

Review Article

## Two-Electron Reactions in Organic and Organometallic Electrochemistry

Dennis H. Evans\* and Mark W. Lehmann

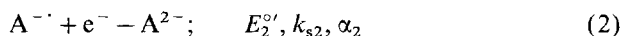
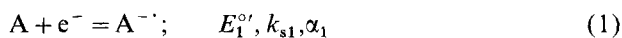
Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

**Dedicated to Professor Henning Lund on the occasion of his 70th birthday.**

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The electrochemical oxidation or reduction of many organic and organometallic compounds proceeds by two or more individual electron-transfer reactions. In this paper, various aspects of such reactions are reviewed. These include the factors that govern the difference between the formal potentials for the two steps ( $E_1^{\circ'} - E_2^{\circ'}$ ), causes of potential inversion ( $E_1^{\circ'} - E_2^{\circ'} < 0$  for reductions) and mass transfer and kinetic effects associated with the disproportionation/comproportionation reaction among the three species involved in the two-step reaction.

It is quite common to observe in the electrochemical reactions of organic and organometallic compounds that the reduction or oxidation proceeds in a series of one-electron steps in which addition or removal of the electron occurs with greater difficulty for a given step than for the one immediately preceding it. As an example, consider the reduction of an aromatic hydrocarbon, A, in an aprotic solvent. Here the addition of the first electron generates the radical anion, which in turn is reduced to the dianion in the second step [reactions (1) and (2)].



Each step has associated with it a reversible formal potential,  $E_j^{\circ'}$ , standard heterogeneous electron-transfer rate constant,  $k_{sj}$ , and transfer coefficient,  $\alpha_j$ . In this paper, we will assume that the formal potentials,  $E^{\circ'}$ , are equal to the standard potentials,  $E^{\circ}$ . For aromatic hydrocarbons it is observed that  $E_2^{\circ}$  lies several tenths of a volt negative of  $E_1^{\circ}$ , i.e.,  $E_1^{\circ} - E_2^{\circ} > 0$ . This condition has been called normal ordering of potentials.

In a number of cases, it has been found that a reversal occurs such that the introduction of the second electron (for reduction reactions) actually occurs with greater facility than the first, i.e.,  $E_2^{\circ}$  is positive of  $E_1^{\circ}$ . This

condition has been called potential inversion. The reasons for this behavior are complex but some generalizations can be made.

In both cases, normal ordering and potential inversion, the disproportionation/comproportionation reaction [reaction (3)] can take place in the diffusion layer.



The relationship among the equilibrium constant for disproportionation,  $K_{\text{disp}}$ , the free energy change,  $\Delta G_{\text{disp}}^{\circ}$ , and the difference between the formal potentials is given by eqn. (4). From eqn. (4) one can see that with normal ordering of potentials disproportionation is not favored whereas with potential inversion disproportionation is thermodynamically favored.

$$\Delta G_{\text{disp}}^{\circ} = -RT \ln K_{\text{disp}} = F(E_1^{\circ} - E_2^{\circ}) \quad (4)$$

The occurrence of reaction (3) often has little effect on the current-potential curves. In fact, it has been shown that for the case of mass transfer only by diffusion, reversible electrode reactions, identical diffusion coefficients for all species, and no other chemical reactions, reaction (3) can have no influence on any voltammetric experiment.<sup>1</sup> However, when one or more of these conditions is not met, reaction (3) can affect the observed response, usually in a subtle manner but sometimes quite spectacularly.

In this review we will discuss the factors that govern the difference between the formal potentials, the causes

\* To whom correspondence should be addressed.

of potential inversion and the effects of disproportionation/comproportionation. No attempt has been made to provide a comprehensive review and literature citations have been chosen based primarily on the ability of their content to illustrate the main points being made in this work.

### Factors affecting the difference in formal potentials. Normal ordering of potentials.

*Delocalized charge in the ions.* The singly charged ion radicals and the doubly charged ions formed by sequential oxidation or reduction of aromatic hydrocarbons tend to have charge density that is delocalized over the entire aromatic system. As such, they offer a vague resemblance to the idealized model used by Born to compute the electrical energy required to charge ions, *viz.*, the ions are considered to be spherical entities with charge distributed uniformly over the surface. Evans and Hu<sup>2</sup> compared disproportionation enthalpies calculated by a semiempirical molecular orbital method (AM1) with the disproportionation free energies calculated by the Born equation assuming that the aromatic hydrocarbon anions were spheres with radii corresponding to the known molecular volume [eqn. (5)]. Here,  $N_A$  is Avogadro's number,  $e_0$  is the charge on the electron,  $\epsilon_0$  is the permittivity of free space and  $r$  is the radius of the particle.

$$\Delta G_{\text{disp,Born}}^{\circ}(\text{vac}) = \frac{N_A e_0^2}{4\pi\epsilon_0 r} \quad (5)$$

Surprisingly good agreement was found indicating that the computed disproportionation enthalpies were mainly governed by the electrostatics of charging the ions, *i.e.*, there are no special chemical effects associated with ion formation, a result that fits the qualitative notion that the two electrons in question are being added or removed from the same molecular orbital.

