

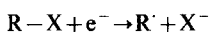
Electron Transfer Reactions in Organic Chemistry. II.*

An Analysis of Alkyl Halide Reduction by Electron Transfer Reagents on the Basis of the Marcus Theory

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The electron transfer reduction of alkyl halides has been discussed in terms of the Marcus theory as a possible model for an irreversible electron transfer process. An important feature of this treatment is a transition state for electron transfer with a virtually broken C–halogen bond, resulting in a prediction of a large value of the bond and solvent reorganization energy parameter λ of the Marcus equation. For such a mechanism it is logical to use E° values pertaining to the half reaction



and accordingly E° values were worked out for a series of alkyl halides in a number of solvents of particular interest.

A number of alkyl halide reductions of varying type (by $e^-(aq)$, aromatic radical anions, Co(I), Co(II), Fe(I), Fe(II), Cr(II), and Mo(0)) was found to conform reasonably well to these postulates; for the whole data set a λ value of 46 kcal mol⁻¹ could be estimated. Further analysis of different sub-sets revealed a weak trend of increasing λ 's in the order RI < RBr < RCl, consistent with a predicted dependence of λ upon the C–halogen bond strength. It was also shown that a typical S_N2 process involving alkyl halides (the Finkelstein reaction) displays a log $k/\Delta G^\circ$ behaviour dramatically different from that of the reactions mentioned above.

In conclusion, the Marcus theory appears to be as well applicable to irreversible as reversible electron transfer in organic systems and hence should constitute a valuable tool in physical organic chemistry.

The Marcus theory was originally adapted for relating kinetic and thermodynamic parameters of *outer-sphere* electron transfer between metal complexes,^{1–4} i.e. for reactions in which the inner coordination shells of the participating metal ions are intact in the transition state. No *ligand-to-metal bond* is broken or formed in the transition state; on the other hand, an outer-sphere mechanism does not exclude *atom or group transfer, such as hydrogen atom transfer, between ligands* in the transition state.

As one tries to adapt the Marcus theory to organic electron transfer processes, the study of which is now a rapidly developing area,⁵ it is found^{5a} that the majority of cases conform reasonably well to its conceptual and mathematical framework, as long as the electron transfer step is *reversible* (1). In eqn. (1) R represents an organic species and Ox (Red)

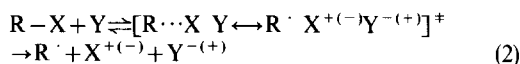


an inorganic or organic oxidant (reductant) capable of accepting (donating) one electron from (to) R. The transition state conforms to the Marcus model: An electron is transferred between two species with very little (<1 kcal mol⁻¹) resonance interaction, and with an energy barrier largely originating from the Franck-Condon restrictions, i.e. that electron transfer takes place on a time scale in which the positions of all atomic nuclei are frozen. In the terminology of Marcus' theory this means that the height of the barrier is made up from two contributions, namely solvent and bond reorganization energy (λ_o and λ_i , respectively). The total reorganization energy λ , the sum of λ_o and λ_i ,

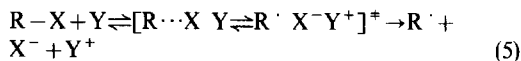
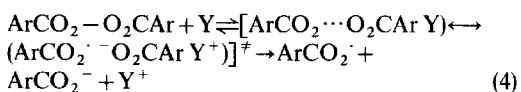
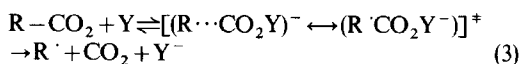
* Part I of this series, see Ref. 5a.

can either be estimated from extrakinetic quantities or determined experimentally.

Problems arise when the limits of the Marcus model are stretched to include *irreversible* processes, involving simultaneous electron transfer and bond cleavage, of which there are several important classes in organic chemistry.^{5a,6} Such reactions are not analogous to the inner-sphere reactions of coordination chemistry, since there is no real analogy to the bridging ligand inherent in this concept. Possible examples of irreversible organic electron processes are the oxidation of carboxylates (3),⁷ the reduction of diaryl peroxides (4)^{6,8} and the reduction of alkyl halides (5).⁹ In these cases, a general description of the transition state can be given as in eqn. (2), where R is an organic moiety, X



is a leaving group of some kind and Y represents a one-electron redox species. The following features of the transition state differ from the original Marcus model: In the reactants' transition state the R-X bond is stretched to the point of breaking and the products' transition state is formulated without any bond between R[·] and X⁺⁽⁻⁾, but with all nuclear positions identical to those of the reactants' transition state. For the three cases mentioned above, the transition states should accordingly be formulated as in eqns. (3)–(5).



If we postulate this model for the transition state of a simultaneous electron transfer/bond cleavage reaction it immediately follows that the reorganization energy (λ) for the process must be large. We actually invoke cleavage of a single bond in the transition state (a large λ_i), and such a drastic change is also likely to involve a large solvent reorganization energy (λ_o). In addition, the E° of the R-X redox half reaction must be the one pertaining to eqns. (6) and (7) (note that the sign convention for

E° values trivially reverses reactions in which RX is oxidized).



