2^\bullet$ [7]. Figure 7 of their review is notable in conveying the various reports on the Henry's law constant for $NO_2^\bullet$, and it provides strong evidence from 6 different sources that the value lies between (6×10^{-3} and 2×10^{-2}) M atm^{-1} {*i.e.* 0.059 to 0.197 M MPa^{-1}}. After detailed consideration of the data in their Fig. 7, Schwartz and White conclude that K_H must lie between (0.7×10^{-2} and 1.3×10^{-2}) M atm^{-1} {*i.e.* 0.069 to 0.128 M MPa^{-1}}.

Cape *et al.* measured the solubility of $NO_2^\bullet$ at 10 °C [4]. Because of the significant temperature dependence of the solubility we prfer to rely on other data obtained at temperatures closer to 25 °C.

Mertes and Wahner [5] derived a value for K_H from the temperature-dependent equation given by Chameides [6]. Chameides, in turn, obtained his equation with data from the 1965 NBS tables. The current (1982) NBS tables do not provide data for $NO_2^\bullet(aq)$, so we infer that NBS decided that the old data were unreliable.

From this discussion, it appears safe to base our evaluation on $K_H = (1.4 \pm 0.2) \times 10^{-2}$ M/bar {*i.e.* 0.14 M MPa^{-1}} at 20 °C. The value for $K_H = (1.2 \pm 0.2) \times 10^{-2}$ M/bar {*i.e.* 0.12 M MPa^{-1}} at 25 °C can be obtained assuming a value for the heat of $NO_2^\bullet$ hydration; following Cheung and co-workers here we use –19 kJ mol^{-1} for this enthalpy of hydration (same as for O_3). This result is within the range recommended by Schwartz and White [7]. Combining this number with the NBS' $\Delta_f G° = +51.31$ kJ mol^{-1} for $NO_2^\bullet(g)$ and assuming ± 0.20 kJ mol^{-1} standard error in this value, we obtain $\Delta_f G° = +(62.3 \pm 0.5)$ kJ mol^{-1} for $NO_2^\bullet(aq)$.

Recommended values:

$K_H = (1.2 \pm 0.2) \times 10^{-2}$ M bar^{-1} at 25 °C {*i.e.* 0.12 ± 0.02 M MPa^{-1}}
$\Delta_f G° = +62.3 \pm 0.5$ kJ mol^{-1} for $NO_2^\bullet(aq)$ at 25 °C

List of auxiliary thermodynamic data: –19 kJ mol^{-1} for the enthalpy of hydration of O_3 [8]; $\Delta_f G° = +51.31$ kJ mol^{-1} for $NO_2^\bullet(g)$ from the NBS tables [9]. 1 bar = 0.987 atm.

Nomenclature: See Data Sheet 91.

References

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Data Sheet 94

Chemical equilibrium: $2HNO_2(aq) \rightleftharpoons NO^\bullet(aq) + NO_2^\bullet(aq) + H_2O$ (94.1)

List of reports:

$K_{eq} = 8.5 \times 10^{-8}$ at 22 °C and $\mu = 0.014$ M [1]. Park and Lee obtained this result from the steady-state gas-phase concentrations of HNO_2, $NO^\bullet$ and $NO_2^\bullet$ generated from an acidified HNO_2 solution under vigorous N_2 bubbling.

Discussion

Park and Lee did not actually report the value of K_{eq} cited above but rather gave the corresponding values for the forward and reverse rate constants, which, in turn, were derived from a complex expression describing the mixed kinetics of gas evolution in a system under dynamic purging. The equation used to derive the equilibrium constant uses the Henry's law constant for $NO_2^\bullet$, but the form of the equation is such that K_{eq} and H_{NO2} are not strictly correlated. Park and Lee also reported a ~10% uncertainty in the rate constants. The equilibrium constant is expected to be independent of ionic strength. Park and Lee also reported results at 10 and 30 °C, from which a pronounced temperature dependence of K_{eq} was demonstrated. From these data we interpolate $K_{eq} = (1.1 \pm 0.1) \times 10^{-7}$ at 25 °C and $\mu = 0$ M.

Recommended value:

$K_{eq} = (1.1 \pm 0.1) \times 10^{-7}$ at 25 °C and $\mu = 0$ M

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 91.

References

1. J.-Y. Park, Y.-N. Lee. *J. Phys. Chem.* **92,** 6294-6302 (1988).

Data Sheet 95

Chemical equilibrium: $2\ \mathrm{NO_2^{\bullet}}(aq) \rightleftharpoons \mathrm{HNO_2} + \mathrm{H^+} + \mathrm{NO_3^-}$ (95.1)

List of reports:

$K_{\mathrm{eq}} = (3.8 \pm 1.5) \times 10^9$ M at $\mu = 0$ and 25 °C. Result obtained by Schwartz and White [1] (1981) by evaluation of the potentiometric data of Vetter [2] (1949).

Discussion

Schwartz and White considered this equilibrium carefully, and there is little we can add to the discussion. There seems to be no direct measurements on this reaction published subsequent to Vetter’s.

Recommended value:

$K_{\mathrm{eq}} = (3.8 \pm 1.5) \times 10^9$ M at $\mu = 0$ and 25 °C

List of auxiliary thermodynamic data: none.

Nomenclature: See Data Sheet 91.

References

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Data Sheet 96

Chemical equilibrium: $PO_3^{\bullet 2-} + PenSH \rightleftharpoons HPO_3^{2-} + PenS^{\bullet}$ (96.1)

PenSH is penicillamine, (Pen = $-CMe_2-C(NH_2)H-CO_2^{-}$)

List of reports:

The equilibrium constant for reaction 96.1 was determined in a pulse radiolysis experiment in neutral, N_2O-saturated solutions by monitoring the yield of $PenS^{\bullet}$ at any concentration ratio HPO_3^{2-}/ PenSH [1]. The plot of $G(HO^{\bullet}) - G(PenS^{\bullet})/G(PenS^{\bullet})$ vs. this ratio yields the equilibrium constant as the slope. $G(HO^{\bullet})$ is obtained simply as the maximum $G(PenS^{\bullet})$. The result was $K_{96.1} = 8 \times 10^2$. No uncertainty was reported; inspection of the figure from which the equilibrium constant was derived suggests that $\pm 1 \times 10^2$ would be a conservative estimate.

The forward rate constant for this reaction was reported previously [2] as $k_f = 3.0 \times 10^8$ L mol^{-1} s^{-1}; this then leads to $k_r = 3.8 \times 10^5$ L mol^{-1} s^{-1}.

Discussion

In this Report, the potential for the couple $PenS^{\bullet}$, H^+/PenSH is reported to be +1.37 ± 0.03 V (Data Sheet S-8). Thus, the potential for the couple $PO_3^{\bullet 2-}$, H^+/ HPO_3^{2-} is $E^o = (1.37 \pm 0.03)$ V + 0.059 V $\log((8 \pm 1) \times 10^2) = +(1.54 \pm 0.04)$ V.

Recommended value:

$E^{\circ\prime}(PO_3^{\bullet 2-}, H^+/HPO_3^{2-}) = +(1.54 \pm 0.04)$ V

List of auxiliary thermodynamic data: none.

Nomenclature: $PO_3^{\bullet 2-}$, trioxidophosphate(•2−); HPO_3^{2-}, hydroxidodioxidophosphate(2−); penicillamine, (2*S*)-2-amino-3-methyl-3-sulfanylbutanoic acid

References

1. K. Schäfer, K.-D. Asmus. *J. Phys. Chem.* **85,** 852-855 (1981).
2. K. Schäfer, K.-D. Asmus. *J. Phys. Chem.* **84,** 2156-2160 (1980).

Data Sheet 97

Chemical equilibrium: $HO^{\bullet} + H_3PO_4 \rightleftharpoons H_2O + H_2PO_4^{\bullet}$ (97.1)

List of reports:

Forward and reverse rate constants were derived from a study of the pulse radiolysis of concentrated (3, 5, and 8) mol L^{-1} phosphoric acid solutions [1]. The sum of initially produced $HO^{\bullet}$ and $H_2PO_4^{\bullet}$ was obtained by allowing these radicals to react with Cl^- and measuring the yield of $Cl_2^{\bullet-}$, taking $\varepsilon_{340nm} = 8200$ L mol^{-1} cm^{-1}. The absorption coefficient of $H_2PO_4^{\bullet}$ at 520 nm was determined to be $\varepsilon_{520nm} = 1850$ L mol^{-1} cm^{-1} [2] , and the radicals were monitored at this wavelength. At these high phosphoric acid concentrations, a substantial fraction of the phosphate radical is formed as a direct result of the pulse. The subsequent build-up of absorbance at 520 nm reflects primarily a competition among the forward reaction above, other loss reactions of $HO^{\bullet}$, and the self-reaction of $H_2PO_4^{\bullet}$. Taking rate constants for critical reactions from the literature, and estimating rate constants for some less critical reactions, the authors modeled their results and concluded the rate constants for the forward and reverse reactions were, in 1 – 6 mol L^{-1} phosphoric acid: $k_f = (4.2 \pm 0.4) \times 10^4$ L mol^{-1} s^{-1} and $k_r = (2.5 \pm 0.2) \times 10^3$ L mol^{-1} s^{-1}.

From these, $K_{97.1} = 16.8$ (where the concentration of water is explicitly included).

(At 8 mol L^{-1} phosphoric acid, slightly lower rate constants were obtained.)

Discussion

From the equilibrium constant, $K_{97.1} = 16.8$, an electrode potential of +2.65 V was calculated, based on +2.72 V for $E°(HO^{\bullet},H^+/H_2O)$.

The reported reverse rate constant takes $[H_2O]$ = number of moles of water per liter of solution. But the correct procedure should be to take the standard state of water, 1 mol L^{-1}. As a first-order reaction, the reverse rate constant becomes $k_r = (1.4 \pm 0.1) \times 10^5$ s^{-1} and $K_{97.1} = (0.30 \pm 0.05)$ L mol^{-1}. If it is assumed that the value of $K_{97.1}$ is not significantly affected by the phosphoric acid concentration, this leads to the correct value of the standard potential: $E° = +2.72 - (0.059 \log 0.3) = +2.75 \pm 0.01$ V, with no uncertainty assumed in $E°(HO^{\bullet})$.

A much larger value of the forward rate constant, $k_f = 2.7 \times 10^6$ mol^{-1} s^{-1}, was reported at pH 0 by Grabner *et al.* [3]. This value does not seem consistent, however, with rate constants reported for the reaction of $HO^\bullet$ with $H_2PO_4^-$ (~2 × 10^4 L mol^{-1} s^{-1} [2]), HPO_4^{2-} (1.5 × 10^5 L mol^{-1} s^{-1} [2]), or with PO_4^{3-} (<1 × 10^7 L mol^{-1} s^{-1} [4]).

The existence of a reasonably fast reverse reaction is supported by the observation of O_2 generation in the continuous photolysis of peroxydiphosphate solutions [5].

Recommended value:

$E°(H_2PO_4^\bullet, H^+/H_3PO_4) = +(2.75 \pm 0.01)$ V

List of auxiliary thermodynamic data: none.

References

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Data Sheet 98

Couple: carbon dioxide/Dioxocarbonate(•1–)

List of reported equilibrium constants:

$$\mathrm{CO_2^{\bullet-} + Tl^+ \rightleftharpoons CO_2(aq) + Tl} \qquad (98.1)$$

Schwarz and Dodson, 1989 [1].
$K = 0.2$, after correction for μ (experimental conditions: $\mu = 0.05$ M, pH 3.7, room temperature). Combined with $E°(\mathrm{Tl^+/Tl°}) = -1.94$ V, estimated, and a K of 140 $\mathrm{M^{-1}}$ for the equilibrium $\mathrm{Tl° + Tl^+ \rightleftharpoons Tl_2^+}$, $E°'(\mathrm{CO_2(aq)/CO_2^{\bullet-}}) = -(1.90 \pm 0.01)$ V.

$$\mathrm{CO_2^{\bullet-} + RSH \rightleftharpoons HCO_2^- + RS^{\bullet}} \qquad (98.2)$$

Surdhar *et al.*, 1989 [2].
For the reactions with lipoamide (LS), penicillamine, and β-mercaptoethanol, equilibrium constants of 61 ± 15 (and 53 ± 20), 256 ± 30, and 2000 ± 250, respectively, were determined. Given electrode potentials $E°(\mathrm{RS^{\bullet}/RSH})$ of +1.43 V (for $E°[\mathrm{LS_2H^{\bullet}, H^+/ L(SH)_2}]$), +1.32 V and +1.33 V, respectively, the standard electrode potential of the couple $\mathrm{CO_2^{\bullet-}/HCO_2^-}$ was estimated at +(1.49 ± 0.03) V. With this value and $2E°(\mathrm{HCO_2^-/CO_2aq}) = -0.364$ V, the authors arrive at −(1.85 ± 0.06) V for $E°(\mathrm{CO_2aq/CO_2^{\bullet-}})$

Corrections:
The potentials involving penicillamine and β-mercaptoethanol were based on equilibria with the the chlorpromazine radical/chlorpromazine couple. The electrode potential of this couple has been revised (see Data Sheet S-9) and, based on these 0.03 V higher values and an independently revised lipoamide electrode potential ($E°[\mathrm{LS_2^{\bullet-}, 2H^+/ L(SH)_2}] = +(1.78 \pm 0.06)$ V, see Data Sheet S-10), the value of $E°(\mathrm{CO_2^{\bullet-}/HCO_2^-})$ changes to +1.52 V, and $E°(\mathrm{CO_2aq/CO_2^{\bullet-}})$ from −1.85 V to −1.89 V. The error is estimated at 0.06 V.

Recommended values: Given the excellent agreement between the two determinations,

$E°'(\mathrm{CO_2(aq)/CO_2^{\bullet-}}) = -(1.90 \pm 0.02)$ V
$\Delta_f G°(\mathrm{CO_2^{\bullet-}}) = -(205 \pm 2)\ \mathrm{kJ\ mol^{-1}}$, see also Data Sheet 100.

List of auxiliary thermodynamic data.

Koppenol and Rush [3] estimated a standard potential of –(1.84 ± 0.22) V based on the electron affinity of carbon dioxide and an solvation Gibbs energy for $CO_2^{\bullet-}$ assumed to be similar to those of other triatomic anions. Older literature values are discussed there. The Gibbs energy of formation of −205 kJ mol^{-1} was also derived by Yu *et al.* [4].

Nomenclature: CO_2, dioxidocarbon, carbon dioxide is allowed; $CO_2^{\bullet-}$, dioxidocarbonate(•–); HCO_3^-, hydroxidodioxidocarbonate(1–); Tl^+, thallium(+); Tl^{2+}, dithallium(+)

References

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4. D. Yu, A. Rauk, D. A. Armstrong. *J. Chem. Soc., Perkin Trans. 2* 2207-2215 (1994).

Data Sheet 99

Couple: trioxocarbonate(•1–)/trioxocarbonate(2–)

List of reported equilibrium constants:

Chemical equilibrium: $Br_2^{\bullet-} + CO_3^{2-} \rightleftharpoons 2Br^- + CO_3^{\bullet-}$ (99.1)

Huie *et al.* [1].

$K = (3.2 \pm 0.7)$ ($\mu = 3$ M, pH 12.0), $\Delta E = 0.030 \pm 0.006$ V.

Based on Reaction 99.1 and $E°(Br_2^{\bullet-}/2Br^-) = +(1.625 \pm 0.02)$ V [2] (see Data Sheet 26), $E^{\circ\prime}(CO_3^{\bullet-}/ CO_3^{2-}) = +(1.59 \pm 0.02)$ V.

Chemical equilibrium: $CO_3^{\bullet-} + 2SCN^- \rightleftharpoons CO_3^{2-} + (SCN)_2^{\bullet-}$ (99.2)

Lymar *et al.*, 2000 [3].

$K = (1.5 \pm 0.3) \times 10^4$ M^{-1} and $(2.1 \pm 0.2) \times 10^4$ M^{-1} at 0.5 M and 1.5 M ionic strength, respectively. Based on these equilibrium constants $E^{\circ\prime}(CO_3^{\bullet-}/CO_3^{2-})$ is 0.25 V higher than $E^{\circ\prime}((SCN)_2^{\bullet-}/2SCN^-)$. The authors have noted that this difference can be somewhat smaller at low ionic strength, as the electrolyte would tend to stabilize CO_3^{2-} the most. Given $E^{\circ\prime}((SCN)_2^{\bullet-}/2SCN^-) = +1.30$ V (see Data Sheet 101), $E^{\circ\prime}(CO_3^{\bullet-}/CO_3^{2-}) = +1.55$ V.

Chemical equilibrium: $CO_3^{\bullet-} + ClO^- \rightleftharpoons CO_3^{2-} + ClO^{\bullet}$ (99.3)

Huie *et al.* [1].

$K = (9.5 \pm 3.0) \times 10^2$ ($\mu = 3.0$ M, pH 12.2, 22.2 °C), $\Delta E = (0.176 \pm 0.010)$ V.

Comments: The equilibrium constant for reaction 99.1 is the average of (3.3 ± 0.3), derived from the absorbance at 360 nm ($Br_2^{\bullet-}$) at equilibrium and of (3.1 ± 0.5) from the rate constants for the decay of $Br_2^{\bullet-}$ to its equilibrium value. The error in the assessment of the $Br_2^{\bullet-}/2Br^-$ electrode potential determines that in $E^{\circ\prime}(CO_3^{\bullet-}/ CO_3^{2-})$. The difference of 0.04 V between two careful measurements may be due to medium effects. The $E^{\circ\prime}$ value derived in this way involves combining data at various ionic strengths and thus is not very well defined.

The standard electrode potential of the $ClO^{\bullet}/ClO^{-}$ couple is not known precisely enough to determine $E^{\circ}(CO_3^{\bullet-}/CO_3^{2-})$; in fact the value of +1.59 V is used to estimate $E^{\circ}(ClO^{\bullet}/ClO^{-})$ [1].

Recommended values:

$E^{\circ\prime}(CO_3^{\bullet-}/CO_3^{2-}) = +(1.57 \pm 0.03)$ V
$\Delta_f G^{\circ}(CO_3^{\bullet-}) = -(89.1 \pm 0.8)$ kcal mol^{-1}, or $-(373 \pm 3)$ kJ mol^{-1}

List of auxiliary thermodynamic data

Based on a review of earlier literature Stanbury proposed a value of +1.5 V [2]. In an *ab initio* study, Armstrong *et al.* [4] suggest a value of +(1.23 ± 0.15) V. While not as accurate as the two experimentally derived values, this result is impressive for an *ab initio* calculation.