The *electrochemistry* of carboxylates¹⁰ and alkyl halides^{9,11} has been discussed as possible synchronous electron transfer/bond cleavage processes already in the 50's and 60's. Both reactions have all the experimental characteristics of being electrochemically irreversible, *i.e.* the rate-determining step is a slow, heterogeneous electron transfer, and calculated E° values for (6) and (7) were in agreement with this finding. In the case of carboxylate oxidation, the E° of eqn. (8) was far too high to be compatible with irreversibility in the electrochemical sense.¹⁰ However, these ideas were not universally

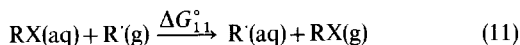
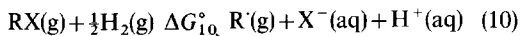
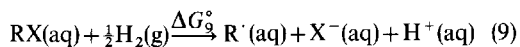


accepted among practitioners of organic electrochemistry, especially not for carboxylate oxidation. For alkyl halide reduction, the problem of the possible stability of (R-X)⁻ has been kept open for discussion for a long time,¹² and still presents an experimental as well as theoretical challenge.^{13,14} In connection with a review of the possible use of the Marcus theory on organic electron transfer reactions,^{5a} it was noted that kinetic data for alkyl halide reduction by different classes of electron transfer reductants could not be completely accommodated within the formalism of the Marcus theory when standard free energy changes were estimated on the basis of Hush's original E° values for alkyl halide reduction.⁹ These were calculated for eqn. (6), R=CH₃, X=Cl, Br, I, in aqueous solution. Since we now have good quantitative measures of how ionic solvation changes with solvent, it was deemed of interest to extend calculations of E° for alkyl halide reductions to organic solvents as well, especially those for which data allowing a comparison between experiment and theory are available. In this paper results from such estimates are reported, and pertinent kinetic data for alkyl halide reduction are analyzed on this basis.

RESULTS

In his calculation of standard electrode potentials of methyl halide reductions, Hush⁹ split the free

energy change of reaction (9) ($R = CH_3$), the required quantity for estimating E° in aqueous solution, into two parts, namely reactions (10) and (11). Then ΔG_9° is simply obtained as the sum of ΔG_{10}° and ΔG_{11}° .



The advantage of this treatment is that ΔG_{10}° can be obtained in terms of easily available thermodynamic data, whereas ΔG_{11}° simply is the difference in the standard free energy of solution in water of $R'(g)$ and $RX(g)$, respectively. For the former species, data for $RH(g)$ was used as a reasonable approximation for those of $R'(g)$.

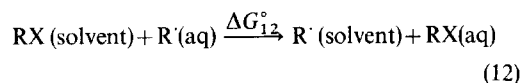
Calculations of E° for $CH_3X/CH_3^\cdot + X^-$ couples in aqueous solution were repeated using modern thermodynamic data¹⁵⁻¹⁸ and are shown in Table 1. The new E° values are slightly more negative than Hush's original ones, which is due to changes in the ΔG_{10}° values. The difference between $\Delta G_9^\circ(CH_3Br)$ and $\Delta G_9^\circ(CH_3I)$ is now -1.7 kcal mol⁻¹ (previously -0.8 kcal mol⁻¹), in satisfactory agreement with the experimental value,¹⁹ -1.66 kcal mol⁻¹. Values for ΔG_{11}° were obtained from a recent critical evaluation of the thermodynamics of gas dissolution in water.²⁰ They are practically identical with those used by Hush.⁹

In Table 2, column 2, this treatment has been extended to ethyl, propyl, isopropyl, butyl, *t*-butyl, allyl and benzyl halides. Almost all data for obtaining ΔG_{10}° are available in standard tables whereas in all cases the ΔG_{11}° values were put equal

to those of the methyl halides. For reasons which will be obvious later it is important to establish the lower limit of E° , and since ΔG_{11}° is expected to exhibit its largest value for the methyl halides, this assumption affects the E° values in the correct direction.

The aqueous E° values were then converted to E° values for a number of solvents of interest in connection with electron transfer reactions of alkyl halides (Table 2, columns 3-7). This was done using the single ion free energies of transfer from water to other solvents listed by Cox *et al.*²² For fluoride ion, only $\Delta G_{tr}^\circ(H_2O \rightarrow DMF)$ and $\Delta G_{tr}^\circ(H_2O \rightarrow MeOH)$ are known, and were therefore approximated by those of AcO^- in the other solvents. This approximation has been shown to be a reasonable one in other context.* No ΔG_{tr}° values for THF are available, so these were approximated for the halide ions as those pertaining to DMF and for H^+ that for transfer to MeOH. For acetonitrile, the most positive value of $\Delta G_{tr}^\circ(H^+)$ is 11 kcal mol⁻¹ (used for calculation of the values in column 6, Table 2),²⁴ but it should be noted that lower values of 3.3 and 6.9 kcal mol⁻¹ have been estimated by other authors,²⁵ leading to values of E° that should be higher than those of column 6, Table 2, by 0.3 and 0.18 V, respectively.