Chemical equilibrium: $HCO_3^{\bullet} \rightleftharpoons H^+ + CO_3^{\bullet-}$ (99.4)

Czapski *et al.* [5].

A pK_a smaller than 0 has been determined [5], as expected for a $HOXO_2$ acid.

Recommended value:

Except that pK_a is negative, no numerical recommendation can be made.

Auxiliary thermodynamic data: Earlier pK_a estimates of 9.6 and 7.0 – 8.2 are discussed by Czapski *et al.* [5]. A recent value of 9.5 [6] was shown to be in error [3]. The result of an *ab initio* calculation [4], −4.1, also does not support the $pK_a \geq 7$ values.

References

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Data Sheet 100

Dioxidocarbonate(•1−)/hydrogendioxidocarbonate(1−)

$$\mathrm{CO_2^{\bullet-} + HSLSH \rightleftharpoons HCO_2^- + HSLS^{\bullet}} \qquad (100.1)$$

Surdhar *et al.* [1].
HSLSH is dihydrolipoamide ($\mathrm{HS\text{-}CH_2\text{-}CH_2\text{-}C(SH)H\text{-}(CH_2)_4\text{-}CONH_2}$). $K = 61 \pm 15$, and 53 ± 20 from kinetic data, at pH 4 and 10 mM formate. $\Delta_{\mathrm{rxn}}G^\circ = -(10 \pm 1)$ kJ mol^{-1}. Given $E^\circ(\mathrm{SLS^{\bullet-}/HSLSH}) = +1.75$ V [2] and a pK_a of 5.5 for HSLSH, $E^\circ(\mathrm{CO_2^{\bullet-}/HCO_2^-}) = +1.52$ V.

$$\mathrm{CO_2^{\bullet-} + PenSH \rightleftharpoons HCO_2^- + PenS^{\bullet}} \qquad (100.2)$$

Surdhar *et al.* [1].
PenSH is penicillamine (Pen = $\mathrm{\text{-}CMe_2\text{-}C(NH_2)H\text{-}CO_2^-}$). $K = (256 \pm 3)$ at pH 6 and 100 mM formate. $\Delta_{\mathrm{rxn}}G^\circ = -(13.6 \pm 0.3)$ kJ mol^{-1}. Given $E^\circ(\mathrm{PenS^{\bullet-}/PenSH}) = +1.32$ V [2], $E^\circ(\mathrm{CO_2^{\bullet-}/HCO_2^-}) = +1.46$ V.

$$\mathrm{CO_2^{\bullet-}} + \beta\text{-}\mathrm{RSH} \rightleftharpoons \mathrm{HCO_2^-} + \beta\text{-}\mathrm{RS^{\bullet}} \qquad (100.3)$$

Surdhar *et al.* [1].
β-RSH is β-mercaptoethanol ($\mathrm{HOCH_2CH_2SH}$). $K = (2000 \pm 250)$ at pH 3 and 0.1 M to 0.3 M formate. $\Delta_{\mathrm{rxn}}G^\circ = -(13.6 \pm 0.3)$ kJ mol^{-1}. Given $E^\circ(\beta\text{-}\mathrm{RS^{\bullet}}/\beta\text{-}\mathrm{RSH}) = +1.33$ V [2], $E^\circ(\mathrm{CO_2^{\bullet-}/HCO_2^-}) = +1.48$ V.

Discussion

The above three reactions are symmetric with respect to reactant and product charges, and thus the equilibrium constants are expected to be minimally affected by ionic strength. For this reason, the derived electrode potentials can be considered to be E° rather than $E^{\circ\prime}$ values. Given the uncertainty in the determination of the standard electrode potentials of the used substituted sulfanyl/sulfane couples, Surdhar *et al.* [1] calculate an average of $+(1.49 \pm 0.06)$ V for $E^\circ(\mathrm{CO_2^{\bullet-}, H^+/HCO_2^-})$. This value can be corrected, given a new evaluation of the chlorpromazine electrode potential (see Data Sheet S-9) which was the reference electrode potential for Reactions 100.2 and 100.3, and a new evaluation of the lipoamide electrode potential (see Data Sheet S-10). On average, the electrode potential of the used substituted sulfanyl/sulfane couples increased by 0.03 V, which yields +(1.52 ± 0.06) V for $E°(CO_2^{\bullet-}, H^+/HCO_2^-)$, see evaluation of $E°(CO_2aq/CO_2^{\bullet-})$ (Data Sheet 98).

Recommended value:

$E°(CO_2^{\bullet-}, H^+/HCO_2^-) = +(1.52 \pm 0.03)$ V.

$$HCO_2^{\bullet} \rightleftharpoons H^+ + CO_2^{\bullet-} \text{ (or } COOH^{\bullet} \rightleftharpoons H^+ + CO_2^{\bullet-}) \qquad (100.4)$$

Fojtik *et al.*, 1970 [3].
$pK_a = (3.0 \pm 0.3)$

Buxton and Sellers, 1973 [4].
$pK_a = 1.4$

Jeevajaran *et al.*, 1990 [5].
$pK_a = -(0.2 \pm 0.1)$

Flyunt *et al.*, 2001 [6].
$pK_a \sim 2.3$

Discussion

Flyunt *et al.* [6] report that the Buxton and Sellers [4] result was an artifact. They also argue that the result of Jeevarajan *et al.* [5] should be attributed to the protonation of $COOH^{\circ}$. Flyunt *et al.* [6] are at a loss to explain the discrepancy between their result and that of Fojtik *et al.* [3].

This pK_a is interpreted by Loeff *et al.* [7] to correspond to the species $^{\bullet}COOH$. The Gibbs energy for the conversion of $^{\bullet}COOH$ to $HCO_2^{\bullet}$ is estimated at larger than 0.6 eV. Given the data of Jeevarajan *et al.* [5], a resemblance in the UV-spectra of HCO_2^- and Cl^-, and a coMParison with electrode potentials of alkylperoxyl/alkylperoxide couples, a standard electrode potential of > 2.4 V is suggested for $HCO_2^{\bullet}/HCO_2^-$ [7]. Rauk and Armstrong calculate, with *ab initio* methods, a potential of +2.3 V for this couple, and +2.5 V for $E°(HCO_2^{\bullet}/HCO_2H)$ [8]. Flyunt *et al.* [6] are in agreement with the interpretation that $CO_2^{\bullet-}$ protonates preferentially on one of its oxygen atoms rather than carbon. We accept this interpretation and recommend a pK_a for $COOH^{\bullet}$ that is the average of the results of Fojtik *et al.* [3] and Flyunt *et al.* [6].

Recommended value:

pK_a = (2.6 ± 0.3) for $COOH^{\bullet} \rightleftharpoons H^+ + CO_2^{\bullet-}$

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Data Sheet 101

Chemical equilibrium: $SCN^{\bullet} + SCN^{-} \rightleftharpoons (SCN)_2^{\bullet -}$ (101.1)

List of reported equilibrium constants:

Baxendale *et al.*, 1968 [1].
Thiocyanate was oxidized by hydroxyl radicals generated by pulse radiolysis. The equilibrium constant is 2.0×10^5 M^{-1} at both pH 2 and 7. Forward and backward rate constants are 7.0×10^9 M^{-1} s^{-1} and 3.4×10^4 s^{-1}, respectively at 22.0 °C. Ionic strength not stated. Given uncertainties of 10% in each rate constant, an error of 0.3×10^5 M^{-1} is estimated.

Baxendale and Bevan, 1969 [2].
Temperature study (22 – 88) °C; the authors use for 22 °C data from previous paper [1]. We interpolate the value of K at 25 °C from a ln$K$ vs. 1/T graph: $K = 1.99 \times 10^5$ M^{-1}.

Elliot and Sopchyshyn, 1984 [3].
Temperature study (10 -90) °C; reports $K = 1.08 \times 10^5$ M^{-1} at 22 °C. Conditions: pH 7 implied, concentrations of SCN^{-} between 0.1 mM and 100 mM. Regarding the difference with the results obtained by Baxendale and coworkers [1, 2], the authors state: "No explanation can be given for this difference…"

Chin and Wine, 1992 [4].
Hydroxyl radicals were generated by flash photolysis of hydrogen peroxide. $K = (2.2 \pm 0.3) \times 10^5$ M^{-1} at 297 K. Forward and backward rate constants are $(6.9 \pm 0.7) \times 10^9$ M^{-1} s^{-1} and $(3.09 \pm 0.25) \times 10^4$ s^{-1}, respectively. Ionic strength is below mM. The pH was not stated, and no buffer was used.

Lymar *et al.*, 2000 [5].
Forward rate constant taken from Nagarajan and Fessenden [6], 9×10^9 M^{-1} s^{-1} combined with 4.2×10^4 s^{-1} at 0.5 M ionic strength, yields $K = 2.1 \times 10^5$ M^{-1}.

Wu *et al.*, 2001 [7].
Temperature study (25 – 400) °C; reports $K = 1 \times 10^5$ M^{-1} at 25 °C. The Van 't Hoff plot shows good agreement with results obtained by Elliot and Sopchyshyn [3].

Recommendation: The choice, in essence, is between $(1 \times 10^5$ and $2 \times 10^5)$ M^{-1} s^{-1} at 25 °C. Given the excellent agreement between an experimental and a simulated increase of absorbance at 472 nm of the $(SCN)_2^{\bullet-}$ radical obtained by Milosavljevic and LaVerne [8], $K_{101.1} = (2.0 \pm 0.3) \times 10^5$ M^{-1} s^{-1} at 25 °C. The standard Gibbs energy of Reaction 101.1 is −(30.3 ± 0.5) kJ. Given the charge-type of reaction 101.1 it is reasonable to expect that the *K* value is independent of ionic strength. Consequently, $E°(SCN^{\bullet}/SCN^-)$ is (314 ± 5) mV higher than $E°((SCN)_2^{\bullet-}/2SCN^-)$.

Chemical equilibrium: $BrSCN^{\bullet-} + SCN^- \rightleftharpoons (SCN)_2^{\bullet-} + Br^-$ (37.1)

List of reported equilibrium constants:

Schöneshofer and Henglein, 1970 [9].

$K = 10^{-3}$. Conditions: 0.3 M to 1.0 M ionic strength, no buffer, pH not known, no estimate of error.

Chemical equilibrium: $BrSCN^{\bullet-} + Br^- \rightleftharpoons Br_2^{\bullet-} + SCN^-$ (36.1)

List of reported equilibrium constants:

Schöneshofer and Henglein, 1970 [9].

$K = 1.1 \times 10^2$. Conditions: 10 mM ionic strength, no buffer, pH not known, no estimate of error.

Reactions 37.1 and −36.1 can be added to yield:

Chemical equilibrium: $Br_2^{\bullet-} + 2SCN^- \rightleftharpoons (SCN)_2^{\bullet-} + 2Br^-$ (101.2)

with $K_{37.1}\, K_{-36.1} = 9 \times 10^{-6}$. This equilibrium constant is expected to be minimally affected by ionic strength, given the ionic charge distribution. It leads to a difference in electrode potential between $E°(Br_2^{\bullet-}/Br^-)$ and $E°((SCN)_2^{\bullet-}/2SCN^-)$ of 298 mV (see also Data Sheet 26). Given estimated errors of 15% in $K_{37.1}$ and $K_{36.1}$, the electrode potential difference has an uncertainty of 7 mV.

Chemical equilibrium: $ISCN^{\bullet-} + SCN^- \rightleftharpoons (SCN)_2^{\bullet-} + I^-$ (55.1)

List of reported equilibrium constants:

Schöneshofer and Henglein, 1970 [9].

$K = 2.5 \times 10^{-3}$. Conditions: 0.3 M to 1.0 M ionic strength, no buffer, pH not known, no estimate of error.

Chemical equilibrium: $ISCN^{\bullet-} + I^- \rightleftharpoons I_2^{\bullet-} + SCN^-$ (56.1)

List of reported equilibrium constants:

Schöneshofer and Henglein, 1970 [9].

$K = 55$. Conditions: 10 mM ionic strength, no buffer, pH not known, no estimate of error.

Reactions 55.1 and −56.1 can be added to yield:

Chemical equilibrium: $I_2^{\bullet-} + 2SCN^- \rightleftharpoons (SCN)_2^{\bullet-} + 2I^-$ (101.3)

with $K_{55.1}\, K_{-56.1} = 4.55 \times 10^{-5}$. Given the ionic charges involved, this equilibrium constant is expected to be minimally dependent on ionic strength. It leads to a difference in electrode potential between $E°(I_2^{\bullet-}/2I^-)$ and $E°(SCN)_2^{\bullet-}/2SCN^-)$ of 257 mV. [see also the evaluation of $E°(I_2^{\bullet-}/2I^-)$, Data Sheet 45]. Given estimated errors of 15% in $K_{55.1}$ and $K_{56.1}$, the electrode potential difference has an uncertainty of 7 mV.

Chemical equilibrium: $TrpH^{\bullet+} + 2SCN^- \rightleftharpoons (SCN)_2^{\bullet-} + TrpH$ (101.4)

Posener *et al.*, 1976 [10].

$K = 0.0125\ \mathrm{M}^{-1}$ at low pH and high ionic strength. The conditions are not clearly stated. The same study gives the pK_a of $\mathrm{TrpH}^{\bullet+}$ as 4.3.

Chemical equilibrium: $\mathrm{TrpH}^{\bullet+} + \mathrm{SCN}^- \rightleftharpoons \mathrm{SCN}^\bullet + \mathrm{TrpH}$ (101.5)

Posener *et al.*, 1976 [10].

$K = 6.3 \times 10^{-8}$ at low pH and high ionic strength. The conditions are not clearly stated. The equilibrium constant was obtained by combining the measured equilibrium constant for reaction 101.4 and a literature value of $2.0 \times 10^{-5}\ \mathrm{M}^{-1}$ for reaction 101.1.

Chemical equilibrium: $(\mathrm{SCN})_2^{\bullet-} + \mathrm{Os(bpy)}_3^{2+} \rightleftharpoons 2\mathrm{SCN}^- + \mathrm{Os(bpy)}_3^{3+}$ (101.6)

Nord *et al.*, 1982 [11].

Forward and backward rate constants are $(2.8 \pm 0.2) \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $(25 \pm 5)\ \mathrm{M}^{-2}\ \mathrm{s}^{-1}$, respectively. Thus, $K = (1.1 \pm 0.2) \times 10^8$ M at 22 °C and 0.1 M ionic strength. The pH for the forward reaction was 3, and the hydron concentration for the backward reaction was 0.5 M, although the ionic strength was reported as 0.1 M! Given $E°'(\mathrm{Os(bpy)}_3^{3+}/ \mathrm{Os(bpy)}_3^{2+}) = +0.857 \pm 0.004$ V at $\mu = 0.1$ M and 22 °C [11], $E°'((\mathrm{SCN})_2^{\bullet-}/2\mathrm{SCN}^-)$ is $+(1.331 \pm 0.008)$ V at $\mu = 0.1$ M.

Chemical equilibrium: $(\mathrm{SCN})_2^{\bullet-} + \mathrm{Ru(bpy)}_3^{2+} \rightleftharpoons 2\mathrm{SCN}^- + \mathrm{Ru(bpy)}_3^{3+}$ (101.7)

DeFelippis *et al.*, 1990 [12].

$K = (1.69 \pm 0.30)$ M at 0.02 M ionic strength. Determined $E°'(\mathrm{Ru(bpy)}_3^{3+}/\mathrm{Ru(bpy)}_3^{2+}) = +1.28$ V, at 25 °C, 0.1 M ionic strength and pH 7. With this electrode potential and the equilibrium constant a value for $E°'((\mathrm{SCN})_2^{\bullet-}/2\mathrm{SCN}^-)$ was calculated as $+(1.29 \pm 0.01)$ V. A value for $E°(\mathrm{SCN}^\bullet/\mathrm{SCN}^-)$ of +1.61 V was calculated by use of a literature value for $K_{101.1}$.

Chemical equilibrium: $\mathrm{CO}_3^{\bullet-} + 2\mathrm{SCN}^- \rightleftharpoons \mathrm{CO}_3^{2-} + (\mathrm{SCN})_2^{\bullet-}$ (99.2)

Lymar *et al.*, 2000 [5].
$K = 2.3 \times 10^4\ \mathrm{M}^{-1}$ near pH 11 and high (1.5 M) ionic strength; $K = 1.7 \times 10^4\ \mathrm{M}^{-1}$ near pH 11 and 0.5 M ionic strength. Experiments performed at 25 °C (Lymar, personal communication). Values obtained by both measuring the position of equilibrium and from the ratio of the forward and reverse rate constants.

Chemical equilibrium: $CO_3^{\bullet -} + SCN^- \rightleftharpoons CO_3^{2-} + SCN^\bullet$ (101.8)

Lymar *et al.*, 2000 [5].
$K = 0.08$ near pH 11 and high (0.5 M) ionic strength. Value obtained by combining the measured equilibrium constants for reactions 99.2 and 101.1. From this equilibrium constant $E°'(CO_3^{\bullet -}/CO_3^{2-})$ is 0.06 V lower than $E°'(SCN^\bullet/SCN^-)$. Given the reevaluation of $E°'(CO_3^{\bullet -}/CO_3^{2-})$, +(1.57 ± 0.03) V (Data Sheet 99), $E°'(SCN^\bullet/SCN^-) = +(1.63 \pm 0.03)$ V.

Indirect determinations and estimates of *E*°(SCN•/SCN⁻)

Sarala *et al.*, 1980 [13].

Based on $E°(I^\bullet/I^-) = +1.33$ V (assumed), $E°(SCN^\bullet/SCN^-)$ is recalculated from the energetics of I – SCN-equilibria determined by Schöneshöfer and Henglein [9]. The result is +1.60 V for $E°'(SCN^\bullet/SCN^-)$.

Butler *et al.*, 1982 [14].

Literature calculation:

$I^- + SCN^\bullet \rightleftharpoons ISCN^{\bullet -}$ $K = 1/(1.3 \times 10^{-8}\ \mathrm{M})$ [9]
$ISCN^{\bullet -} \rightleftharpoons SCN^- + I^\bullet$ $K = 4.8 \times 10^{-4}$ M [9]
$I^\bullet + e^- \rightleftharpoons I^-$ $E° = +1.3$ V [15]

The sum of these three equations leads to $E°'(SCN^\bullet/SCN^-) = +1.56$ V, and, consequently, $E°'((SCN)_2^{\bullet -}/2SCN^-) = +1.25$ V. The authors indicate an error of 0.22 V.

Schwarz and Bielski, 1986 [16].

From the kinetics of the reaction of $HO_2^{\bullet}$ with I_2 at $\mu = 1$ M and a value of 1.1 kcal mol^{-1} (4.6 kJ mol^{-1}) for $\Delta_f G°$ of $HO_2^{\bullet}$ these authors determined a standard Gibbs energy of formation of $I_2^{\bullet-}$ of −0.9 kcal mol^{-1} (−3.8 kJ mol^{-1}). Via reactions 55.1 and 56.1 they arrive at $\Delta_f G°(SCN)_2^{\bullet-} = +74.0$ kcal mol^{-1} (+310 kJ mol^{-1}), $E°'((SCN)_2^{\bullet-}/2SCN^-) = +1.31$ V, and $E°'(SCN^{\bullet}/SCN^-) = +1.62$ V. These potential are approximate because of the various ionic strengths used in their derivation.

Merényi *et al.*, 1988 [17].

From the kinetics of the reaction of $ClO_2^{\bullet}$ with tryptophan, the authors derive a value of 1.08 ± 0.02 V for $E°'(trp^{\bullet}/trpH)$ at pH 7. With an equilibrium constant of 6.3×10^{-8} for reaction 101.5 ($TrpH^{\bullet+}/SCN^-$) determined by Posener *et al.* [10], see above, there is a 426 mV difference between $E°(trpH^{\bullet+}/trpH)$ and $E°(SCN^{\bullet}/SCN^-)$. Given a pK_a of 4.3 of $TrpH^{\bullet+}$, this leads to $E°'(SCN^{\bullet}/SCN^-) = +1.67$ V, although the authors list +1.66 ± 0.02 V. More recent investigations of the $TrpH^{\bullet+}/TrpH$ couple indicate that its potential is ~0.05 V lower (see Supplementary Data Sheet S-12.

Discussion

There are only two direct determinations (the reactions with $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$) [11, 12] of which the one by Nord *et al.* [11] is based on a rather large equilibrium constant under uncertain ionic strength conditions. We therefore give more weight to the determination by DeFelippis *et al.* [12]. Unfortunately, the results from DeFelippis *et al.* were obtained by combining data at differing ionic strengths; we consider that accurate correction of the values to the same ionic strength would be unreliable. As a result, the derived potentials are $E°'$ values at an undefined ionic strength. Fortunately and surprisingly, the indirect determinations yield values that are very similar.

A consistency test can be performed by considering the equilibrium constants for the following reactions:

$$BrSCN^{\bullet-} + SCN^- \rightleftharpoons (SCN)_2^{\bullet-} + Br^- \qquad (37.1)$$
$$BrSCN^{\bullet-} + Br^- \rightleftharpoons Br_2^{\bullet-} + SCN^- \qquad (36.1)$$
$$Br_2^{\bullet-} + CO_3^{2-} \rightleftharpoons 2Br^- + CO_3^{\bullet-} \qquad (99.1)$$

$$CO_3^{\bullet-} + 2SCN^- \rightleftharpoons CO_3^{2-} + (SCN)_2^{\bullet-} \qquad (99.2)$$

This leads to $K_{99.1}/(K_{37.1}K_{36.1}) = 3.4 \times 10^4$ M^{-1}, which is equivalent to the equilibrium constant for reaction 99.2. The directly-measured value for $K_{99.2}$ is 2.3×10^4 M^{-1}, which demonstrates excellent self-consistency.

Recommended values:

$E°'(SCN^{\bullet}/SCN^-) = +(1.61 \pm 0.02)$ V
$E°'((SCN)_2^{\bullet-}/2SCN^-) = +(1.30 \pm 0.02)$ V
$\Delta_f G°(SCN^{\bullet}) = +248 \pm 2$ kJ mol^{-1}
$\Delta_f G°(SCN)_2^{\bullet-} = +310 \pm 2$ kJ mol^{-1}

Nomenclature: SCN^-, nitridosulfidocarbonate(1−), thiocyanate is allowed; $SCN^{\bullet}$, nitridosulfidocarbon(•); $(SCN)_2^{\bullet-}$, bis(nitridosulfidocarbonate)(*S*–*S*)(•1−); $ISCN^{\bullet-}$, (iodosulfato)nitridocarbonate(•1−)

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Data Sheet 102

Chemical equilibrium: $HgCl_2(aq) + MV^{\bullet+} \rightleftharpoons HgCl(aq) + Cl^- + MV^{2+}$ (102)
(MV^{2+} = methyl viologen)

List of reports:

$1/K_{eq} = 2.5$, presumably at room temperature, with 0.05 M Cl^- and an unspecified concentration of phosphate buffer at pH ~ 6 [1]. Result obtained by pulse radiolysis, measuring the equilibrium absorbance of $MV^{\bullet+}$. The reported equilibrum constant (2.5) is actually for the reaction when written as $Hg(I) + MV^{2+} \rightleftharpoons Hg(II) + MV^{\bullet+}$, and thus is dependent on the chloride concentration.

Discussion

The authors convert the conditional equilibrium constant into a conditional electrode potential of –0.47 V (at 0.05 M Cl^-) by use of $E° = –0.45$ V for $MV^{2+}/MV^{\bullet+}$. They then derive a formal potential of –0.55 V for $HgCl_2(aq) + e^- \rightleftharpoons HgCl(aq) + Cl^-$. This potential is expected to be dependent on ionic strength, but without knowledge of the ionic strength employed we are unable to estimate the magnitude of the correction. Given the uncertainties about the speciation of Hg(I), the uncertainty in the formal potential must be at least 20 mV.

The authors then use solvation energy estimates to derive $E° < –2.0$ V for Hg^{2+}/Hg^+, but we consider this outcome to be contrary to expectations based on stability constant estimates: chloride should stabilize Hg(II) more than Hg(I) and thus $E°(Hg^{2+}/Hg^+)$ is expected to be positive of $E°(HgCl_2/HgCl, Cl^-)$.

Recommended value:

$E°' = –(0.55 \pm 0.02)$ V for $HgCl_2(aq) + e^- \rightleftharpoons HgCl(aq) + Cl^-$

List of auxiliary thermodynamic data: none.

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Data Sheet 103

$E°(NO_3^•(aq)/NO_3^-)$

Published reports:

The electrode potential $E°(NO_3^•/NO_3^-)$ has been evaluated by two methods:

a) Through the estimation of the Gibbs energy of formation of $NO_3^•$ in the gas phase and in water. In chronological order: $E°$ = +2.3 ± 0.1 V [1]; 1.9 V [2]; 2.28 V [3]; 2.49 V [4].

b) From the positions of three equilibria with other radicals:

$HO^• + HNO_3(aq) \rightleftharpoons H_2O + NO_3^•(aq)$ (104.1)

$E°'$ = +2.67 V [5]; $E°'$ = +(2.48 ± 0.01) V [6]; $E°'$ = +(2.58 ± 0.02) V [7].

$SO_4^{•-} + NO_3^- \rightleftharpoons SO_4^{2-} + NO_3^•(aq)$ (14.1)

$E°'$ = +(2.45 ± 0.05) V [8].

$NO_3^•(aq) + Cl^- \rightleftharpoons NO_3^- + Cl^•(aq)$ (16.1)

$E°'$ = +(2.47 ± 0.01) V [7].

Discussion

Historically, the thermodynamicchemical estimates preceded the equilibrium data. These estimates have been reviewed by Stanbury [4] and are not considered or discussed here. We only note a large spread in the $E°$ values obtained by that method, although some of them come close to the recommended value given below.

The electrode potentials for reference radicals and the literature reports on their equilibria with $NO_3^•$ have been individually assessed in this work. The following values are recommended:

$K_{104.1}$ = none (see Data Sheet 104).

Accordingly, all $E°(NO_3^•/NO_3^-)$ reported from this equilibrium are to be considered unreliable.

$K_{14.1}$ = (0.28 ± 0.1) at μ = 0 M; $E°(SO_4^{•-}/SO_4^{2-})$ = +(2.43 ± 0.02) V (see Data Sheet 14)

From these values, $E°(NO_3^•/NO_3^-)$ = +(2.46 ± 0.02) V.

$K_{16.1}$ = (3.33 ± 0.24) at μ = 0 M; $E°(Cl^•/Cl^-)$ = +(2.43 ± 0.02) V (see Data Sheet 16)

From these values, $E°(NO_3^•/NO_3^-)$ = +2.46 ± 0.02 V.

Excellent agreement between the last two evaluations gives significant confidence in the result.

The electrode potential $E°(NO_3^•, H^+/HNO_3)$ = +(2.39 ± 0.02) V can be calculated from the equilibrium evaluated in this work:

$SO_4^{•-} + HNO_3 \rightleftharpoons HSO_4^- + NO_3(aq)$ (15.1)

$K_{15.1} = (5 \pm 2) \times 10^2$, and

$pK_a(HSO_4^-)$ = 1.96 [9].

The latest printed NBS tables [10] give an erroneous value for $\Delta_f G°(NO_3^-)_{aq}$, while the previous version contains the correct value of −111.3 kJ mol^{-1} [11, 12]. With this value, $E°(NO_3^•/NO_3^-)$ = +(2.46 ± 0.02) V corresponds to $\Delta_f G°(NO_3^•)_{aq}$ = +(126 ± 2) kJ mol^{-1}. Accepting $K_a(HNO_3)$ = 20 M [13], we calculate $E°(NO_3^•, H^+/HNO_3)$ = +2.38 V, which is within the uncertainty of the estimate based on $K_{3.21}$.

Recommended values:

$NO_3^•(aq) + e^- \rightleftharpoons NO_3^-(aq)$ $E°$ = +(2.46 ± 0.02) V
$NO_3^•(aq) + H^+ + e^- \rightleftharpoons HNO_3(aq)$ $E°$ = +(2.39 ± 0.02) V
$NO_3^•$(aq) $\Delta_f G°$ = +(126 ± 2) kJ mol^{-1}

Nomenclature: $NO_3^•$, trioxidonitrogen(•), NO_3^-, trioxidonitrate(1−), nitrate is acceptable.

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7. G. A. Poskrebyshev, R. E. Huie, P. Neta. *J. Phys. Chem. A* **107,** 1964-1970 (2003).
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13. O. Redlich, R. W. Duerst, A. Merbach. *J. Chem. Phys.* **49,** 2986-2994 (1968).

Data Sheet 104

Chemical equilibrium: $HO^\bullet + HNO_3(aq) \rightleftharpoons H_2O + NO_3^\bullet(aq)$ (104.1)

List of reports:

$K_{eq} = 1 \times 10^2$, dimensionless, in 0.2-1.5 M HNO_3, was estimated from the ratio of the rate constants $k_f = 5.3 \times 10^7$ M^{-1} s^{-1} and $k_r = 5.3 \times 10^5$ M^{-1} s^{-1} obtained by pulse radiolysis [1]. Both k_r and K_{eq} have been reported in improper units because water was explicitly included in the reverse reaction rate law; this inclusion was also performed in an improper manner using water activity around 1 M.

$K_{eq} = (2.8 \pm 0.4) \times 10^5$, dimensionless at $\mu = 0$ M, was obtained from the ratio of the rate constants $k_f = (8.6 \pm 1.3) \times 10^7$ M^{-1} s^{-1} and $k_r = (3 \pm 1) \times 10^2$ M^{-1} s^{-1} derived from pulse radiolysis in solutions of HNO_3 [2]. As in the previous report by Katsumura and co-workers, water was explicitly included in the reverse reaction rate law and k_r and K_{eq} had improper units. In the subsequent paper from the same laboratory [3], these values have been converted using water concentration of 55.6 M to have appropriate dimensionalities, that is $k_r = (1.7 \pm 0.6) \times 10^4$ s^{-1} and $K_{eq} = (5.0 \pm 1.5) \times 10^3$ M^{-1}.

Discussion

In the earlier of these reports by Katsumura and co-workers [1], activities of the reagents instead of their concentrations were used in the rate law for the reaction approach to equilibrium. This treatment is kinetically incorrect.

Poskrebyshev *et al.* also treated the rate laws in terms of activities [2], but our concerns about the validity of this approach are overshadowed by the concerns regarding the dose dependence. Three methods for the evaluation of K_{eq} were applied by these authors. The first method was the same as used by Katsumura and co-workers [1] and was based on the approach to equilibrium; it yielded $K_{eq} = (5.5 \pm 2.2) \times 10^4$ M^{-1}. In the second method, a K_{eq} ranging from about (2.5×10^4 to 7×10^4) M^{-1}at various radiation doses was obtained from the $NO_3^\bullet$ absorption maximum in its kinetic profile, where a complete equilibration was assumed. From the dose dependence shown by this latter method, the authors properly concluded that a significant loss of radicals due to the radical-radical reactions had occurred and resorted to kinetic modeling, which gave $K_{eq} = (2.8 \pm 0.4) \times 10^5$ and this value was considered as the most reliable. However, just as with the absorption maximum, the modeling result is heavily dependent upon the rates of the radical-radical reactions. It appears that the major radical loss should occur through the $HO^\bullet + NO_2^\bullet$ reaction, but reasonable kinetic fits could be obtained only with the rate constant for this reaction that was more than an order of magnitude below the well-supported literature values [4-6]. These considerations seem to imply that there is insufficient reversibility in the reaction of $HO^\bullet$ with $NO_3^\bullet$ for accurate equilibrium measurements, unless exceedingly small doses can be employed.

In summary, neither of the reported K_{eq} can be recommended with reasonable confidence.

Recommended value:

None

List of auxiliary thermodynamic data: none

References

1. P.-Y. Jiang, Y. Katsumura, K. Ishigure, Y. Yoshida. *Inorg. Chem.* **31,** 5135-5136 (1992).
2. G. A. Poskrebyshev, P. Neta, R. E. Huie. *J. Geophys. Res.* **106,** 4995-5004 (2001).
3. G. A. Poskrebyshev, R. E. Huie, P. Neta. *J. Phys. Chem. A* **107,** 1964-1970 (2003).
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Data Sheet 105

Chemical equilibria:

$$H_2NO^\bullet \rightleftharpoons HNO^{\bullet-} + H^+ \quad (105.1)$$

$$H_3NO^{\bullet+} \rightleftharpoons H_2NO^\bullet + H^+ \quad (105.2)$$

List of reports:

pK_a($H_2NOH^{\bullet+}$) = (4.2 ± 0.1), at ~ 22 °C with ionic strength uncontrolled and as high as 0.01 M [1]. From pulse radiolysis of NH_2OH, by monitoring the absorbance at 240 nm of the radical intermediate between pH 2 and 10.

pK_a($H_2NOH^{\bullet+}$) = (4.0 ± 0.1), presumably at room temperature, with ionic strength uncontrolled and as high as 0.5 M [2]. From pulse radiolysis of NH_2OH, monitoring the absorbance of the radical intermediate as a function of pH at 230 nm. A similar pH dependence of the absorbance was obtained from flash photolysis, although the pH range was limited to less than 4.

pK_a($H_2NO^\bullet$) = (12.6 ± 0.3), presumably at room temperature, with ionic strength uncontrolled and as high as 1 M [3]. Result from pulse radiolysis, monitoring the kinetics as a function of pH for the recombination of $H_2NO^\bullet$, with the reaction of $H_2NO^\bullet$ with $MV^{\bullet+}$ (MV is methylviologen, 1,1′-dimethyl-4,4′-bipyridinium(2+)) as an indicator. Experiments were performed between pH 8 and 14.

Discussion

The two early reports give spectral evidence for a radical pK_a at about 4.1, while the recent report from Lind and Merényi [3] gives kinetic evidence for a radical pK_a of 12.6. None of the three studies gives data over a sufficiently broad pH range to encoMPass both pK_a regions, so one might argue that the radical has two successive pK_a values. However, Lind and Merényi [3] argue that $H_3NO^{\bullet+}$ (or $NH_2OH^{\bullet+}$) should be a strong acid with pK_a < –5; they base their argument on two lines of evidence: 1) The reactions of hydroxylamine with Fe^{3+} and Pu^{4+} have rate laws that require the radical to be unprotonated even in 1 M acid, and 2) by analogy with TEMPO and related nitroxyl radicals, which are protonated only in concentrated H_2SO_4 solutions. Lind and Merényi also argue that the spectral changes that were previously interpreted in terms of a pK_a near 4.1 were due instead to a diminished yield of the radical at low pH. We are pursuaded by the results and interpretations of Lind and Merényi and thus recommend their values.

Recommended values:

$NH_2OH^{\bullet +} \rightleftharpoons NH_2O^{\bullet} + H^+$ p$K_a < -5$

$NH_2O^{\bullet} \rightleftharpoons NHO^{\bullet -} + H^+$ p$K_a = 12.6 \pm 0.3$

List of auxiliary thermodynamic data:

Nomenclature: NH_2OH, dihydridohydroxidonitrogen or azanal, hydroxylamine is acceptable; $NH_2OH^{\bullet +}$,dihydridohydroxidonitrogen(•1+); $NH_2O^{\bullet}$, dihydridooxidonitrogen(•); $NHO^{\bullet -}$, hydridoxidonitrate(•1−)

References

1. M. Simic, E. Hayon. *J. Am. Chem. Soc.* **93,** 5982-5986 (1971).
2. D. Behar, D. Shapira, A. Treinin. *J. Phys. Chem.* **76,** 180-186 (1972).
3. J. Lind, G. Merényi. *J. Phys. Chem. A.* **110,** 192-197 (2006).

Data Sheet 106

Chemical equilibrium: $HPO_3^{\bullet-} \rightleftharpoons PO_3^{\bullet 2-} + H^+$ (106.1)

List of reports:

Over the wavelength range 230 nm to 290 nm, the optical absorptivity of $PO_3^{\bullet 2-}$ was found to be significantly higher than that for $HPO_3^{\bullet-}$ [1]. This allowed a simple determination of the second pK_a of this radical by measuring the absorptivity subsequent to the pulse irradiation of phosphite solutions at various pH values. From the inflection point of the S-shaped curve, p$K_{106.1}$ = 5.75 was obtained, in excellent agreement with earlier ESR measurements of p$K_{106.1}$ = 5.8 [2].