In all cases no estimates were made of the free energies of transfer of the neutral species of eqn. (9) from water to the appropriate solvent. Instead, it is assumed that ΔG_{12}° (see eqn. (12)) is 0 which is in



* Ref. 23a; one might also use data^{23b} for the "fluoride-like" O_2^- ($\Delta G_{tr}^\circ[H_2O \rightarrow DMF] \approx 13.5$ kcal mol⁻¹, $\Delta G_{tr}^\circ[H_2O \rightarrow DMSO] \approx 12.3$ kcal mol⁻¹) but the result would be almost identical.

Table 1. Calculation of E° values for $CH_3X(aq) + e^- \rightarrow CH_3^\cdot(aq) + X^-(aq)$ according to the method given by Hush. Hush's original values are given within brackets.⁹ Data were taken from Refs. 15-18 unless otherwise stated.

X	$\Delta G_{10}^\circ/\text{kcal mol}^{-1a}$	$\Delta G_{11}^\circ/\text{kcal mol}^{-1}$	$\Delta G_9^\circ/\text{kcal mol}^{-1}$	$-E^\circ/\text{V vs. NHE}$
F	18.1[-]	2.2[-]	20.3[-]	0.88[-]
Cl	18.1[15.2]	2.6[2.6]	20.7[17.8]	0.90[0.77]
Br	17.9[14.1]	2.8[2.9]	20.7[17.0]	0.90[0.74]
I	19.3[14.9]	3.1[2.9]	22.4[17.8]	0.97[0.77]

^a A recent estimate of $\Delta H_f^\circ[CH_3^\cdot(g)] = 34.9$ kcal mol⁻¹ was used.

Table 2. Estimated E° values for $RX(\text{solv}) + e^- \rightarrow R^-(\text{solv}) + X^-(\text{solv})$ in different solvents, together with available $E_{1/2}$ values for the cathodic reduction of RX at the dropping Hg electrode. All potentials are given vs. NHE.^a

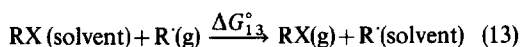
RX	$-E^\circ/\text{V}$ in						$-E_{1/2}/\text{V}$ (solvent)
	H ₂ O	MeOH	DMF	DMSO	MeCN	THF	
MeF	0.88	1.16	1.33	1.17	1.93	1.59	
MeCl	0.90	1.14	1.23	1.10	1.82	1.49	1.99 (DO-H ₂ O)
MeBr	0.90	1.12	1.06	0.97	1.71	1.32	1.72 (DMF)
MeI	0.97	1.15	1.07	0.88	1.64	1.28	1.39 (DO-H ₂ O); 1.15 (50% EtOH)
EtF	0.75	1.03	1.20	1.04	1.80	1.46	
EtCl	0.82	1.06	1.15	1.02	1.74	1.41	>2.1 (no wave) (DMF)
EtBr	0.74	0.97	0.90	0.81	1.55	1.16	1.89 (DMF)
EtI	0.82	1.00	0.92	0.73	1.49	1.13	1.43 (DO-H ₂ O)
PrF	0.82	1.10	1.27	1.11	1.87	1.53	
PrCl	0.79	1.03	1.12	0.99	1.71	1.38	
PrBr	0.77	1.00	0.93	0.84	1.58	1.19	1.98 (DMF)
PrI	0.82	1.00	0.92	0.73	1.49	1.13	1.39 (50% EtOH)
i-PrF	0.74	1.02	1.19	1.03	1.79	1.45	
i-PrCl	0.77	1.01	1.10	0.97	1.69	1.36	
i-PrBr	0.71	0.94	0.87	0.78	1.52	1.13	2.02 (DMF)
i-PrI	0.71	0.89	0.81	0.62	1.38	1.06	
BuCl	0.72	0.96	1.05	0.92	1.64	1.31	
BuBr	0.74	0.92	0.90	0.81	1.55	1.16	1.99 (DMF); 2.03 (DO-H ₂ O)
t-BuF	0.85	1.13	1.29	1.14	1.90	1.55	
t-BuCl	0.74	0.98	1.07	0.94	1.64	1.33	
t-BuBr	0.66	0.89	0.82	0.73	1.47	1.08	1.95 (DMF); 1.84 (DMSO)
t-BuI	0.67	0.85	0.77	0.56	1.34	1.34	0.98
Allyl-Cl	0.32	0.56	0.65	0.52	1.24	0.87	1.89 (DMSO)
Allyl-Br	0.28	0.51	0.44	0.35	1.09	0.70	0.97 (DMSO)
Allyl-I	0.42	0.60	0.52	0.33	1.09	0.73	
PhCH ₂ Cl ^b	0.32	0.56	0.65	0.52	1.24	0.91	1.70 (DO-H ₂ O)
PhCH ₂ Br	0.30	0.53	0.46	0.37	1.11	0.72	0.98 (DMF); 0.89 (MeOH) ^e
PhCH ₂ I ^c	0.55	0.73	0.65	0.46	1.22	0.86	
CCl ₄ ^d	0.25 (0.05)	0.49 (0.29)	0.58 (0.28)	0.45 (0.25)	1.25 (1.0)	0.84 (0.64)	0.54 (DO-H ₂ O); 0.51 (MeOH-H ₂ O); 0.01 (DMF)