Discussion

The authors gave no uncertainty estimate. Based on the good agreement with the previous results, the large difference between the absorption coefficients for the two forms and the quality of the results, we recommend p$K_{106.1}$ = (5.75 ± 0.05).

Recommended value:

p$K_{106.1}$ = (5.75 ± 0.05)

Nomenclature: $HPO_3^{\bullet-}$, hydroxidodioxidophosphate(•−); $PO_3^{\bullet 2-}$, trioxidophosphate(•2−).

References

1. K. Schäfer, K.-D. Asmus. *J. Phys. Chem.* **84,** 2156-2160 (1980).
2. O. P. Chawla, R. W. Fessenden. *J. Phys. Chem.* **79,** 2693-2700 (1975).

Data Sheet 107

Chemical equilibrium: $H_2PO_3^{\bullet} \rightleftharpoons HPO_3^{\bullet-} + H^+$ (107.1)

Chemical equilibrium: $H_3PO_3^{\bullet+} \rightleftharpoons H_2PO_3^{\bullet} + H^+$ (107.2)

List of reports:

The shift in the ^{31}P hyperfine constant in the ESR spectrum of $HPO_3^{\bullet-}$ was measured as a function of acidity from pH 2.4 to 61.2% $HClO_4$ [1]. It was argued that a plot of the reciprocal of the shift would be directly proportional to an acidity function applicable to this high acidity. An approach that assumes that each acid proton is associated with four water molecules to form $H_9O_4^+$ was taken, and the function h/w^4 utilized, where $h = [H_9O_4^+]$ and $w = [H_2O]/[H_2O]_0$, the total water concentration relative to pure water [2]. Although a linear relation between the reciprocal of the shift in the hyperfine constant and this acidity function was found for the ascorbate radical, which confirmed a single proton-transfer equilibrium, a non-linear relationship was found for hydroxidodioxidophosphate(•–) ($HPO_3^{\bullet-}$). This was taken to indicate the presence of two protonation equilibria, 107.1 and 107.2.

The observed curve could be fit to a more complex expression involving these two equilibria. The equilibrium constant $K_{107.1}$ and its associated splitting constant were derived by a straight-line fit to the lowest four acid concentrations and similar parameters for reaction 107.2 were obtained from a fit to the highest acid concentrations.

$K_{107.1} = 1.1 \text{ mol L}^{-1}$

$K_{107.2} = 54 \text{ mol L}^{-1}$

Discussion

These parameters and the splitting constants provided a good fit to the observations, but due to the nature of their derivation and their relative closeness, these values should be considered only approximate.

Recommended values:

$K_{107.1} = 1.1 \text{ mol L}^{-1}$
$K_{107.2} = 54 \text{ mol L}^{-1}$

Nomenclature: $H_3PO_3^{\bullet+}$, trihydroxidophoshorus(•1+); $H_2PO_3^{\bullet}$, dihydroxidooxidophosphorus(•), $HPO_3^{\bullet-}$, hydroxidodioxidophosphate(•1−).

References

1. H. F. Davis, H. J. McManus, R. W. Fessenden. *J. Phys. Chem.* **90,** 6400-6404 (1986).
2. W. T. Dixon, D. Murphy. *J. Chem. Soc., Faraday Trans. 2* **74,** 432-439 (1978).

Data Sheet 108

Chemical equilibrium: $H_2PO_4^{\bullet} \rightleftharpoons H^+ + HPO_4^{\bullet-}$ (108.1)

Chemical equilibrium: $HPO_4^{\bullet-} \rightleftharpoons H^+ + PO_4^{\bullet 2-}$ (108.2)

List of reports:

The three acid-base forms of the phosphate radical were generated through the pulse radiolysis of bis(tetraoxidophosphate)(*O-O*)(4−) ($P_2O_8^{4-}$) solutions at pH 4, 7, and 11 [1]. The absorption spectra were measured over the range 400 nm to 600 nm. The maximum absorption shifted from about 520 nm at pH 4, to 510 nm at pH 7, and 530 nm at pH 11. These shifts allowed the two pK_a values to be determined by monitoring the absorption at a convenient wavelength, 540 nm, over the pH range 4 to 11. The best-fit curve gave $pK_{108.1} = (5.7 \pm 0.2)$ and $pK_{108.2} = (8.9 \pm 0.1)$, where the error estimates are from the authors.

Discussion

The differences among the spectra are not too large, and the fact that there is a blue shift going from $H_2PO_4^{\bullet}$ to $HPO_4^{\bullet-}$, but a red shift for $H_2PO_4^{\bullet}$ to $PO_4^{\bullet 2-}$ suggests a somewhat greater uncertainty in these results. The general positions for these forms on the pH scale are supported by kinetic results. Generally, it appears that the order of electrode potential is: $H_2PO_4^{\bullet} > HPO_4^{\bullet-} > PO_4^{\bullet 2-}$.

Recommended values:

$pK_{108.1} = (5.7 \pm 0.4)$
$\mathrm{pK}_{108.2} = (8.9 \pm 0.2)$

Nomenclature: $H_2PO_4^{\bullet}$, dihydroxidodioxidophosphorus(•); $HPO_4^{\bullet-}$, hydroxidotrioxidophosphate(•1−); $PO_4^{\bullet 2-}$, tetraoxidophosphate(•2−)

References

1. P. Maruthamuthu, P. Neta. *J. Phys. Chem.* **82,** 710-713 (1978).

Data Sheet 109

Chemical equilibrium: $HPO_5^{\bullet-} \rightleftharpoons PO_5^{\bullet 2-} + H^+$ (109.1)

List of reports:

The trioxidophosphate(•2−) radical, or its hydronated form,which absorb over the wavelength range 230 nm to 290 nm, react rapidly with dioxygen [1].

$$PO_3^{\bullet 2-}, HPO_3^{\bullet -} + O_2 \rightarrow PO_5^{\bullet 2-}, HPO_5^{\bullet -}$$

The peroxy radicals have a weaker absorption over the wavelength range 240 nm to 340 nm, with the doubly-charged anion somewhat red-shifted coMPared to the singly-charged anion. Transient conductivity measurements confirmed the formation of the two types of anions, and a point of inflection was observed in a plot of the conductivity against pH over the range 2 – 5. This results in the value $pK_{109.1} = 3.4$.

Discussion

No uncertainty was quoted in the paper, but we estimate ± 0.2, due to the lack of confirmation by other experiments and to the observation that not quite full conductance appears to be attained at the highest pH. The basic observation seems to be quite reliable, however.

Recommended value:

$pK_{109.1} = (3.4 \pm 0.2)$.

Nomenclature: $HPO_3^{\bullet -}$, hydroxidodioxidophosphate(•1−); $PO_3^{\bullet 2-}$, trioxidophosphate(•2−); $HPO_5^{\bullet -}$, (dioxido)hydroxidodioxidophosphate(•1−); $PO_5^{\bullet 2-}$, (dioxido)trioxidophosphate(•2−).

References

1. K. Schäfer, K.-D. Asmus. *J. Phys. Chem.* **84,** 2156-2160 (1980).

Data Sheet 110

Chemical equilibrium: $As(OH)_4^{\bullet} \rightleftharpoons As(OH)_3O^{\bullet-} + H^+$ (110.1)

Chemical equilibrium: $HAsO_3^{\bullet-} \rightleftharpoons AsO_3^{\bullet 2-} + H^+$ (110.2)

Chemical equilibrium: $HAsO_3^{\bullet-} + H_2O \rightleftharpoons As(OH)_3O^{\bullet-}$ (110.3)

Chemical equilibrium: $HAsO_3^{\bullet-} + H_2O + H^+ \rightleftharpoons As(OH)_4^{\bullet}$ (110.4)

List of reports:

As(IV) species were generated through the pulse radiolysis of N_2O-saturated arsenite or arseneous acid solutions [1].

$As(III) + HO^{\bullet} \rightarrow As(IV)$

Spectra corresponding to four different protonation forms of As(IV) were recorded. These species exhibit a somewhat complicated relationship that depended on pH and time, and appear to be related through protonation and hydration equilibria.

Below pH 3, only one species was observed, which is formed in a rapid reaction and underwent a second order decay. Between pH 3 and 6, this species also decayed by first-order reaction to other absorbing species. A second, rapidly formed species was observed in the pH 8.5 to 10 range, which also decayed by a combination of first- and second-order processes. In the pH range 7 to 8, the two species that were formed in a rapid, primary reaction existed in an acid-base equilibrium.

Because the pK_a indicated for these two species is characteristic of weak oxyacids, Kläning, *et al.* [1] suggested that $HO^{\bullet}$ reacts with As(III) by addition

$As(OH)_3 + HO^{\bullet} \rightarrow As(OH)_4^{\bullet}$

$As(OH)_2O^- + HO^{\bullet} \rightarrow As(OH)_3O^{\bullet-}$

And the protolytic equilibrium between the two is

$As(OH)_4^{\bullet} \rightleftharpoons As(OH)_3O^{\bullet-} + H^+$ (110.1)

The anion in 110.1 has a spectrum red-shifted from the spectrum of the neutral form. From a plot involving the logarithm of the absorption ratio against pH, the acid dissociation constant at an ionic strength of 0.1 mol L^{-1} was determined to be $pK_{110.1} = 7.26$. This was corrected to (7.38 ± 0.06) at zero ionic strength.

Both $As(OH)_4^{\bullet}$ and $As(OH)_3O^{\bullet-}$ decay through first-order reactions to two species with considerably changed spectra. One species appears to exist in equilibrium with $As(OH)_4^{\bullet}$ in the pH range 5 to 6. A p*K* value could be derived from an analysis of the molar absorption of these species after attainment of equilibrium. Values of $pK = (3.78 \pm 0.05)$ at ionic strength 0.002 mol L^{-1} and $pK = (3.64 \pm 0.05)$ at 0.1 mol L^{-1} were derived. These values corrected to zero ionic strength become 3.82 and 3.88, identical within experimental error. This supports the identification of the initially formed As(IV) species as this uncharged $As(OH)_4^{\bullet}$. The authors suggest that this equilibrium corresponds to the dehydration reaction

$As(OH)_4^{\bullet} \rightleftharpoons HAsO_3^{\bullet-} + H_2O + H^+$ (110.5)

which proceeds through the intermediate formation of $H_2AsO_3^{\bullet}$. Thus, $pK_{110.5} = (3.85 \pm 0.05)$ and $pK_{-110.5} = -(3.85 \pm 0.05)$.

Similarly, $As(OH)_3O^{\bullet-}$ decays through a dehydration reaction

$As(OH)_3O^{\bullet-} \rightarrow HAsO_3^{\bullet-} + H_2O$

followed by deprotonation

$HAsO_3^{\bullet-} \rightleftharpoons AsO_3^{\bullet 2-} + H^+$ (110.2)

with $pK_{110.2} = (7.81 \pm 0.04)$.

The equilibrium constant for reaction 110.3 is obtained as $K_{110.3} = K_{110.1} \times K_{110.4} = 3 \times 10^{-4}$ or $pK_{110.3} = 3.53$.

Discussion

Recommended values:

$As(OH)_4^{\bullet} \rightleftharpoons As(OH)_3O^{\bullet-} + H^+$ $\quad pK_{110.1} = (7.38 \pm 0.06)$
$HAsO_3^{\bullet-} \rightleftharpoons AsO_3^{\bullet 2-} + H^+$ $\quad pK_{110.2} = (7.81 \pm 0.04)$
$HAsO_3^{\bullet-} + H_2O \rightleftharpoons As(OH)_3O^{\bullet-}$ $\quad pK_{110.3} = (3.53 \pm 0.11)$
$HAsO_3^{\bullet-} + H_2O + H^+ \rightleftharpoons As(OH)_4^{\bullet}$ $\quad pK_{110.4} = -(3.85 \pm 0.05)$

References

1. U. K. Kläning, B. H. Bielski, K. Sehested. *Inorg. Chem.* **28,** 2717-2724 (1989).

Data Sheet 111

Chemical equilibrium: $HOSCN^{\bullet-} + SCN^- \rightleftharpoons (SCN)_2^{\bullet-} + HO^-$ (111.1)

List of reports:

$K_{eq} = 6.45 \times 10^3$ at an unspecified temperature and ionic strength [1]. From pulse radiolysis with optical measurement of the position of equilibrium.

Discussion

The results were obtained with $[HO^-]$ varying from 0.2 M to 0.8 M, so the ionic strength might not have been constant, and μ certainly was rather high. On the other hand, K_{eq} is expected to be insensitive to ionic strength. The study probably was performed at room temperature. No uncertainty was specified for K_{eq}; given the usual accuracy of such measurements we assign an uncertainty of ± 20%.

We presently recommend an association constant of $(2.0 \pm 0.3) \times 10^5$ M^{-1} for the reaction of $SCN^\bullet$ with SCN^- (See Data Sheet 101) Taking $K_w = 1 \times 10^{-14}$ M^2 then leads to $pK_a = 12.5 \pm 0.1$ for $SCN^\bullet + H_2O \rightleftharpoons SCNOH^{\bullet-} + H^+$.

Recommended values:

$K_{eq} = (6.5 \pm 1.3) \times 10^3$ at 22 °C and zero ionic strength.
$pK_a = (12.5 \pm 0.1)$ for $SCN^\bullet + H_2O \rightleftharpoons HOSCN^{\bullet-} + H^+$

Nomenclature: SCN^-, nitridosulfidocarbonate(1−), thiocyanate is allowed; $(SCN)_2^{\bullet-}$, bis(nitridosulfidocarbonate)(*S*-*S*)(•1−); $HOSCN^{\bullet-}$, cyanidohydroxidosulfate(•1−).

List of auxiliary thermodynamicchemical data: none.

References

1. D. Behar, P. L. T. Bevan, G. Scholes. *J. Phys. Chem.* **76,** 1537-1542 (1972).

Data Sheet 112

Chemical equilibrium: $Tl + Tl^{+} \rightleftharpoons Tl_2^{+}$ (112.1)

List of reports:

$K_{eq} = 2.3 \times 10^{3}$ M^{-1}, with μ ranging from 0.1 mM to 0.1 M, presumably at room temperature [1]. Obtained from the equilibrium optical absorbance as a function of $[Tl^{+}]$. Result confirmed by Butler and Henglein (1980) [2].

$K_{eq} = (140 \pm 5\%)$ M^{-1}, with μ ranging from 0.1 mM to 0.1 M, presumably at room temperature [3]. Obtained from the equilibrium optical absorbance as a function of $[Tl^{+}]$.

Discussion

The disagreement between the two above results is substantial. Schwarz and Dodson [3] presented convincing arguments that the original absorbance data of Cercek *et al.* [1] were misinterpreted and that proper manipulation of the data yield a value for K_{eq} that is in agreement with the more recent determination. Schwarz and Dodson [3] were less confident in their explanation of the discrepant results of Butler and Henglein [2], but they suggest that the absorbance data of Butler and Henglein [2] may have been distorted by subsequent reactions. Overall, we favor the results of Schwarz and Dodson [3]. Although these experiments were performed at various ionic strengths, the magnitude of K_{eq} is expected not to be sensitive to this variation.

Recommended values:

$K_{eq} = (140 \pm 7)$ M^{-1}

List of auxiliary thermodynamic data: none.

Nomenclature: Tl, thallium, Tl_2^{+}, dithallium(+)

References

1. B. Cercek, M. Ebert, A. J. Swallow. *J. Chem. Soc. (A)* 612-615 (1966).
2. J. Butler, A. Henglein. *Radiat. Phys. Chem.* **15,** 603-612 (1980).

3. H. A. Schwarz, R. W. Dodson. *J. Phys. Chem.* **93,** 409-414 (1989).

Data Sheet 113

Chemical equilibrium: $Tl^{2+} + Cl^{-} \rightleftharpoons TlCl^{+}$ (113.1)

List of reports:

$K_{eq} = (6.2 \pm 0.7) \times 10^{4}\ M^{-1}$ at $\mu = 1.0$ M and room temperature [1]. Data obtained by pulse radiolysis with optical detection. Equilibrium constant determined from the position of equilibrium.

Discussion

The experiments appear to have been conducted properly and reliably. No other conflicting data are known. Thus we recommend the equilibrium constant as given.

With use of this equilibrium constant, the NBS value [2] of $\Delta_f G^\circ$ for Cl^{-}(*aq*) and the recommended value of $\Delta_f G^\circ$ for Tl^{2+} (+182 ± 20 kJ mol^{-1} from reaction 113.1 ($Tl^{2+} + Fe^{3+}$) we derive $\Delta_f G^\circ = +(23.3 \pm 0.3)$ kJ mol^{-1} for $TlCl^{+}$. From the NBS values for $\Delta_f G^\circ$ for $TlCl^{2+}$ and TlCl we derive $E^{\circ\prime} = +(0.179 \pm 0.004)$ V for the $TlCl^{2+}/TlCl^{+}$ couple and $E^{\circ\prime} = +(1.972 \pm 0.004)$ V for the $TlCl^{+}/TlCl$ couple. These electrode potentials are not corrected for ionic strength effects and thus are designated $E^{\circ\prime}$ values.

Recommended values:

$Tl^{2+} + Cl^{-} \rightleftharpoons TlCl^{+}(aq)$	$K_{eq} = (6.2 \pm 0.7) \times 10^{4}\ M^{-1}$ in 1 M H^{+}.
$TlCl^{+}$	$\Delta_f G^\circ = +(23.3 \pm 0.4)$ kJ mol^{-1}
$TlCl^{2+} + e^{-} \rightleftharpoons TlCl^{+}$	$E^{\circ\prime} = +(0.179 \pm 0.004)$ V
$TlCl^{+} + e^{-} \rightleftharpoons TlCl$	$E^{\circ\prime} = +(1.972 \pm 0.004)$ V

List of auxiliary thermodynamic data: $\Delta_f G^\circ$ for Tl^{2+}(*aq*), $TlCl^{2+}$(*aq*), TlCl(*aq*) and Cl^{-}(aq).

Nomenclature: Tl^{2+}, thallium(2+); $TlCl^{+}$, thallium chloride(1+).

References

1. R. W. Dodson, H. A. Schwarz, *J. Phys. Chem.* **78,** 892-899 (1974).

2. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall, *J. Phys. Chem. Ref. Data* **11,** Suppl. No. 2 (1982).

Data Sheet 114

Chemical equilibrium: $TlCl^+ + Cl^- \rightleftharpoons TlCl_2$ (114.1)

List of reports:

$K_{eq} = (1.9 \pm 0.4) \times 10^3\ M^{-1}$ at $\mu = 1.0$ M and room temperature [1]. Data were obtained by pulse radiolysis with optical detection. The equilibrium constant was determined from the position of equilibrium.

Discussion

The experiments appear to have been conducted properly and reliably. No other conflicting data are known. Thus we recommend the equilibrium constant as given.

With use of this equilibrium constant, the NBS value [2] of $\Delta_f G°$ for Cl^- and the recommended value of $\Delta_f G°$ for $TlCl^+$ (23.3 ± 0.4) kJ mol^{-1} from reaction 113.1 ($Tl^{2+} + Cl^-$) we derive $\Delta_f G° = -(126.6 \pm 0.7)$ kJ mol^{-1} for $TlCl_2$. From the NBS values for $\Delta_f G°$ for $TlCl_2^+$ and $TlCl_2^-$ we derive $E°' = +(0.029 \pm 0.008)$ V for the $TlCl_2^+/TlCl_2$ couple and $E°' = +(1.754 \pm 0.008)$ V for the $TlCl_2/TlCl_2^-$ couple.

Recommended values:

$TlCl^+ + Cl^- \rightleftharpoons TlCl_2(aq)$	$K_{eq} = (1.9 \pm 0.4) \times 10^3\ M^{-1}$ in 1 M H^+.
$TlCl_2$	$\Delta_f G° = -(126.6 \pm 0.7)$ kJ mol^{-1}
$TlCl_2^+ + e^- \rightleftharpoons TlCl_2$	$E°' = +(0.029 \pm 0.008)$ V
$TlCl_2 + e^- \rightleftharpoons TlCl_2^-$	$E°' = +(1.754 \pm 0.008)$ V

List of auxiliary thermodynamic data: $\Delta_f G°$ for $TlCl^+$, $TlCl_2^+$, $TlCl_2^-$ and Cl^-.

Nomenclature: $TlCl^+$, thallium chloride(1+); $TlCl_2$, thallium dichloride.

References

1. R. W. Dodson, H. A. Schwarz. *J. Phys. Chem.* **78,** 892-899 (1974).
2. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall. *J. Phys. Chem. Ref. Data* **11,** Suppl. No. 2 (1982).

Data Sheet 115

Chemical equilibrium: $TlCl_2 + Cl^- \rightleftharpoons TlCl_3^-$ (115.1)

List of reports:

$K_{eq} = (13 \pm 3)\ M^{-1}$ at $\mu = 1.0$ M and room temperature [1]. Data obtained by pulse radiolysis with optical detection. Equilibrium constant determined from the position of equilibrium.

Discussion

The experiments appear to have been conducted properly and reliably. No other conflicting data are known. Thus we recommend the equilibrium constant as given.

With use of this equilibrium constant, the NBS value [2] of $\Delta_f G°$ for Cl^- and the recommended value of $\Delta_f G°$ for $TlCl_2$ (–126.6 ± 0.4) kJ mol^{-1} from reaction 114.1 ($TlCl^+ + Cl^-$) we derive $\Delta_f G° = -(264.2 \pm 0.7)$ kJ mol^{-1} for $TlCl_3^-$. From the NBS value for $\Delta_f G°$ for $TlCl_3$ we derive $E°' = -(0.106 \pm 0.007)$ V for the $TlCl_3/TlCl_3^-$ couple. Corrections for the effect of ionic strength were not applied, and hence the electrode potential is designated an $E°'$ value.

Recommended values:

$TlCl_2 + Cl^- \rightleftharpoons TlCl_3^-$ $K_{eq} = (13 \pm 3)\ M^{-1}$ in 1 M H^+.
$TlCl_3^-$ $\Delta_f G° = -(264.2 \pm 0.7)$ kJ mol^{-1}
$TlCl_3 + e^- \rightleftharpoons TlCl_3^-$ $E°' = -(0.106 \pm 0.007)$ V

List of auxiliary thermodynamic data: $\Delta_f G°$ for $TlCl_2$(*aq*), $TlCl_3$(*aq*) and Cl^-(aq).

Nomenclature: $TlCl_2$, thallium dichloride; $TlCl_3^-$, trichloridothallate(1−).

References

1. R. W. Dodson, H. A. Schwarz. *J. Phys. Chem.* **78,** 892-899 (1974).
2. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall. *J. Phys. Chem. Ref. Data* **11,** Suppl. No. 2 (1982).

Data Sheet 116

Chemical equilibrium: $HO^\bullet(aq) \rightleftharpoons O^{\bullet-}(aq) + H^+(aq)$ (106.1)

List of reports:

$pK_a = (11.9 \pm 0.2)$ at 23 °C. Result obtained by pulse radiolysis determination of the kinetics of oxidation of $[Fe(CN)_6]^{4-}$ by $HO^\bullet/O^{\bullet-}$ [1].

$pK_a = (11.9 \pm 0.2)$ at 23 °C (?) and low ionic strength. Result obtained by pulse radiolysis determination of the kinetics of oxidation of $[Fe(CN)_6]^{4-}$ by OH/O^- [2].

$pK_a = (11.8 \pm 0.2)$ at ~23 °C at low ionic strength. Result obtained by pulse radiolysis determination of the kinetics of oxidation of CO_3^{2-} by $HO^\bullet/O^{\bullet-}$ [3].

$K_a/K_w = (56 \pm ?)(pK_a = 12.2)$ at 25 °C at ~0.01 M ionic strength. Baxendale *et al.* obtained this result by pulse radiolysis determination of the kinetics of oxidation of BH_4^- by $HO^\bullet/O^{\bullet-}$ [4].

$pK_a = (11.9 \pm ?)$ presumably at room temperature at ~0.01 M ionic strength. Result obtained by pulse radiolysis determination of the kinetics of oxidation of IO_3^- by $HO^\bullet/O^{\bullet-}$ [5].

$pK_a = (11.8 \pm ?)$ at 25 °C without control of ionic strength. Result obtained by pulse radiolysis determination of the kinetics of oxidation of CO_3^{2-} by $HO^\bullet/O^{\bullet-}$ [6]. Value of pK_a obtained by inspection of Figure 3 in the paper.

$pK_a = (11.7 \pm 0.1)$ at zero ionic strength and 25 °C. Elliot and McCracken obtained this result by pulse radiolysis determination of the kinetics of oxidation of $[Fe(CN)_6]^{4-}$ by $HO^\bullet/O^{\bullet-}$ [7]. pK_a values obtained from measurements of K_a/K_w and then using K_w values at appropriate temperature and ionic strength. Value of pK_a at 25 °C interpolated from data at 20 °C and 30 °C.

$pK_a = (12.0 \pm 0.2)$ at 22 °C and ~0.01 M ionic strength. Hickel *et al.* obtained this result by pulse radiolysis determination of the ratio of the forward and reverse rate constants as revealed by the kinetics of addition of $O^{\bullet-}$ to O_2 at $P(O_2) = (10 - 140)$ atm {*i.e.* (1.01-14.2) MPa} [8]. An essentially identical result was obtained from the pH dependence of the addition reaction under conditions where proton transfer was at equilibrium at $P(O_2) = 0.2$ atm (*i.e.* 0.02) MPa. Both calculations depended on pK_w, for which a value of 14.08 was selected.

pK_a = (11.54 ± 0.04) at 25 °C and ~0.01 M ionic strength. Poskrebyshev *et al.* obtained this result by pulse radiolysis determination of the kinetics of oxidation of benzoate by $HO^•/O^{•-}$ [9]. A value of (1.01×10^{-14}) M^2 for K_w was used in deriving pK_a from the measured K_b.

Discussion

The result of Baxendale *et al.* can be converted into a *p*K_a by use of $K_w = (1.01 \times 10^{-14})$ M^2: pK_a = 12.2. With this addition, the extensive list of measurements of the pK_a of $HO^•$ gives considerable confidence that the value lies in the range of 11.5 to 12.2; most of the reports suggest a value near 11.9.

We exclude from detailed consideration the three early reports from the Rabani group [1-3] because the results were obtained without temperature control and not extrapolated to zero ionic strength. Likewise we exclude the result from Barat *et al.* [5], which also failed to report an uncertainty analysis.

We exclude the result of Buxton *et al.* [6] because the pK_a was derived from experiments spanning a wide range of ionic strengths and no appropriate correction was applied. Moreover, there is no meaningful analysis of uncertaintes.

One of the extreme values, as inferred from the work of Baxendale *et al.* [4], was not actually reported in the original work, was not assigned an uncertainty, and was not coMPared to prior work; for these reasons we exclude it from further consideration.

Another of the extreme pK_a values (11.54 ± 0.04) [9] requires discussion. The unusually high precision assigned to the measurement appears only in the abstract of the paper. The high assigned precision implies that the deviation of the pK_a value from the prior determinations is statistically significant; however, the paper presents no discussion of this fact, nor does it provide any suggestions as to the origins of the deviation. We note that Figure 1 of the paper presents plots of k_{obs} vs [benzoate] at various pH values, where the pH values are given to only 0.1 unit precision. It seems likely that the uncertainty in the derived pK_a is overly optimistic. In view of these concerns we consider this report [9], although the most recent, not necessarily the best.

Of the remaining reports, those of Elliot and McCracken [7] and of Hickel *et al.* [8] are significant in that they include data at 25 °C with well-defined uncertainty estimates. The work of Elliot and McCracken [7] shows substantial temperature dependence for pK_a, which underscores the importance of obtaining data at 25 °C. The work of Hickel *et al.* [8] is important because it is the only study to determine pK_a from the ratio of the forward and reverse proton-transfer rate constants (rather than just from the pH dependence of an irreversible $HO^•/O^{•-}$ reaction); as such it provide strong additional support that the quantity being determined is actually the pK_a. One weakness in the paper by Hickel *et al.* [8] is in the way that [HO^-] was obtained: for pH > 11 it was calculated "from the weight of NaOH in the solutions", which is a quite unreliable method. For pH < 11 it was calculated from the pH, but the details of the calculation are not described. In contrast, the work of Elliot and McCracken determined [OH^-] by titration [7]. Of these two papers, the one by Elliot and McCracken [7] is preferrred because of its greater precision, its more reilable method of determining [OH^-], and its use of ionic-strength dependent K_w values.

In comparing the results from the papers of Poskrebyshev *et al.* [9] and of Elliot and McCracken [7] it is difficult to find any flaws in either, with the exception of the weak handling of uncertainties in the former. However, since the Poskrebyshev paper [9] yields a value that is so far from the values reported elsewhere we regard it as anomalous and recommend the result of Elliot and McCracken [7].

Recommended values:

$HO^{\bullet}(aq) \rightleftharpoons O^{\bullet-}(aq) + H^+(aq)$ p$K_a = (11.7 \pm 0.1)$

List of auxiliary thermodynamic data: K_w

References

1. J. Rabani, M. S. Matheson. *J. Am. Chem. Soc.* **86,** 3175-3176 (1964).
2. J. Rabani, M. S. Matheson. *J. Phys. Chem.* **70,** 761-769 (1966).
3. J. L. Weeks, J. Rabani. *J. Phys. Chem.* **70,** 2100-2106 (1966).
4. J. H. Baxendale, M. D. Ward, P. Wardman. *Trans. Faraday Soc.* **67,** 2532-2537 (1971).
5. F. Barat, L. Gilles, B. Hickel, B. Lesigne. *J. Phys. Chem.* **76,** 302-307 (1972).
6. G. V. Buxton, N. D. Wood, S. Dyster. *J. Chem. Soc., Faraday Trans. 1* **84,** 1113-1121 (1988).
7. A. J. Elliot, D. R. McCracken. *Rad. Phys. Chem.* **33,** 69-74 (1989).
8. B. Hickel, H. Corfitzen, K. Sehested. *J. Phys. Chem.* **100,** 17186-17190 (1996).
9. G. A. Poskrebyshev, P. Neta, R. E. Huie. *J. Phys. Chem. A* **106,** 11488-11491 (2002).

Data Sheet 117

Chemical equilibrium:

$$S^{\bullet -} + SH^{-} \rightleftharpoons HSS^{\bullet 2-} \quad (117.1)$$

List of reports:

$K = 1 \times 10^4$ M^{-1}, determined by pulse radiolysis of H_2S solutions at pH 7.0 in 2 mM phosphate buffer [1].

$K = 8 \times 10^3$ M^{-1}, determined by flash photolysis of H_2S solutions buffered at pH 7 and 7.5, calculated from the ratio of k_f and k_r [2]. The ionic strength was not specified; (20 ± 2) °C.

Discussion

The two determinations are in good agreement despite the likely differing ionic strengths. We recommend the average value: 9×10^3 M^{-1}, and we suggest an uncertainty of ± 20 % given the unknown effect of ionic strength. The first determination was performed at rather low ionic strength, so the ionic strength correction could be negligible. Although the exact pK_as of $HS^{\bullet}$ and $HSSH^{\bullet -}$ are unknown, Das *et al.* [2] provide evidence that they are low enough that the protonated species do not affect the measurements at pH 7 significantly.

Recommended value:

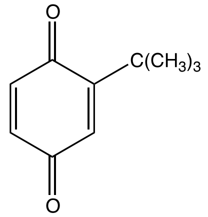
$$K(117.1) = (9 \pm 2) \times 10^3\ M^{-1}.$$

References

1. G. Mills, K. H. Schmidt, M. S. Matheson, D. Meisel. *J. Phys. Chem.* **91,** 1590-1596 (1987).
2. T. N. Das, R. E. Huie, P. Neta, S. Padmaja. *J. Phys. Chem. A* **103,** 5221-5226 (1999).

Supplementary Data Sheet S-1

Subject: 2-*tert*-butyl-1,4-benzosemiquinone (TBQ)



The radical derived from 2-*tert*-butyl-1,4-benzoquinone:
IUPAC PIN: 3-*tert*-butyl-4-hydroxyphenoxyl

Couple: $2\text{-}C_4H_9\text{-}C_6H_3O_2/2\text{-}C_4H_9\text{-}C_6H_3O_2^{\bullet-}$

Method: ESR **Solvent:** 1% acetone in water

Measurements by comproportionation equilibrium:

Equilibrium: $\mathrm{TBQ + TBQH_2 \rightleftharpoons 2TBQH^{\bullet}}$ (pH considerations not designated) (S-1)

Other solutes: NaCl, phosphate buffer

Gas: argon

pH = 6.5 - 9.5. **Temperature:** 22 °C. **Ionic strength:** 0.12 M.

Equilibrium constant from position of equilibrium: log K'(S-1) = –(8.8 ± 0.1), at pH 7, not corrected for ionic strength [1].

Supporting measurements: The authors measured potentiometrically $E°'(\mathrm{TBQ/TBQH_2})$ = +(0.232 ± 0.003) V vs NHE at pH 7, which is the potential for the 2-electron reduction of TBQ at pH 7. At this pH the semiquinone is fully deprotonated (pK_a(TBQH$^{\bullet}$ = 4.3) and the hydroquinone is doubly protonated (pK_a($\mathrm{TBQH_2}$) = 10.6). Combination of K'(S-1) and $E°'(\mathrm{TBQ/TBQH_2})$ gives $E°'(\mathrm{TBQ/TBQ^{\bullet-}})$ = –(0.025 ± 0.006) V, which is the formal potential of the $\mathrm{TBQ/TBQ^{\bullet-}}$ couple at μ = 0.12 M. A correction for the activity coefficient of $\mathrm{TBQ^{\bullet-}}$ then leads to $E°(\mathrm{TBQ/TBQ^{\bullet-}})$ = –(0.032 ± 0.006) V. Note that eqs 20 and 22 in the paper by Dohrman and Bergmann have typos: the right-hand terms should be divided by 2. Apparently the results were calculated without making this mistake.

Derived potentials: The standard electrode potential of the $\mathrm{TBQ,H^+/TBQH^{\bullet}}$ couple was derived from the above $E°$ value by use of the pK_a of $\mathrm{TBQH^{\bullet}}$ equals (4.3 ± 0.1) at essentially zero ionic strength. The pK_a was determined by pulse radiolysis of TBQ in 1 M 2-propanol, measuring the pH dependence of the absorbance of the semiquinone at 430 nm. The outcome was $E°(\mathrm{TBQ,H^+/TBQH^{\bullet}})$ = +(0.219 ± 0.015) V.

The standard electrode potential of the $\mathrm{TBQ^{\bullet-},2H^+/TBQH_2}$ couple $E°$ = +(1.315 ± 0.006) V was determined as above from the measured $E°'$ and K' values at pH 7 with a correction for the activity coefficient of $\mathrm{TBQ^{\bullet-}}$, and $E°$ = +(1.061 ± 0.015) V for the $\mathrm{TBQH^{\bullet},H^+/TBQH_2}$ couple was calculated by using the pK_a of $\mathrm{TBQH^{\bullet}}$. A value for $E°(\mathrm{TBQ^{\bullet-}/TBQ^{2-}})$ of –(0.112 ± 0.015) V was obtained by use of p$K_{a,1}$ and p$K_{a,2}$ for $\mathrm{TBQH_2}$, but in this case the accuracy of the result is overstated, since activity coefficients are not reliably estimated for di-anions at μ = 0.12 M.

Discussion: The comproportionation equilibrium was also investigated by Roginsky *et al.* [2]. Roginsky *et al.* used ESR to determine the equilibrium constant in 50 mM phosphate buffer, and they obtained a value approximately 4-fold greater than reported by Dohrmann and Bergmann. The origin of the discrepancy is not understood, but the consequence is a 36 mV difference in the derived potentials. We thus recommend the potentials derived by Dohrmann and Bergman after adjusting them by 36/2 mV; we increase the incertainties accordingly by 10 mV. In the case of $E°(TBQ^{•-}/TBQ^{2-})$ we add another 5 mV of uncertainty because of the ionic strength issues. The E_m values recommended below are from Dohrmann and Bergmann, adjusted again by 18 mV and with a correspondingly increased uncertainty.