^aData were taken from Refs. 15–18, 22 and 26, unless otherwise stated. See also text. ^b $S^\circ[\text{PhCH}_2\text{Cl}(\text{g})]$ was estimated to be 3 cal mol⁻¹ K⁻¹ less than $S^\circ[\text{PhCH}_2\text{Br}(\text{g})]$. ^c $S^\circ[\text{HPhCH}_2\text{I}(\text{g})]$ was estimated to be 1 cal mol⁻¹ K⁻¹ greater than $S^\circ[\text{PhCH}_2\text{Br}(\text{g})]$. ^dValues in parentheses are derived with a value of $\Delta H_f^\circ[\text{CCl}_3 \cdot (\text{g})] = 14$ kcal mol⁻¹.²⁷ ^eRef. 28.

keeping with the goal of establishing the lower limits of the E° values. This assumption is equivalent to putting the differences in solvation energy between RX and R^- in the non-aqueous solvents (eqn. (13)) equal to those for water (for the X^- , column 3 of Table 1). Clearly, this treatment establishes an upper limit for ΔG_{13}° since ΔG_{13}° generally must be

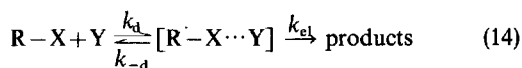
smaller than ΔG_{11}° due to the weaker interactions between neutral organic species and non-aqueous solvent molecules.

The last column of Table 2 gives available half-wave potentials for reduction of alkyl halides, taken from the extensive compilations in Ref. 26.



DISCUSSION

As outlined in the introduction, it is the purpose of this paper to discuss known and/or suspected cases of non-bonded electron transfer between alkyl halides and various reductants in terms of the Marcus theory, assuming that the carbon-to-halogen bond is almost broken in the transition state (eqn. (5)). With this postulate the kinetic form of eqn. (5) is the simple one of eqn. (14), in which k_d and k_{-d}



are the rate constants for diffusing together and apart, respectively, of the reactants, and k_{el} is the rate constant for electron transfer. Using the Marcus expression (eqn. (15)) for ΔG^\ddagger and converting it to k_{el} via the Eyring equation, k_{obs} can be written as in eqn. (16), assuming that electrostatic factors are negligible (as usually done for reactions in which one reactant is neutral). In eqn. (16) A is of the order

$$\Delta G^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G^{\circ'}}{\lambda} \right)^2 \quad (15)$$

$$k_{obs} = \frac{k_d}{1 + A \exp \left[\frac{\lambda}{4} \left(1 + \frac{\Delta G^{\circ'}}{\lambda} \right)^2 / RT \right]} \quad (16)$$

of 1 and $\Delta G^{\circ'}$ the free energy change for the reaction under the actual conditions of the experiment. For the further treatment A is put equal to 0.2 (a normally used value; calculations are not sensitive to variations of this parameter).^{5a} Hence we can express $\log k_{obs}$, the variable of interest, as in eqn. (17), the expression to be used in the analysis of electron transfer reactions of alkyl halides to follow.

$$\log k_{obs} = \log k_d - \log \left(1 + 0.2 \exp \left[\frac{\lambda}{4} \left(1 + \frac{\Delta G^{\circ'}}{\lambda} \right)^2 / RT \right] \right) \quad (17)$$

Before we embark on this endeavour a comment on the data of Table 2 is necessary. An attempt to discuss alkyl halide reductions^{5a} (by metal complexes as well as purely organic reductants) in terms of the Marcus theory led to major incon-

sistencies, when the original aqueous E° values of Hush (Table 1) were used in eqn. (17). In particular, these rather high values — in addition being contra-intuitively almost independent of the nature of X — imply that alkyl halides are fairly “strong” oxidants, capable of oxidizing many anionic, in particular carbanionic, species in very fast reactions. In spite of this, the by far strongest reductants used, aromatic radical anions, showed far too low experimental rate constants to be compatible with values calculated by the Marcus treatment using Hush’s E° values. Even if aqueous E° values come out slightly more negative now (Table 1), it is to be expected that they should not be well suited for estimates of reaction rates in non-aqueous systems. The solvation of halide ions is strongly dependent on the nature of the ion, fluoride ion on the one extreme being strongly destabilized in non-aqueous solvents, especially dipolar aprotic ones, and iodide ion on the other extreme being relatively little affected by a change of solvent.²² This order of stabilization by solvation is responsible for the invariance of aqueous E° values with the nature of the halide ion; the large differences in bond dissociation energies between C–X bonds are compensated by the solvation energy of X^- operating in the opposite direction.

We are now in a position to explain the need for establishing a lower limit for the E° values. Since we want to discuss radical anion reduction of alkyl halides in terms of non-bonded electron transfer, we must use E° values that are biased on the negative side; otherwise one might object that the experimental evidence has been unfairly stacked against using the Marcus theory for what are considered *the most typical* non-bonded electron transfer reactions of the alkyl halides. Thus, as an example, the most positive value of $\Delta G_{tr}^\circ(\text{H}^+)$ from water to acetonitrile of 11 kcal mol⁻¹ was used, in spite of the fact that considerably lower estimates are available.

A comparison between E° values and available $E_{1/2}$ data (last column of Table 2) shows that in all cases but one (CCl₄ in DMF) the cathodic reduction of alkyl halides is electrochemically irreversible, requiring a considerable overpotential to proceed at a measurable rate. The cathodic behaviour of methyl halides in terms of E° values for eqn. (9) (R=Me) has been carefully analyzed by Hush.⁹

Finally, it should be noticed that the crucial assumption that step (3) is dissociative in the case of simple alkyl halides is still under active scrutiny by several groups,^{13,14,29–36} and it is by no means

Table 3. Halide (excluding fluorides) reductions by organic and inorganic species, as analyzed by Marcus' theory.

No.	Reductant	Solvent	E°/V of reductant	No. of data pairs	$\lambda_5/kcal\ mol^{-1}$	$\lambda_{18}/kcal\ mol^{-1}$	Ref. ^a
1	e^-	H ₂ O	-2.77	9	53 (40)		38
2	Aromatic radical anions	THF	-(1.08-1.99)	15	54 (4)	90(8) ^b	39; 5a
3	(Anthracene) ^{·-}	DMSO	-1.07	4			40; 5a
4	Bu ₃ P-Co(I) cobaloxime	MeOH	-0.51	13	48(4)	66-86	41; 42
5	B _{12s}	MeOH	-0.59	10	46 (3)	62-82	41
6	Co(I)tetraphenylporphin	DMF/PrOH	-0.56	1			43
7	Co(I)salen	DMF	-0.82	2			44
8	Co(I)phthalocyanine	MeOH	-0.39	2			45; 46
9	Co(CN) ₃ ³⁻	MeOH/H ₂ O	-0.83	7	48 (8)	66-86	47; 48
10	Fe(I)porphins	DMF	-(0.88-0.995)	8	51 (5)	72-92	49
11	Fe(II)deuteroporphine IX	MP/HOAc ^c	0.00 ^d	3			50
12	Cr(II)	H ₂ O/EtOH	-0.41	2			51
13	Cr(II)([15]ane N ₄) ²⁺	<i>t</i> -BuOH/H ₂ O	-0.58	10	43 (3)	56-76	52
14	Mo(CO) ₂ (dmpe) ₂	CH ₃ CN	0.00	1			53
15	(C ₅ Me ₅) ₂ UCl	THF	-1.06	8	25 (12)		54

^aFirst reference to kinetic data, second to source of E° value, unless it is listed in standard tables. ^b λ for self-exchange of aromatic radical anions (ion paired) was set equal to 18 kcal mol⁻¹ (see Ref. 5a). ^c*N*-Methylpyrrolidone-acetic acid; data for DMF were used. ^dSet equal to that of Fe(II)tetraphenylporphin.

definitively settled that discrete (R-X)^{·-} do not exist.^{12,29} Presently, it seems, however, that most experimental evidence favours dissociative electron transfer for simple alkyl halides^{30,31} whereas for certain polyhalogenated methanes the existence of radical anions has been demonstrated.^{32,33} Theoretical studies present diverging conclusions,^{13,14,34-36} but it is of interest to note for the discussion to follow that (CH₃F)^{·-} is predicted to be capable of finite existence.^{14,34} In one *ab initio* study a barrier for solvent assisted bond cleavage of (CH₃-Cl)^{·-} has been inferred,³⁵ but estimated to be low (≤ 16 kcal mol⁻¹), whereas another one favours dissociative electron transfer with direct formation of a loose complex of C_{3v} symmetry between CH₃· and Cl.¹⁴ Introduction of a nitro substituent in CH₃Cl removes the barrier for dissociative electron transfer.¹³

Table 3 lists a number of alkyl halide reductions by inorganic and organic species for which kinetic data are available in one or several of the cases listed in Table 2. In most cases the possibility of an electron transfer reduction mechanism has been discussed, although not necessarily favoured as the ultimate mechanistic choice. The reactions cover a wide variety of reducing reagents and reaction conditions, ranging from hydrated electrons to transition metal complexes in acetonitrile. For those

reactions where a reasonable number of data pairs is available (1, 2, 4, 5, 9, 10 and 13) a value of λ for the individual reaction was calculated by non-linear regression analysis,* using expression (17) with an adequate value of k_d . These values are given as λ_5 in column 6 of Table 3.