A further check on the TBQ potential is provided by data in the Dohrmann and Bergmann paper, where they use pulse radiolysis to measure the redox equilibrium constant for the reaction of $TBQ^{•-}$ with 4-(dimethylamino)phenoxyl (DMAP): $TBQ^{2-} + DMAP^{•} = TBQ^{•-} + DMAP^{-}$. They obtain an equilibrium constant of $(1.1 \pm 0.5) \times 10^3$ at 22 °C and $\mu \sim 0.5$ M in 0.9 M ethylene glycol at pH 13.5. Then they use their $E°$ value for $TBQ^{•-}/TBQ^{2-}$ and estimated activity coefficients for $TBQ^{•-}$ and TBQ^{2-} to obtain $E°'(DMAP^{•}/DMAP^{-}) = +(0.10 \pm 0.02)$ V at 22 °C and $\mu \sim 0.5$ M in 0.9 M ethylene glycol. This differs by 70 mV from the DMAP potential reported by Steenken and Neta. Dohrmann and Bergmann sugested various sources for the disagreement and principal among them seems to be the possibility that the organic cosolvents affect the equilibria. Given the doubts introduced by these considerations, the uncertainties presented below may be highly optimistic.

Recommended values:

$E°(TBQ/TBQ^{•-}) = -(0.014 \pm 0.016)$ V.
$E°(TBQ,H^+/TBQH^{•}) = +(0.237 \pm 0.025)$ V
$E°(TBQ^{•-},2H^+/TBQH_2) = +(1.297 \pm 0.016)$ V
$E°(TBQ^{•-}/TBQ^{2-}) = -(0.130 \pm 0.030)$ V
$E°'(TBQ/TBQ^{•}) = -(0.007 \pm 0.016)$ V at pH 7 and $\mu = 0.12$ M
$E°'(TBQ^{•}/TBQH_2) = +(0.471 \pm 0.016)$ V at pH 7 and $\mu = 0.12$ M

References

1. J. K. Dohrmann, B. Bergmann. *J. Phys. Chem.* **99**, 1218-1227 (1995).
2. V. A. Roginsky, L. M. Pisarenko, W. Bors, C. Michel. *J. Chem. Soc., Perkin Trans. 2* 871-876 (1999).

Supplementary Data Sheet S-2

Chemical equilibrium: $ClO_2^{\bullet} + PhO^{-} \rightleftharpoons ClO_2^{-} + PhO^{\bullet}$ (S-2)

PhOH = phenol

$K = 2.2 \times 10^2$ from absorbance, $(2.5 \pm 0.9) \times 10^2$ from kinetics, pH 13 [1].
Taking $E°(ClO_2^{\bullet}/ClO_2^{-}) = +0.936$ V at 298 K [2].
$E°(PhO^{\bullet}/PhO^{-}) = +(0.796 \pm 0.010)$ V
$k_f = (1.6 \pm 0.3) \times 10^7$ L mol^{-1} s^{-1}, $k_r = (6.3 \pm 1.2) \times 10^4$ L mol^{-1} s^{-1}

$K = 3.0 \times 10^2$ from absorbance, 2.7×10^2 from kinetics, pH 11-12, $\mu = 1$ M [3].
Taking $E°(ClO_2^{\bullet}/ClO_2^{-}) = +0.936$ V [2].
$E°(PhO^{\bullet}/PhO^{-}) = +(0.791 \pm 0.010)$ V
$k_f = 3.5 \times 10^7$ L mol^{-1} s^{-1}, $k_r = 1.3 \times 10^5$ L mol^{-1} s^{-1}

$K = (2.1 \pm 0.3) \times 10^2$ from absorbance, pH 11.5, $\mu = 0.12$ M [4].
Taking $E°(ClO_2^{\bullet}/ClO_2^{-}) = +0.934$ V [5].
$E°(PhO^{\bullet}/PhO^{-}) = +(0.796 \pm 0.005)$ V

Electrochemistry

$E°' = +0.803$ V, by cyclic voltametry, from a Pourbaix diagam, at an ionic strength estimated near 0.15 M (0.05 M Britton-Robinson buffer) at, presumably, room temperature. The concentration of phenol was 0.2 mM, the scan rate 0.2 V s^{-1} [6].

Discussion

Average of all 5 K's is $(2.5 \pm 0.5) \times 10^2$. Assuming all measured equilibrium constants at 295 K are the same as that at 298 K, and taking $E°(ClO_2^{\bullet}/ClO_2^{-}) = +(0.935 \pm 0.003)$ V (Data Sheet 24), we find $E°(PhO^{\bullet}/PhO^{-}) = +(0.793 \pm 0.008)$ V, a value in excellent agreement with the very solid study on the electrochemistry of phenol [6]. As the value of K(S-2) is expected to be independent of ionic strength, the derived electrode potential can be regarded as a standard potential.

Recommended value

$E°(PhO^{\bullet}/PhO^{-}) = +(0.793 \pm 0.008)$ V

List of auxiliary thermodynamic data

$pK_a(\mathrm{PhOH}) = 10.0$
$pK_a(\mathrm{PhOH}^{\bullet+}) = -2.0$ [7] or -2.75 [8]
$E°(\mathrm{PhO}^{\bullet}, \mathrm{H}^+/\mathrm{PhOH}) = +1.38$ V or $+1.42$ V
$E°'(\mathrm{pH}\ 7) = +0.97$ V.

Das [8] argues that the pK_a of –2.0 previously reported for $\mathrm{PhOH}^{\bullet+}$ is in error because the prior report overlooked the association of PhOH with $\mathrm{PhOH}^{\bullet+}$; the revised pK_a is –(2.75 ± 0.05).

References

1. G. Merényi, J. Lind, X. Shen. *J. Phys. Chem.* **92**, 134-137 (1988).
2. N. V. Troitskaya, K. P. Mishchenko, I. E. Flis. *Russ. J. Phys. Chem.* **33**, 77-79 (1959).
3. J. Lind, X. Shen, T. E. Eriksen, G. Merényi. *J. Am. Chem. Soc.* **112**, 479-482 (1990).
4. T. N. Das, R. E. Huie, P. Neta. *J. Phys. Chem. A* **103**, 3581-3588 (1999).
5. D. M. Stanbury. *Adv. Inorg. Chem.* **33**, 69-138 (1989).
6. C. Costentin, C. Louault, M. Robert, J.-M. Savéant. *Proc. Natl. Acad. Sci. U.S.A.* **106**, 18143-18148 (2009).
7. W. T. Dixon, D. Murphy. *J. Chem. Soc., Faraday Trans. 2* **72**, 1221-1230 (1976).
8. T. N. Das. *J. Phys. Chem. A* **109**, 3344-3351 (2005).

Supplementary Data Sheet S-3

Chemical equilibrium: $PhO^{\bullet} + MePhO^{-} \rightleftharpoons PhO^{-} + MePhO^{\bullet}$ (S-3.1)

PhOH = phenol

MePhOH = 3-methylphenol

$K = (12.4 \pm 1.2)$ from absorbance, pH 13, $I = 0.1$ M [1].

Taking $E°(PhO^{\bullet}/PhO^{-}) = +0.80$ V (Data Sheet S-2)

The equilibrium constant for reaction S-3.1 is expected to be insensitive to ionic strength, which enables the derived electrode potential to be regarded as a standard potential.

Recommended value:

$E°(MePhO^{\bullet}/MePhO^{-}) = +(0.74 \pm 0.01)$ V at $\mu = 0$

List of auxiliary thermodynamic data:

$pK_a(MePhOH) = 10.0$

References

1. T. N. Das, R. E. Huie, P. Neta, *J. Phys. Chem. A* **103,** 3581-3588 (1999).

Supplementary Data Sheet S-4

tyrosine

Chemical equilibrium: $PhO^{\bullet} + TyrO^{-} \rightleftharpoons PhO^{-} + TyrO^{\bullet}$ (S-4.1)

PhOH = phenol, TyrOH = tyrosine

$K_{S\text{-}4.1}$ = 21 from absorbance, 18 from kinetics, pH 11-12, μ = 0.5 M [1].
The authors took $E°(PhO^{\bullet}/ PhO^{-})$ = +0.80 V to derive $E°(TyrO^{\bullet}/ TyrO^{-})$ = +(0.72 ± 0.02) V.
$k_f = 4.9 \times 10^8$ L mol^{-1} s^{-1}, $k_r = 2.8 \times 10^7$ L mol^{-1} s^{-1}

$K_{S\text{-}4.1}$ = (12.0 ± 1.2) from absorbance, pH 11.3, μ = 0.076 M [2].
The authors took $E°(PhO^{\bullet}/ PhO^{-})$ = +0.80 V to derive $E°(TyrO^{\bullet}/ TyrO^{-})$ = +(0.736 ± 0.005) V at μ = 0.

$K_{S\text{-}4.1}$ = (11.5 ± 1.2) from absorbance, pH 11.3, μ = 0.5 M [2].
The authors took $E°(PhO^{\bullet}/ PhO^{-})$ = +0.80 V to derive $E°(TyrO^{\bullet}/ TyrO^{-})$ = +(0.737 ± 0.005) V at μ = 0.

Chemical equilibrium: $TyrO^{\bullet} + ABTS^{2-} + H^{+} \rightleftharpoons TyrOH + ABTS^{\bullet-}$ (S-4.2)

ABTS = 2,2'-azinobis(3-ethylbenzothiazoline-6-sulphonate)

$K_{S\text{-}4.2}$ was determined at pH 9.08, 10.00, and 11.03 by pulse radiolysis, both from the equilibrium absorbance and from the ratio of the forward and reverse rate constants [3]. Taking $E°(ABTS^{\bullet-}/ABTS^{2-})$ = +0.68 V and a pK_a of 10.4 for the TyrOH phenolic dissociation the authors calculated $E°(TyrO^{\bullet}/TyrO^{-})$ = +(0.717 ± 0.002) V, and $E°'$ = +(0.93 ± 0.02) V at pH 7. We note that Table 1 of this publication has several typos: k_6 and k_{-6} should be reversed, K_6 should be $1/K_6$, and ΔE_6 should be $-\Delta E_6$.; E_m, however, is correct.

Discussion

The various determinations of $E°(TyrO^{\bullet}/TyrO^{-})$ span a range of 20 mV, which exceeds some of the stated uncertainties. On the other hand, the smaller stated uncertainties seem overly optimistic. In the case of the ABTS reaction (S-4.2) the uncertainty in $E°(ABTS^{\bullet-}/ABTS^{2-})$ was not included in calculating $E°(TyrO^{\bullet}/TyrO^{-})$; that uncertainty is probably at least 10 mV. Thus, the various reports of $E°(TyrO^{\bullet}/TyrO^{-})$ are in reasonable agreement.

An indirect calculation of $K_{S\text{-}4.1}$ can be performed by combining the equilibrium constants for two reactions involving sulfite:

$SO_3^{\bullet-} + PhO^- \rightleftharpoons SO_3^{2-} + PhO^\bullet$ $K_{63.1} = 0.056$ at $\mu = 0$ M. (Data Sheet 63)
$TyrO^\bullet + SO_3^{2-} \rightleftharpoons TyrO^- + SO_3^{\bullet-}$ $K_{64.1} = 0.61$ at pH 11.6 (independent of μ) (Data Sheet 64)

The sum of the two reactions gives the reverse of reaction S-4.1: $1/K_{S\text{-}4.1} = (K_{63.1})(K_{64.1}) = 3.4 \times 10^{-2}$ (or $K_{S\text{-}4.1} = 29$) at $\mu = 0$ M. This result is in reasonable agreement with the direct measurements of $K_{S\text{-}4.1}$ summarized above, given the effects of propagation of error.

Overall, the value of $K_{S\text{-}4.1}$ determined by Das *et al.* appears to be the most reliable, while the uncertainty is probably best estimated by considering all of the above reports. Thus we recommend a value of (12 ± 5) for $K_{S\text{-}4.1}$ (or $\Delta E° = 64$ mV). We currently recommend $E°(PhO^\bullet/PhO^-) = (0.793 \pm 0.008)$ (Data Sheet S-2), and thus we derive $E°(TyrO^\bullet/TyrO^-) = +(0.729 \pm 0.01)$ V from $K_{S\text{-}4.1}$. Combining this result with that derive from reaction S-4.2 leads to $E°(TyrO^\bullet/TyrO^-) = +(0.723 \pm 0.01)$ V.

Recommended values:
$K_{S\text{-}4.1} = 12 \pm 5$
$E°(TyrO^\bullet/TyrO^-) = (0.723 \pm 0.010)$ V

List of auxiliary thermodynamic data
pK_a(tyrosine) = 2.18, 9.21, 10.1 [4]
$E°'$(pH 7) = +0.91 V (assuming pK_as of amino and carboxyl group are the same in the radical as in the parent tyrosine).
$E°(ABTS^{\bullet-}/ABTS^{2-}) = +0.68$ V.

Further comments:

During the 1980s proton-coupled electron transfer from tyrosine to the tryptophan radical in peptides and proteins has been observed at pH 7 by pulse radiolysis [5-8]. Given the values that we find for the equilibrium constants of those reactions, the difference in electrode potential is at most 60 mV; this inference excludes the data of Faraggi *et al.* because it is unclear whether the reactions reached equilibrium [6]. As the couple $Trp^\bullet$, $H^+/TrpH$ has an electrode potential of +(1.03 ± 0.02) V at pH 7 (see Data Sheet S12), that of the $TyrO^\bullet,H^+/TyrOH$ couple is expected to be near +0.97 V. However, the values cited above yield a value of +0.91 V. Of course, one can accept a value of +0.91 V, but then the electrode potential of the $\text{Trp}^{\bullet}$, H^{+}/TrpH couple would be incorrect. The origin of this discrepancy is not known. Recent cyclic voltammetry experiments yield +0.97 ± 0.01 V for $E^{\circ\prime}(\text{TyrO}^{\bullet}, \text{H}^{+}/\text{TyrOH})$ at pH 7 (L. Mahmoudi, R. Kisner, T. Nauser, W. H. Koppenol, 2014, unpublished.), quite close to that obtained for a tyrosine in an artificial protein, +0.98 V [9].

Experimental measurements at pH 7 [10] gave $E^{\circ}(\text{TyrO}^{\bullet}/\text{TyrO}^{-})$ between +0.90 and +0.97 V, but it is not clear whether real equilibrium was achieved in those cases (because of the slow electron transfer with neutral phenols). The results were:

Reference	Ref. $E^{\circ\prime}$/V	$E^{\circ\prime}(\text{TyrO}^{\bullet}/\text{TyrO}^{-})$/V from kinetics	$E^{\circ\prime}(\text{TyrO}^{\bullet}/\text{TyrO}^{-})$/V from absorbance
$\text{IrBr}_6^{2-/3-}$	+0.80	+0.92	+0.92
$\text{Os(bpy)}_3^{3+/2+}$	+0.83	+0.97	+0.94
$\text{IrCl}_6^{2-/3-}$	+0.91	+0.94	+0.96
$\text{ClO}_2^{\bullet}/\text{ClO}_2^{-}$	+0.92	+0.94	
$\text{Os(terpy)}_2^{3+/2+}$	+0.93		+0.90

Harriman [11] and DeFilippis *et al.* [12] determined electrode potentials of +0.93 V and +0.94 V, respectively, by cyclic voltammetry and differential pulse polarography. As the tyrosyl radical dimerizes rapidly, the cathodic peak is hardly observable in a cyclic voltammogram. Still, with an equation derived by Nicholson [13], an electrode potential can be derived from the CV data. However, that equation was incorrectly modified by Harriman [11], and used as such by DeFillipis *et al.* [12]. While differential pulse polarography is very sensitive, it does not yield a reliable potential if the oxidation product undergoes subsequently a rapid reaction; for this reason we do not trust the value of +0.83 V by Nocera and coworkers [14].

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Supplementary Data Sheet S-5

Chemical equilibrium: $PhO^{\bullet} + PhNMe_2 \rightleftharpoons PhO^{-} + PhNMe_2^{\bullet+}$ (S-5.1)

$PhNMe_2$ = *N,N*-dimethylaniline
PhOH = phenol

$K = (69 \pm 7)$ from absorbance measurements, pH 12, $\mu = 0.18$, 2.7 mol L^{-1} ethylene glycol [1].
Taking $E°(PhO^{\bullet}/PhO^{-}) = +0.80$ V
$E^0(PhNMe_2^{\bullet+}/PhNMe_2) = +(0.69 \pm 0.01)$ V at $I = 0$

Discussion

The authors used a high concentration of ethylene glycol to help dissolve *N,N*-dimethylaniline, Furthermodynamicre, they used a linear accelerator, not a Febetron, thus the dose per pulse was lower.

Holcman and Sehested [2] report $PhNMe_2^{\bullet+} + HO^{-} \rightarrow PhNMeCH_2^{\bullet} + H_2O$ with $k \approx 1 \times 10^5$ L mol^{-1} s^{-1}, thus, at pH 12, $k \approx 1 \times 10^3$ s^{-1}

Earlier study:
Chemical equilibrium: $ClO_2^{\bullet} + PhNMe_2 \rightleftharpoons ClO_2^{-} + PhNMe_2^{\bullet+}$ (S-5.2)
$K = (15 \pm 5)$ from kinetics measurements at pH 9.6 [3].
Taking $E°(ClO_2^{\bullet}/ ClO_2^{-}) = +0.936$ V [4], $E°(PhNMe_2^{\bullet+}/PhNMe_2) = +(0.87 \pm 0.02)$ V.
The authors used a Febetron with a high dose per pulse. The limited solubility of $PhNMe_2$ is an issue here as the authors did not use ethylene glycol, with the consequence that, if not all $PhNMe_2$ was dissolved, K will be higher. We will not use this value.

Recommended value:

$E°(PhNMe_2^{\bullet+}/PhNMe_2) = +(0.69 \pm 0.01)$ V at $\mu = 0$.

List of auxiliary thermodynamic data
$pK_a(PhNMe_2H^{+}) = 5.1$

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Supplementary Data Sheet S-6

Chemical equilibrium: $I_2^{\bullet-} + CNPhO^- \rightleftharpoons 2I^- + CNPhO^\bullet$ (S-6.1)

CNPhOH = 4-cyanophenol

$K = 0.1$ M from absorbance measurements, 0.07 M from kinetics, pH 11 – 12 , $\mu = 1$ M [1].
Taking $E°(I_2^{\bullet-}/2I^-) = +1.03$ V (from Data Sheet 45)
$E°(CNPhO^\bullet/CNPhO^-) = +(1.09 \pm 0.03)$ V (the paper uses $E°(I_2^{\bullet-}/2I^-) = +1.06$ V and gives $E° = +1.12$ V)

$k_f = 7 \times 10^4$ L mol^{-1} s^{-1}, $k_r = 1 \times 10^6$ L mol^{-2} s^{-1}

This equilibrium constant is expected to be insensitive to ionic strength, so the derived electrode potential at 1 M H^+ may be regarded a standard potential.

List of auxiliary thermodynamic data
$pK_a(CNPhOH) = 7.95$

Recommended values:

$E°(CNPhO^\bullet/CNPhO^-) = +(1.09 \pm 0.03)$ V
$E°(CNPhO^\bullet, H^+/CNPhOH) = +1.56$ V
$E°'(\text{pH } 7) = +1.14$ V

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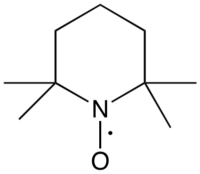
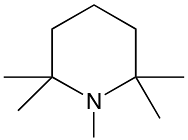
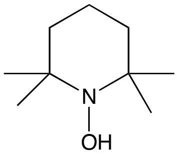
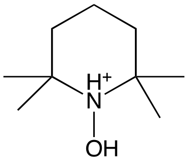
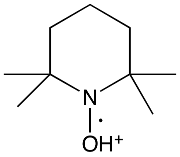
Supplementary Data Sheet S-7

Aqueous electrode potentials involving the nitroxyl radical TEMPO$^\bullet$.

Nitroxyl radicals: $R_2ON^\bullet$, TEMPO$^\bullet$ = 2,2,6,6-tetramethylpiperidine-1-oxyl

Abbreviations used here:

TEMPO$^\bullet$ =  TEMPO$^+$ =  TEMPOH = 

TEMPHOH$^+$ =  TEMPOH$^{\bullet+}$ = 

List of Reports.

Neimann *et al.* reported on the polarography (reduction at Hg) of TEMPO$^\bullet$ [1]. They note some specific medium effects, but these effects are not severe in alkaline media. Their data (Fig. 2) suggest $E°'$ ~ –250 mV vs SCE at pH 11 for reduction of TEMPO$^\bullet$ to TEMPOH, but the exact results are not clearly stated.

Golubev *et al.* [2] reported in 1975 on the acid-induced disproportionation of TEMPO$^\bullet$ and its reverse, both for kinetics and equilibrium constants. From the ratio of the forward and reverse rate constants they obtained $K_{\mathrm{disp}} = (3.3 \pm 0.2) \times 10^4\ \mathrm{M}^{-2}$ at 25 °C for the reaction

$$2\mathrm{TEMPO}^\bullet + 2\mathrm{H}^+ \rightleftharpoons \mathrm{TEMPO}^+ + \mathrm{TEMPHOH}^+ \qquad \text{(S-7.1)}$$

From the equilibrium concentration of TEMPO$^\bullet$ they obtained $K_{\mathrm{disp}} = (1.0 \pm 0.4) \times 10^4\ \mathrm{M}^{-2}$, in reasonable agreement with the kinetics result.

In 1976, Golubev *et al.* used potentiometry to determine $E°$ for TEMPO$^+$/TEMPO$^\bullet$: +(750 ± 5) mV vs NHE at 25 °C, extrapolating data at various ionic strengths to get a value at $\mu = 0$ M [3].

In 1977, Golubev *et al.* (1977) reported on the reaction of alcohols with oxoammonium ions [4]. These studies lead to a value for the comproportionation constant for TEMPO$^\bullet$: $K_{\text{disp}} = (3 \pm 1) \times 10^4$ M^{-2} at 25 °C for the following reaction:

$$2\text{TEMPO}^\bullet + 2\text{H}^+ \rightleftharpoons \text{TEMPO}^+ + \text{TEMPHOH}^+ \qquad \text{(S-7.2)}$$

This result is in good agreement with that of Golubev *et al.* from (1975) [2]. From this equilibrium constant, their prior value for $E°(\text{TEMPO}^{+/0})$, and their prior value for pK_a(TEMPOH) they [4] derived a value for the two-electron $E°$ for TEMPO$^+$/TEMPOH of +0.68 V vs NHE.

In 1986, Petrov and Kozlov used the reaction of tetranitromethane with nitroxyls to measure a rate constant k, which is assigned in terms of the following mechanism [5]:

$$\text{NO}_2^\bullet + \text{TEMPO}^\bullet \rightleftharpoons \text{NO}_2^- + \text{TEMPO}^+ \qquad K_{\text{et}} \qquad \text{(S-7.3)}$$
$$2\text{NO}_2^\bullet + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{NO}_2^- + \text{NO}_3^- \qquad k_{\text{NO2}} \qquad \text{(S-7.4)}$$

Thus, $k = k_{\text{NO2}}K_{\text{et}}$. With use of a literature value for k_{NO2} they derive $K_{\text{et}} = 8.8 \times 10^4$. An alternative method, using the steady-state concentration of TEMPO$^\bullet$, gave a value for K_{et} of 7×10^4. They combined K_{et} with a literature electrode potential for TEMPO$^{+/0}$ to derive $E° = +1.04$ V for NO$_2^\bullet$/NO$_2^-$, which is in good agreement with alternative determinations. Note that Goldstein *et al.* [6] subsequently reported rate constants for this reaction that disagree drastically with those of Petrov and Kozlov [5]; as discussed by Goldstein *et al.* [6], this disagreement does not, however, extend to the values of the equilibrium constant.

Fish *et al.* reported CV data on the TEMPO$^{+/0}$ redox couple [7]. They obtain $E°' = +0.49$ V vs SCE at $\mu = 0.08$ M, presumably at room temperature. We correct their potential to +0.73 V vs NHE.

Krishna *et al.* reported CV data on $\text{R}_2\text{NO}^+ + \text{e}^- \rightleftharpoons \text{R}_2\text{NO}$ for TEMPO$^\bullet$ [8]. They report $E°' = +722$ mV vs NHE at $\mu = 0.15$ M and 23 °C.

Kato *et al.* reported reversible CVs for reduction of TEMPO$^\bullet$ [9]. Inspection of their CV's, however, reveals that the reduction process is irreversible, with the two CV waves having a peak-to-peak separation of ~1.4 V. It is highly unlikely that thermodynamic data can be derived from such voltammograms.

Baur *et al.* reported CVs of nitroxyls, giving $E_{1/2} = +0.62$ V vs Ag/AgCl for $\text{TEMPO}^\bullet$ [10]. The data were obtained by rapid-scan voltammetry and hence the difference between the peak potentials is +360 mV. Accordingly, such data should not be used for obtaining accurate thermodynamic cell potentials.

Goldstein *et al.* reported the equilibrium constant for the following reaction, as determined from the ratios of the forward and reverse rate constants [11].

$$\text{TEMPO}^\bullet + \text{HO}_2^\bullet \rightleftharpoons \text{TEMPO}^+ + \text{HO}_2^- \qquad K = 0.86 \pm 0.22 \tag{S-7.5}$$

From this equilibrium constant and the $\text{HO}_2^\bullet/\text{HO}_2^-$ electrode potential they [11] derived $E°(\text{TEMPO}^+/\text{TEMPO}^\bullet) = +0.75$ V.

Goldstein *et al.* reported the equilibrium constant for reduction of TEMPO^+ by $\text{NO}^\bullet$ [12]:

$$\text{TEMPO}^+ + \text{NO}^\bullet + \text{H}_2\text{O} \rightleftharpoons \text{TEMPO}^\bullet + \text{HNO}_2 + \text{H}^+ \quad K = 0.045 \pm 0.005\ \text{M} \tag{S-7.6}$$

From this equilibrium constant and the $\text{NO}^\bullet/\text{HNO}_2$ electrode potential, they [12] derived $E°(\text{TEMPO}^+/\text{TEMPO}^\bullet) = +0.74$ V.

Sen and Golubev (2009) report on the kinetics of disproportionation of TEMPO in strong acid [13]. From the pH dependence in strongly acidic H_2SO_4 media they obtained the pK_a of the protonated TEMPO radical: p$K_a = -(5.8 \pm 0.3)$. This is in good agreement with Malatesta and Ingold's [14] prior estimate.

Meaningful interpretation of the comproportionation/disproportionation data requires knowledge of the pK_a's of R_2NHOH^+. Reports on this are summarized below.

Golubev *et al.* [2] reported for TEMPOH that $K_a = 1.26 \times 10^{-7}$ M at 25 °C and $\mu = 0$ M (pK_a = 6.90). They used the classical potentiometric titration method.

Kato *et al.* obtained pK_a = 7.95 for TEMPOH from the pH dependence of the reductive CVs of $\text{TEMPO}^\bullet$ [9]. The theoretical basis for obtaining pK_as from such data is not indicated, and we suspect that the results may refer to the pK_a of surface species at the graphite electrode.

Sosnovsky and Bell determined the pK_a potentiometrically at 20 °C, and obtained pK_a = 6.29 for TEMPOH [15].

Israeli *et al.* determined pK_a = (7.5 ± 0.2) by an electrochemical method [16]. The electrochemical determination used essentially the same method as was used by Kato *et al.* [9], and it likewise lacks theoretical justification.

Israeli *et al.* also determined pK_a = (7.5 ± 0.1) at 25 °C and unspecified ionic strength by a kinetic method [16]. The kinetics determination was based on the pH-dependence of the rate of comproportionation of $TEMPO^+$ with TEMPOH.

Discussion

The electrochemical data on the oxidation of $TEMPO^•$ to $TEMPO^+$ generally agree that $E°$ is near +730 mV vs NHE. The most reliable study appears to be that of Golubev *et al.* [3]; these workers used potentiometry, rather than CV, thermodynamic stated their solutions, and obtained data as a function of ionic strength. Support for this result also comes from the equilibrium constants determined for the reactions with $HO_2^•$, $NO_2^•$, and $NO^•$, but none of these can be considered as accurate as the direct potentiometric measurement of Golubev *et al.* [3].

Of the four reports on the pK_a of TEMPOH, the one by Kato *et al.* [9] can be rejected on the grounds that it has no theoretical justification. The electrochemical determination by Israeli *et al.* [16] used essentially the same method as was used by Kato *et al.* [9] and is likewise rejected. The kinetic determination by Israeli *et al.* [16] appears reliable but differs substantially from the two potentiometric determinations. The other two (Golubev *et al.* [2] and Sosnovsky and Bell [15] used the same method, potentiometric titration, and would be expected to give highly accurate results; the outcome, however, is unsatisfactory, with the two pK_a reports differing by 0.6 units. The temperature difference between the two studies is unlikely to cause such a large difference in pK_a. This outcome is rather unsatisfactory, with the reports of Israeli *et al.* [16], Golubev *et al.* [2], and Sosnovsky and Bell [15] leading to an average pK_a of 6.9 ± 0.6. Sen and Golubev have reinvestigated this problem very recently [13]. They claim that the addition of OH^- to $TEMPO^+$ in alkaline media was not taken into account in the voltammetric and kinetic studies of Israeli *et al.*, and that this will perturb the apparent pK_a significantly. Thus, they place great confidence in their pK_a of (6.90 ± 0.02).

The Golubev *et al.* reports [2, 4] on the disproportionation of $TEMPO^•$ are in good agreement, leading to a recommended value of $K_{disp} = (3 \pm 1) \times 10^4$ M^{-2}. If we then use the recommended values for $E°(\text{TEMPO}^{+/0})$ and $\mathrm{p}K_\mathrm{a}$(TEMPOH), we derive $E° = +(0.61 \pm 0.04)$ V for $\text{TEMPO}^\bullet,\text{H}^+/\text{TEMPOH}$.

Recommended values:

$\text{TEMPO}^+ + e^- \rightleftharpoons \text{TEMPO}^\bullet$ $E° = +(0.750 \pm 0.005)$ V.
$\text{TEMPHOH}^+ \rightleftharpoons \text{TEMPOH} + \text{H}^+$ $\mathrm{p}K_\mathrm{a} = (6.90 \pm 0.02)$
$\text{TEMPO}^\bullet + \text{H}^+ + \text{e}^- \rightleftharpoons \text{TEMPOH}$ $E° = +(0.61 \pm 0.04)$ V
$2\text{TEMPO}^\bullet + 2\text{H}^+ \rightleftharpoons \text{TEMPO}^+ + \text{TEMPHOH}^+$ $K_\mathrm{disp} = (3 \pm 1) \times 10^4\ \mathrm{M}^{-2}$

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Supplementary Data Sheet S-8

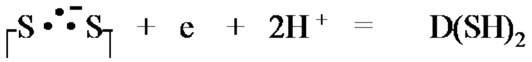
Penicillamine Thiyl Radical.
Couple: $PenS^{\bullet}$, H^{+}/PenSH, (Pen = $-CMe_2-C(NH_2)H-CO_2^{-}$).

Published value(s):
Method: Pulse radiolysis **Solvent:** Water
Measurement by electron transfer equilibrium:

$$PenS^{\bullet} + D(SH)_2 = PenSH + H^{+} + DS_2^{\bullet-}$$

(S-8.1)

Reference: Dithiothreitol (dithiothreitol = (*2S,3S*)-1,4-bis(sulfanyl)butane-2,3-diol, $C_4H_{10}O_2S_2$):



$$DS_2^{\bullet-} + e + 2H^{+} = D(SH)_2$$

(S-8.2)

Other solutes: Gas: N_2O Buffer: Phosphate
pH = 7.0. Ambient temperature stated to be: (296.2 ± 2) K. Ionic strength: 0.01 M.
Ionic strength effects estimated: Yes.
Observed equilibrium constant/measurement corresponds to ΔE = (0.38 ± 0.02) V [1].

Reference electrode potential: $E°(DS_2^{\bullet-},2H^{+}/D(SH)_2) = +(1.75 \pm 0.03)$ V vs NHE [2].
Standard electrode potential of couple: +(1.37 ± 0.03) V vs NHE.

Recommended value:

$$E°(PenS^{\bullet},H^{+}/PenSH) = +(1.37 \pm 0.03)\ V$$

Comments:

The thiyl radical of penicillamine and other thiols abstracts, to a limited extent ($K \sim 0.1$ for penicillamine), H from the α-carbon [3]. This hydrogen-atom transfer equilibrates rather rapidly ($k_f + k_r = 1.5 \times 10^{6}\ s^{-1}$ for $PenS^{\bullet}$ [4]), and thus, on the time-scale that bimolecular redox equilibria are attained by pulse radiolysis, the equilibrium constants for reaction S-8.1 and others involving "$PenS^{\bullet}$" will reflect the contribution of the carbon-centered form of the "thiyl" radical. Thus, the recommended value given above for $E°(PenS^{\bullet},H^{+}/PenSH)$ is not strictly a thiyl radical potential. Nevertheless, when this redox couple is used in establishing electron-transfer equilibria for the $CO_2^{\bullet-}$ and $PO_3^{\bullet2-}$ radicals (Data Sheets 96 and 98) the net result should not be compromised by this effect.

An estimate of (1.63 ± 0.03) V for $E^{o}(DS_2^{\bullet-}/D(SH)_2)$ can be obtained by extrapolation of $E^{o\prime}$ = +0.81 V at pH 7 [5]. The value at pH 7 was obtained by combining several quantities: one was obtained by making the assumption that $E^{o\prime}(D(S^{\bullet})(SH),H^{+}/D(SH)_2) = E^{o\prime}(GS^{\bullet},H^{+}/GSH) =$ 0.92 V at pH 7. Another was the equilibrium constant (K_1) for formation of $DS_2^{\bullet-}$ from $D(S^{-})(S^{\bullet})$ ($= 7.9 \times 10^{3}$), which was calculated from two other reactions:

$$D(S_2H^{\bullet}) \rightleftharpoons D(S_2^{\bullet-}) + H^{+} \qquad K_a(DS_2H^{\bullet}) \qquad \text{(S-8.3)}$$

$$D(SH)(S^{\bullet}) \rightleftharpoons D(S^{-})(S^{\bullet}) + H^{+} \qquad K_a(D(SH)(S^{\bullet}) \qquad \text{(S-8.4)}$$

$$D(S^{-})(S^{\bullet}) \rightleftharpoons D(S_2^{\bullet-}) \qquad K_1 = K_a(DS_2H^{\bullet})/K_a(D(SH)(S^{\bullet}) \qquad \text{(S-8.5)}$$

A value of 6.3×10^{-6} M was used for $K_a(DS_2H^{\bullet})$, as measured by Akhlaq and von Sonntag [6]; it should be noted that Akhlaq and von Sonntag expressed the opinion that their K_a value actually is an overall acid dissociation constant for the sum of $D(S_2H^{\bullet})$ and $D(SH)(S^{\bullet})$. A value of 7.9×10^{-10} M was used for $K_a(D(SH)(S^{\bullet})$, assumed to be equal to the first K_a of $D(SH)_2$. Given the approximations made, the estimate of +1.63 V [5] should be regarded as support for the experimental value of +1.75 V [2].

pK_a values:
Radical values (lowest first): pK_{s1} None [7].
Reductant values (lowest first): pK_{s1} = 7.9; pK_{s2} = 10.46 [8].

References

1. P. S. Surdhar, D. A. Armstrong. *J. Phys. Chem.* **91**, 6532-6537 (1987).
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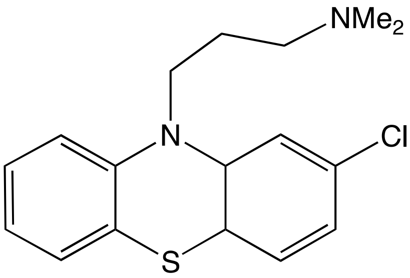
5. T. Nauser, D. Steinmann, G. Grassi, W. H. Koppenol. *Biochemistry* **53**, 5017-5022 (2014).
6. M. S. Akhlaq, C. von Sonntag. *Z. Narturforsch.* **42c**, 134-140 (1987).
7. J. W. Purdie, H. A. Gillis, N. V. Klassen. *Can. J. Chem.* **51**, 3132-3142 (1973).
8. E. W. Wilson, R. B. Martin. *Arch. Biochem. Biophys.* **142**, 445-454 (1971).

Supplementary Data Sheet S-9

Subject: Chlorpromazine radical cation.