The similarity of the λ values may at first sight seem surprising in view of the widely differing reagents and reaction conditions. However, using the corollary of the Marcus theory that λ for a heteronuclear reaction (*e.g.* eqn. (5)) can be expressed as the mean value of the λ 's of the two individual self-exchange reactions (those pertaining to eqn. (5) are formally shown in eqns. (18) and (19)),



the transition state model postulated in eqn. (5) involves a large λ_{18} value, as discussed in the introduction, and hence will be predominant in determining λ_5 . The reagents employed have relatively small λ_{19} values, *e.g.* 15-20 kcal mol⁻¹ for

* By Marquardt's method (Hewlett-Packard System 35 Nonlinear Regression Program).

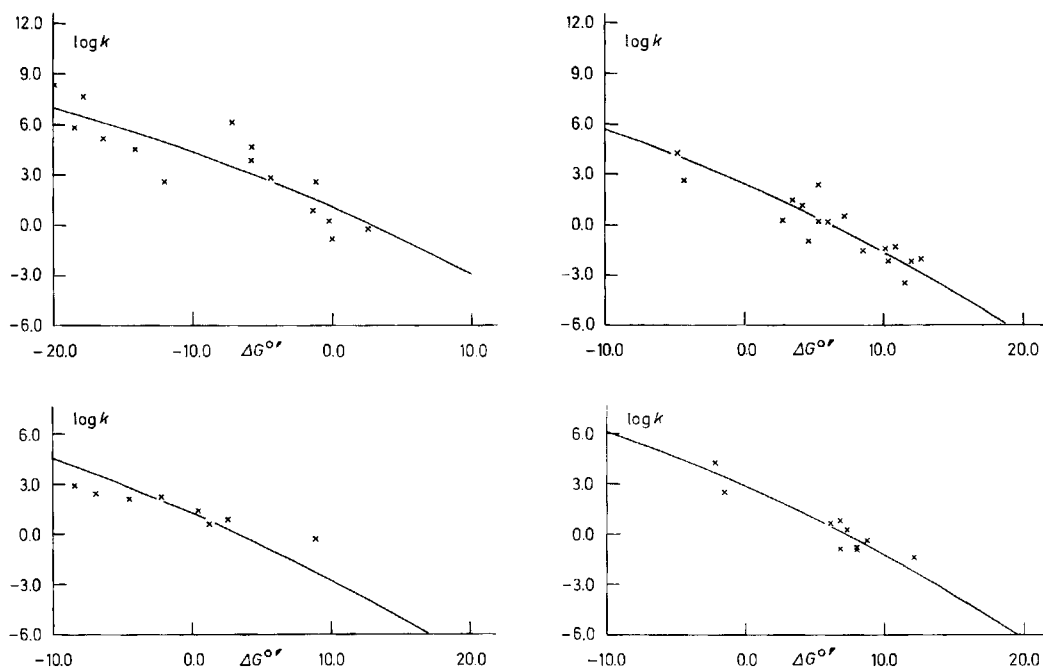


Fig. 1. Marcus plots for the reaction between alkyl halides and a, radical anions; b, Bu_3P -cobaloxime and B_{12}s ; c, Fe(I)porphins; and d, $\text{Cr(II)}([\text{15}] \text{jane N}_4)^{2+}$.

ion-paired radical anions,^{5a} or can be assumed to have relatively small λ_{19} values.^{4,37} Experimental values are unfortunately not available for Co(I)/Co(II) and Fe(I)/Fe(II) couples, but current generalizations regarding structural effects upon λ dictate that the presence of large polarizable ligands should result in low λ values.³⁷ This means that λ_5 will largely be determined by λ_{18} . With the assumption that λ_{19} lies in the region of 10–30 kcal mol⁻¹ we can give limits of λ_{18} for the self-exchange reactions

(last column of Table 3) of alkyl halides (eqn. (18)).

Apart from calculating λ values for the individual reactions of Table 3 (a few examples of Marcus plots of these reactions are shown in Fig. 1) the data, except for those of reaction (15) (see below), were analyzed in various aggregated forms to look for possible trends (Table 4). It is first to be noted that one can indeed construct a master plot of all data pairs (Fig. 2) and obtain a reasonable λ_5 of 46(3) kcal mol⁻¹. A closer look at the points that deviate

Table 4. Marcus analysis of aggregated forms of the data referred to in Table 3, except for those of reaction 15.