Chlorpromazine IUPAC PIN: 3-(2-chloro-10*H*-phenothiazin-10-yl)-*N*,*N*-dimethylpropan-1-amine

Couple type: $CPZH^{\bullet 2+} + e^{-} \rightleftharpoons CPZH^{+}$



= CPZ

The conjugate acid of the amine sidechain of CPZ has pK_a ~ 8, and the pK_a of the radical cation is ~ 7, so below pH 6 both components of the redox couple are protonated [1]. Wardman (1989) cited four reports published prior to 1989 on *E*° for CPZ, the values ranging from 766 mV to 844 mV, and he recommended *E*° = +0.78 V [2]. Madej and Wardman (2006) have reinvestigated this system carefully, both by pulse radiolysis and cyclic voltammetry, and they arrived at a significantly revised potential [1].

List of reports:

E°' = +0.541 V vs NCE (normal calomel electrode) in 0.1 N H_2SO_4, presumably at room temperature. Kabasakalian and McGlotten [3] obtained this result polarographically. Correction of this to NHE (+0.280 V) leads to *E*°' = +0.821 V vs NHE. Later workers argue that the radical is unstable at this pH [4, 5].

Polarographic oxidation of $CPZH^+$ to the radical occurs with *E*°' ~ +0.4 V vs SCE in 12 N H_2SO_4, presumably at room temperature [4]. The high acid concentration was used to stabilize the radical.

$E_{1/4}$ = +0.570 V vs Ag/AgCl in 3 M H_2SO_4, presumably at room temperature [5]. Result obtained by chronopotentiometry. Correction of $E_{1/4}$ to NHE (addition of 0.197 V) leads to $E°'$ = +0.767 V vs NHE. Patriarche and Lingane [5] cited the prior work of Merkle and Discher [4], claimed the oxidation of $CPZH^+$ to be reversible, and made no comment regarding apparent irreversibility in the work of they cited.

$E°'$ = +0.78 V in 1.0 M $HClO_4$ at 25.0 °C [6]. Obtained from the equilibrium constant for the oxidation of $CPZH^+$ by Fe^{3+} and taking $E°'$ = +0.738 V for Fe(III)/Fe(II) in this medium. Note that no tests were performed to determine whether Fe(III) or Fe(II) binds CPZ in any of its forms.

$E°'$ = +0.83 V in 0.01 M phosphate buffer at pH 6 [7]. Surdhar and Armstrong cite unpublished CV results of Hinman and Surdhar for this value.

$E°$ = +0.859 – +0.864 V vs NHE at room temperature (23 ± 2 °C), extrapolated from data in 0.1 M KCl [1]. Data obtained by cyclic voltammetry with a sweep rate of 100 mV s^{-1} with a macroelectrode and 10 mV s^{-1} with a microelectrode. The CV experiments showed that the couple is reversible and that $E°$ is constant over the pH range from 3 to 6.

$E°'$ = +0.614 V vs SCE in 0.1 M phosphate buffer at pH 2 at (20 ± 2) °C, by cyclic voltammetry [8]. We adjust this value to NHE by adding 0.241 V to obtain $E°'$ = +0.855 V.

Discussion

Madej and Wardman used pulse radiolysis to measured equilibrium constants for electron transfer between $CPZH^+$ and 5 other phenothiazines [1]. They also used cyclic voltammetry to determine $E°$ for these 5 other phenothiazines, and they got excellent agreement between the 5 measured electron-transfer equilibrium constants and the equilibrium constants calculated from $\Delta E°$.

The results of Mielech-Lukasiewicz *et al.* [8] are in good agrement with those of Madej and Wardman [1], but the former were not obtained with the objective of determining an accurate value of $E°$. For this reason we prefer the result of Madej and Wardman.

The disagreement between the results of Madej and Wardman and the prior studies most likely reflects the combined effects of unrecognized radical reactions at the relatively long time scales of the prior studies, the high acidity of the prior studies, and the possibility of Fe^{3+} binding to CPZ. The mild disagreement between the results of Madej and Wardman and those cited by Surdhar and Armstrong [7] is disregarded because of the incomplete publication status of the latter. Overall, we recommend the result of Madej and Wardman, including their indicated uncertainty of ± 10 mV.

Recommended value:

$CPZH^{\bullet 2+} + e^- \rightleftharpoons CPZH^+$ $E° = +(0.860 \pm 10)$ mV between pH 5 to 7.

References:

1. E. Madej, P. Wardman. *Rad. Phys. Chem.* **75**, 990-1000 (2006).
2. P. Wardman. *J. Phys. Chem. Ref. Data* **18**, 1637-1755 (1989).
3. P. Kabasakalian, J. McGlotten. *Analyt. Chem.* **31**, 431-433 (1959).
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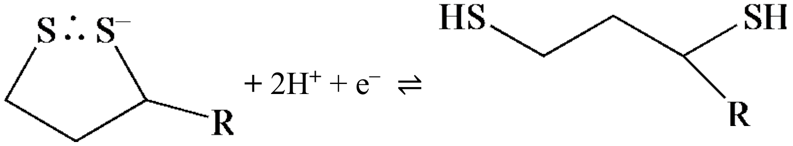
Supplementary Data Sheet S-10

Disulphide Anion Radical of Lipoamide,
Dihydrolipoamide = HS-CH_2-CH_2-C(SH)H-$(CH_2)_4$-$CONH_2$, (L$(SH)_2$).

Couple:



References:

Armstrong, D. A., “*Thermodynamicchemistry of Sulfur Radicals*” in “*S-Centered Radicals*”, Chapter 2, Alfassi, Z. B. Ed., Wiley, New York 1999;
Surdhar, P. S.; Armstrong, D. A. *J. Phys. Chem*. **1987**, *91*, 6532.

Published value(s):

Method: Pulse radiolysis Solvent: Water

Measurements by electron transfer equilibrium:

$$\text{S}\dot{\because}\text{S}^{-} + \text{PhOH} + \text{H}^{+} = \text{HS}\text{———}\text{SH} + \text{PhO}\bullet$$

Reference: PhO$^\bullet$, H$^+$/PhOH

Other solutes:

Gas: N_2O Buffer: Phosphate

pH = 9. Temperature: Ambient temperature stated to be: (296 ± 2) K. Ionic strength: 0.010 M.

Uncorrected equilibrium constant from concentrations: 3.2×10^{-8}.

Ionic strength effects estimated: Yes.

Corrected equilibrium constant given: 2.5×10^{-8} (calculated allowing for ionisation of reactants and ionic strength effects on the redox reaction).

Observed equilibrium constant/measurement corresponds to $\Delta E = (0.45 \pm 0.03)$ V.

Reference potential assumed: $E° = +(1.38 \pm 0.03)$ V.

Standard electrode potential of the couple as indicated by author: +(1.83 V ± 0.03) V vs NHE.

Discussion

No correction for ionic strength effects is nececessary. Surdhar and Armstrong's paper does not mention whether one of the enantiomers of dihydrolipoamide or a racemic mixture was used; however, the results should not depend on this aspect of the stereochemistry.

References:

Armstrong, D. A, “*Thermodynamicchemistry of Sulfur Radicals*” in “*S-Centered Radicals*”, Chapter 2, Alfassi, Z. B. Ed., Wiley, New York 1999.
Surdhar, P. S.; Armstrong, D. A. *J. Phys. Chem*. **1987**, *91*, 6532.

Method: Pulse radiolysis Solvent: Water

Measurements by electron transfer equilibrium:

$$\mathrm{RS^{\bullet} + L(SH)_2 = RSH + H^{+} + \ulcorner S \overset{\bullet}{\bullet\bullet} \bar{S} \urcorner}$$

RSH = β-mercaptoethanol = $HSCH_2CH_2OH$

Reference: $RS^{\bullet}$, H^{+}/RSH

Other solutes: Gas: N_2O Buffer: Phosphate

pH = 7. Temperature: Ambient temperature stated to be: (296.2 ± 2) K. Ionic strength: 0.01 M.

Ionic strength effects estimated: Yes.

Corrected equilibrium constant given: 4.3×10^{-7} (calculated for pH = 0.0).

Observed equilibrium constant/measurement corresponds to $\Delta E° = 0.37$ V.

Reference potential assumed: $E° = +(1.35 \pm 0.03)$ V

Standard electrode potential of couple indicated by author: +1.72 V vs NHE.

Reviewer's revised calculations

No correction for ionic strength effects is nececessary.

Average from the two equilibria = (1.78 ± 0.06) V.

Other data

Oxidant pK_a values (lowest first): pK_{o1} PhOH = 1×10^{-10}

References: Biggs, A. I.; Robinson, R. A. *J. Chem. Soc.* **1961**, 388; Chen, D. T. Y.; Laidler, K. J. *Trans. Faraday. Soc.* **1962**, *58*, 480.

Radical values (lowest first): $L(S)_2H^{\bullet}$, pK_{s1} = 5.85.

Reference: von Sonntag, C. "*The Chemical Basis of Radiation Biology*", Taylor and Francis, London (1987), p 359.

$L(SH)_2$ values (lowest first): pK_{s1} = 10.4; pK_{s2} = 11.0.

References: Gascoigne, I. M.; Radda, G. K. Biochim. Biophys. Acta **1967**, *131*, 498; Szajewski, R. P.; Whitesides, G. M.; *J. Am. Chem. Soc.* **1980**, *102*, 2011.

Reviewers' evaluation

There are sufficient experimental details available to evaluate data

Supplementary Data Sheet S-11

Chemical equilibrium

$$\mathrm{MeOPhNH_2^{\bullet+} + Pz^{+} = MeOPhNH_2 + Pz^{\bullet 2+}} \qquad \text{(S11.1)}$$

$\mathrm{MeOPhNH_2}$ = 4-methoxyaniline;

Pz = promethazine; IUPAC PIN: N,N-dimethyl-2-(10H-phenothiazin-10-yl)propan-2-amine

List of Reports

$K = 9.3 \times 10^{-3}$ from absorbance, ($\approx 6.7 \times 10^{-3}$ from kinetics), pH 5.7, $\mu \approx 0.010$ M [1]. Data obtained by pulse radiolytic generation of the $\mathrm{N_3^{\bullet}}$ as the primary oxidant.

Discussion

Jonsson *et al.* derived $E°(\mathrm{MeOPhNH_2^{\bullet+}/MeOPhNH_2}) = +(0.79 \pm 0.02)$ V by using a value of +0.91 V for $E°(\mathrm{Pz^{\bullet 2+}/Pz^{+}})$ [1] and assuming that the value of K(S11.1) is independent of ionic strength. This latter assumption was based on the concept that the net charge on a side chain of promethazine, remote from the reactive site, does not introduce ionic strength dependence (see footnote 33 of [1]). However, this concept overlooks that the activity coefficients of the reactants and products in equilibrium such as S11.1 are independent of the structure of the transition state, and, for the calculation of activity coefficients with the Debye-Hückel theory, it is the net charge that counts. On the other hand, the measurement of K(S11.1) was performed at a rather low ionic strength (0.01 M), so the correction to zero ionic strength should be rather small.

Subsequent to the work of Jonsson *et al.* the promethazine potential has been extensively reinvestigated [2]. If we adopt the revised $E°(\mathrm{Pz^{\bullet 2+}/Pz^{+}}) = +0.925$ V [2], then we obtain $E°(\mathrm{MeOPhNH_2^{\bullet+}/MeOPhNH_2}) = +(0.80 \pm 0.02)$ V. The 20 mV uncertainty encompasses the uncertainties introduced by the ionic-strength issue noted above, enabling the potential to be regarded as a standard potential.

Recommended value:

$E°(\mathrm{MeOPhNH_2^{\bullet+}/MeOPhNH_2}) = +(0.80 \pm 0.02)$ V

List of auxiliary thermodynamic data:

$pK_\mathrm{a}(\mathrm{MeOPhNH_3^{+}}) = 5.3$; $pK_\mathrm{a}(\mathrm{MeOPhNH_2^{\bullet+}}) = 9.6$ [1]

References

1. M. Jonsson, J. Lind, T. E. Eriksen, G. Merényi. *J. Am. Chem. Soc.* **116**, 1423-1427 (1994).
2. E. Madej, P. Wardman. *Rad. Phys. Chem.* **75**, 990-1000 (2006).

Supplementary Data Sheet S-12

Tryptophan

Chemical equilibrium

$$\mathrm{ClO_2^{\bullet} + TrpH \rightleftharpoons ClO_2^{-} + TrpH^{\bullet +}} \tag{S-12.1}$$

TrpH = tryptophan

$K = (1.6 \pm 0.6) \times 10^{-5}$ from kinetics, pH 4, $\mu = 0.5$ M [1].
At $\mu = 0$, $K = (8.1 \pm 3.2) \times 10^{-6}$.
Taking $E°(\mathrm{ClO_2^{\bullet}/ClO_2^{-}}) = 0.936$ V (Data Sheet 24 recommends 0.935 ± 0.003 V)
$E°(\mathrm{TrpH^{\bullet +}/TrpH}) = +(1.24 \pm 0.01)$ V
$k_\mathrm{f} = (8.8 \pm 3.1) \times 10^{3}$ L mol^{-1} s^{-1}, $k_\mathrm{r} = (5.5 \pm 0.2) \times 10^{8}$ L mol^{-1} s^{-1}

List of auxiliary thermodynamic data
pK_a (Trp) = 2.38, 9.39
pK_a ($\mathrm{TrpH^{\bullet +}}$) = 4.3 [2]
$E(\mathrm{Trp^{\bullet}, H^{+}/TrpH})$(pH 7) = +1.08 V (assuming pK_a values of amino and carboxyl groups are the same in the radical and parent molecule).

Chemical equilibrium

$$\mathrm{(tacn)_2Ni^{3+} + TrpH \rightleftharpoons (tacn)_2Ni^{2+} + Trp^{\bullet} + H^{+}} \tag{S–12.2}$$

$\mathrm{(tacn)_2Ni^{3+}}$ = bis(1,4,7-triazacyclononane)Ni(III)

$K = (0.10 \pm 0.03)$ from absorbance, (0.104 ± 0.03) from kinetics, pH 7, $\mu = 0.1$ M [3]
Taking $E°(\mathrm{(tacn)_2Ni^{3+}/(tacn)_2Ni^{2+}}) = +0.95$ V [4]
$E(\mathrm{Trp^{\bullet}, H^{+}/TrpH})$(pH 7) = 1.01 V
$k_\mathrm{f} = (5 \pm 1) \times 10^{4}$ L mol^{-1} s^{-1}, $k_\mathrm{r} = (4.8 \pm 0.5) \times 10^{5}$ L mol^{-1} s^{-1}

Chemical equilibrium

$$\mathrm{Pz^{\bullet 2+} + TrpH \rightleftharpoons Pz^{+} + Trp^{\bullet} + H^{+}} \tag{S-12.3}$$

Pz = promethazine

$K = 5.5 \times 10^{-3}$ from absorbance, $(5.7 \pm 1) \times 10^{-3}$ from kinetics, pH 6, $\mu = 0.1$ M [3]
Taking $E°(\mathrm{Pz^{\bullet 2+}/Pz^{+}}) = +0.925$ V [5]

$E(\mathrm{Trp}^{\bullet}, \mathrm{H}^{+}/\mathrm{TrpH})(\mathrm{pH}\ 6) = +1.06$ V, $E(\mathrm{Trp}^{\bullet}, \mathrm{H}^{+}/\mathrm{TrpH})(\mathrm{pH}\ 7) = +1.00$ V
$k_\mathrm{f} = (6.2 \pm 1) \times 10^{5}\ \mathrm{L\ mol^{-1}\ s^{-1}}$, $k_\mathrm{r} = (1.1 \pm 0.1) \times 10^{8}\ \mathrm{L\ mol^{-1}\ s^{-1}}$

Chemical equilibrium

$$\mathrm{X}^{\bullet} + \mathrm{TrpH} \rightleftharpoons \mathrm{X}^{-} + \mathrm{Trp}^{\bullet} + \mathrm{H}^{+} \qquad \text{(S-12.4)}$$

K values not given, experiments at pH 7 [6]

Based on $E°(\mathrm{X}^{\bullet}/\mathrm{X}^{-})$/V		$E(\mathrm{Trp}^{\bullet}, \mathrm{H}^{+}/\mathrm{TrpH})$/V at (pH 7)	
		from kinetics	from absorbance
$\mathrm{ClO_2}^{\bullet}/\mathrm{ClO_2}^{-}$	+0.92	+1.03	+1.04
$\mathrm{Os(terpy)_2}^{3+/2+}$	+0.93	+1.06	+1.03
$\mathrm{NO_2}^{\bullet}/\mathrm{NO_2}^{-}$	+1.03	+1.07	
$\mathrm{Fe(bpy)_3}^{3+/2+}$	+1.05	+1.09	+1.00

Average value given $E(\mathrm{Trp}^{\bullet}, \mathrm{H}^{+}/\mathrm{TrpH})(\mathrm{pH}\ 7) = (+1.05 \pm 0.01)$ V at 298 K

Recommended values:

$E°(\mathrm{TrpH}^{\bullet+}/\mathrm{TrpH}) = +(1.24 \pm 0.01)$ V at $\mu = 0$.
$E°'(\mathrm{Trp}^{\bullet},\mathrm{H}^{+}/\mathrm{TrpH})$ at pH 7: $+(1.03 \pm 0.02)$ V.

Harriman [7] and DeFelippis *et al.* [8] determined electrode potentials of +1.015 V and +1.02 V at pH 7, respectively, by cyclic voltammetry and differential pulse polarography. Although these values fit with the recommended value, they are based on a formula derived by Nicholson [9] that was incorrectly modified by Harriman [7]. Recent cyclic voltammetry experiments yield $+(0.99 \pm 0.01)$ V at pH 7 (L. Mahmoudi, R. Kisner, T. Nauser, W. H. Koppenol, 2014, unpublished.)

Nomenclature: tryptophan, (2*S*)-2-amino-3-(1*H*-indol-3-yl)propanoic acid.

References

1. G. Merényi, J. Lind, X. Shen. *J. Phys. Chem.* **92**, 134-137 (1988).

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5. E. Madej, P. Wardman. *Rad. Phys. Chem.* **75**, 990-1000 (2006).

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9. R. S. Nicholson. *Analyt. Chem.* **37**, 667-671 (1965).