Compound type	No. of data pairs	$\lambda_5/\text{kcal mol}^{-1}$
All compounds	87	46 (3)
All compounds, except methyl halides	76	48 (2)
Methyl halides	11	29 (9)
$i\text{-PrX} + t\text{-BuX} + \text{PhCH}_2\text{X} + \text{allyl-X}$	27	47 (4)
All chlorides	31	50 (4)
All bromides	34	47 (3)
All iodides	22	38 (5)
Established non-bonded electron transfer reactions (1–3, 9 and 14 of Table 3)	36	52 (3)

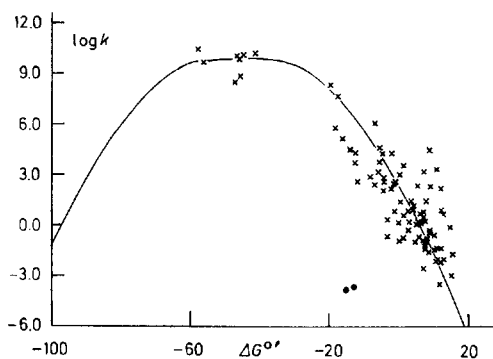


Fig. 2. Marcus plot of all reactions of Table 3, except reaction 15. The two points marked by filled circles refer to alkyl fluoride reactions.

most strongly from the curve revealed a high percentage of methyl halide reactions with Co(I) complexes (the so-called supernucleophiles).^{41,45} Hence all reactions of MeX were left out and a second master plot (Fig. 3) was drawn ($\lambda_5 = 48[2]$ kcal mol⁻¹). This is slightly better than the first one, and a plot of the methyl halide data alone considerably worse ($\lambda_5 = 29[3]$ kcal mol⁻¹). Reasons for this behaviour might be that (a) methyl halides have lower E° values and (b) are sterically less hindered than all the other halides of Table 2, both factors combining to make a nucleophilic reaction with the metal center favoured over electron transfer in the case of MeX. To test this possibility, data for *i*-PrX and *t*-BuX (sterically hindered) and PhCH₂X and allyl-X (low E° values; see Table 2) were combined to give the plot of Fig. 4 (λ_5 is now 47[4] kcal mol⁻¹). It is however hardly possible to

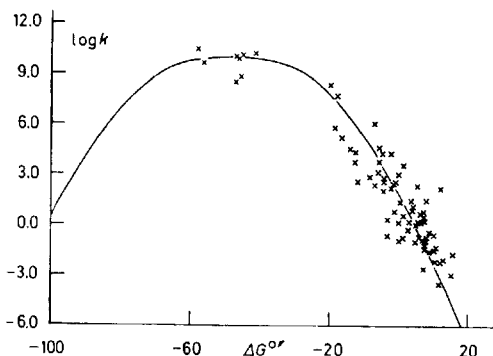


Fig. 3. Marcus plot of all reactions of Table 3, except reaction 15 and excluding all methyl halide reactions.

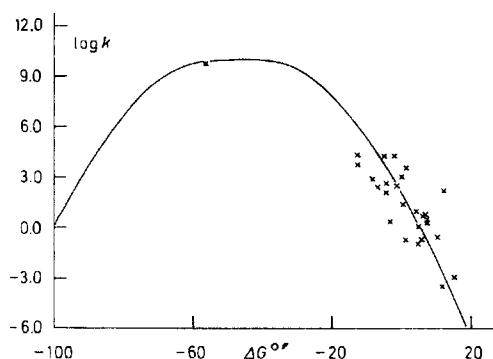


Fig. 4. Marcus plot of all reactions of Table 3, involving isopropyl, tert-butyl, benzyl and allyl halides (except reaction 15).

claim that this sub-set is more well-behaved than the total set; a more definitive analysis of the problem in these terms must rest on a more homogeneous experimental material. It does differ significantly from the sub-set of MeX reactions, though.

A test for differences according to halogen type (see Table 4) revealed a weak trend in the expected direction, namely that λ_5 should decrease with decreasing bond energy of the R-X bond; again the same reservation as above is valid. A last sub-set collected "established" non-bonded electron transfer reactions, *i.e.* such reactions for which an electron transfer mechanism has been deemed most likely, showing practically no difference in behaviour from that of the whole set (Fig. 5).

It is of interest to see how an established S_N2 process is related to the master plot, just to make

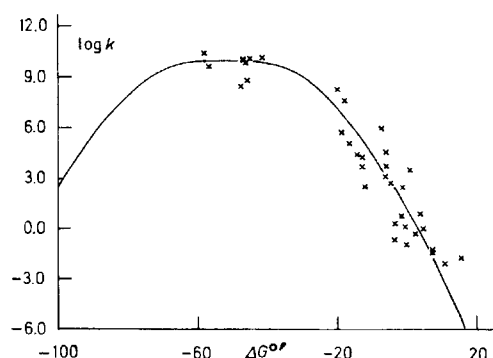


Fig. 5. Marcus plot of "established" electron transfer processes of alkyl halides (reactions 1-3, 9 and 14 of Table 3).

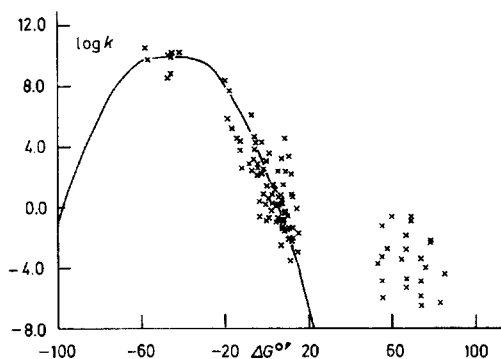
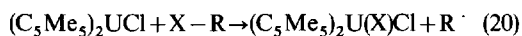


Fig. 6. Master Marcus plot of Fig. 2 with a set of 23 Finkelstein reactions included (domain to the right).

sure that we really are dealing with qualitatively different phenomena. A suitable S_N2 reference process is the Finkelstein reaction ($RX + X^- \rightarrow RX + X^-$) for which a rate constant of $0.6 \text{ M}^{-1} \text{ s}^{-1}$ has been determined in acetone⁵⁵ for the exchange of I^- with EtI. From E° of I^-/I^\cdot ($\approx 1.3 \text{ V}$) and of $\text{Et}-I$ (estimated at -1.2 V) we obtain $\Delta G^\circ \sim 2.5 \text{ V}$ or 58 kcal mol^{-1} , a situation that is drastically illustrated in Fig. 6 where a set of 23 Finkelstein reactions⁵⁵ has been represented in the same plot as Fig. 1, but with a different scale on the x axis.

Another interesting feature is the failure of alkyl fluoride reductions (with aromatic radical anions as reductants) to conform with the Marcus plot, assuming the same reduction mechanism as for chlorides, bromide and halides (see Fig. 2). An obvious explanation is that $(RF)^\cdot$ exists as a relatively stable species and that accordingly the E° values should refer to $RF + e/(RF)^\cdot$ and not to $RF + e/R^\cdot + F^-$. Clearly the former half reaction would have a more negative E° value, although it is not possible to make any quantitative estimate. There is thus a reasonable chance that radical anions of simple alkyl fluorides should be stable enough for experimental detection and study.

Reaction (15), reduction of alkyl halides by a U(III) compound, was recently discussed in some detail.⁵⁴ An atom transfer mechanism (eqn. (20)) was preferred, partly since it was thought that the reaction would be far too endergonic for non-



bonded electron transfer to occur. This estimate was, however, based on cathodic peak potentials of

alkyl halides which generally are much more negative than the corresponding E° values (see Table 2). With E° values from Table 2 reaction (15) actually emerges as a possible borderline case of electron transfer; the kinetic data are themselves badly correlated (see Table 3) with the Marcus equation (17) and inclusion of these 8 data pairs in the total data set of Fig. 2 gives a slightly worse fit to the Marcus parabola (λ_s is then $46[5] \text{ kcal mol}^{-1}$). Thus it is not possible to dismiss an electron transfer mechanism from this point of view.

Concluding, it has been shown that kinetic data for alkyl halide reduction by electron transfer reagents can be consistently interpreted on the basis of the Marcus theory, provided a transition state structure with an almost completely broken C-halogen bond is postulated. In view of the inhomogeneity and imperfectness of the data base, a fully quantitative treatment has not been possible, but the correlations already established show that the Marcus theory may provide an efficient device for sorting out possible electron transfer mechanisms also in irreversible cases. Similar conclusions, although phrased somewhat differently, were reached in a recent study.⁶

One important difference is to be noted, however, in that Scandola *et al.*⁶ excluded the possibility of fixing the zero of the free energy axis due to the difficulty in estimating E° for processes involving almost complete bond breaking in the transition state. As shown above, this seems to be possible, and may be extendable to other systems, *e.g.* alkanecarboxylates, tetraalkyl metals⁵⁶ and diacyl peroxides.⁵⁷

Finally, it should be noted that carbon tetrachloride (see Table 2), as judged by its E° value, should be a reasonably strong electron transfer oxidant, as has indeed been very nicely demonstrated by Meyers and coworkers.⁵⁸ In general, polyhalogenated organic compounds should resemble carbon tetrachloride in this respect, and this is also qualitatively indicated by the fact that these compounds have half-wave potentials for reduction^{11,26} in the region of 0 to -1 V . Assuming that these values have a rather large component of overpotential, polyhalogenated organic compounds would emerge as fairly strong electron transfer oxidants. It is not unreasonable to ascribe the often high but nonselective biological activity of these compounds to their oxidizing properties; in fact, one could build a good case for the view that a polyhalogen compound could act as an excellent

suicide inactivator^{59,60} toward a wide range of redox enzymes. Following electron transfer, a very reactive neutral radical would be formed close to the active center, thus opening a pathway for indiscriminate attack on atoms in its vicinity.⁶¹

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