When the disproportionation is considered to occur in a solvent of dielectric constant  $D$ , the Born treatment predicts that the free energy of disproportionation will be given by eqn. (6), *i.e.*, the unfavorable disproportionation free energy experienced in a vacuum is attenuated in solution by  $1/D$ .

$$\Delta G_{\text{disp,Born}}^{\circ}(\text{sol}) = \frac{N_A e_0^2}{4\pi D \epsilon_0 r} \quad (6)$$

In reality the Born equation overstates the solvation effect, the experimental results for the anions of six aromatic hydrocarbons in DMF correspond to an effective dielectric constant,  $D_{\text{eff}}$ , of only about three.<sup>2</sup> Nevertheless, the experimental values of  $\Delta G_{\text{disp}}^{\circ}(\text{DMF})$ , as reflected in  $E_1^{\circ} - E_2^{\circ}$ , do tend to follow eqn. (6) as regards the effective radius,  $r$ , with the largest hydrocarbons having the smallest experimental free energies of disproportionation and the smallest  $E_1^{\circ} - E_2^{\circ}$ .

*Localized charge in the ions.* Many compounds that undergo two-step oxidation or reduction do so because they contain two, usually identical, electroactive groups. In such cases, the charge on the ions of these compounds will tend to be concentrated on those groups and the Born model with its assumption of delocalized charge is even less relevant than for aromatic hydrocarbons. The qualitative effect is the same. Larger molecules tend to have smaller values of  $E_1^{\circ} - E_2^{\circ}$ . However, it may be useful to use a slightly different model in this case, *viz.*, charge localized on the two electroactive groups separated by a distance  $R$ .

Two idealized cases may be distinguished. In the first, the spacer separating the electroactive groups allows electronic interaction between them through a  $\pi$ -bonded framework. In the second the linker is a saturated hydrocarbon chain through which such electronic interactions will be strongly attenuated. The family of compounds given in Table 1 provides an example of the first type of system. The Born treatment<sup>3</sup> extended to the case of two spheres separated by distance  $R$  predicts that the disproportionation free energy will be given by eqn. (7).

$$\Delta G_{\text{disp,Born}}^{\circ}(\text{sol}) = \frac{N_A e_0^2}{4\pi D \epsilon_0 R} \quad (7)$$

Here  $D$  is the dielectric constant of the medium in which the spheres are located. In their classic papers on the related problem of the dissociation constants of diprotic acids, Kirkwood and Westheimer<sup>10</sup> included a dielectric constant for the molecular cavity containing the charged groups, the cavity modeled as a sphere or ellipsoid. They noted that the results of this more sophisticated treatment could be reproduced by an equation of the form of eqn. (7) where  $D$  is replaced by  $D_{\text{eff}}$ , the effective dielectric constant. Thus, eqn. (7) should provide a guide for interpreting the dependence of  $E_1^{\circ} - E_2^{\circ}$  on the distance between the electroactive groups. Note that the radius of the electroactive groups does not appear in eqn. (7) for the reason that the energy to charge the cation radical is considered to be the Born energy for charging just one of the groups. When this is combined with the electrostatic energy for the dication, dependence on the group radius is lost.

In Fig. 1, the observed values  $E_1^{\circ} - E_2^{\circ}$  are plotted vs.  $1/R$  for four of the five compounds for which data are presented in Table 1. A satisfactorily linear relationship with almost zero intercept is found for three of the compounds (2-4) that have a fairly large separation between the charges, which are arbitrarily considered to reside precisely on the nitrogen atoms. The slope corresponds to  $D_{\text{eff}}=4.7$ . Data for the compound with the smallest distance between nitrogen atoms, the dication of 9,9'-bis-9-azabicyclo[3.3.1]nonane (1), is not plotted in Fig. 1 but its point would fall about 1 V below the line defined by 2-4. In 1 the two charged centers are directly bonded to one another and it is not surprising that eqn. (7) should fail. In this case, the charge is likely to be pushed out into the bicyclic groups attached to

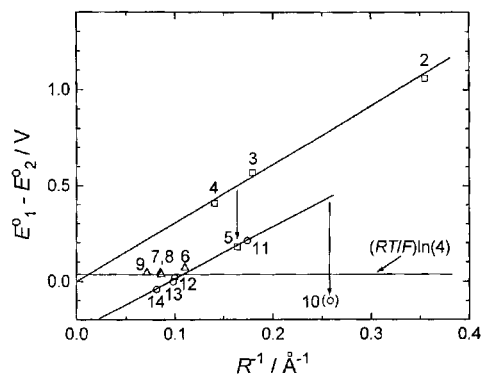


Fig. 1. Difference between first and second formal potentials as a function of inverse distance between electroactive groups for compounds listed in Table 1 (squares) and Table 2 (saturated linkages: triangles; unsaturated linkages: circles).

nitrogen. In fact, an increase of charge-charge distance of only about 1.1 Å would bring the result for **1** in compliance with the line. Ion pairing may be playing a role as well (see below). It would be futile to attempt to read too much quantitative meaning into the correlations in Fig. 1. The result for **1** is included here because of the unusually large value of  $E_1^\circ - E_2^\circ$ , +1.19 V, which is one of the largest values ever reported. There are extremely few examples of two-electron reactions in which the charge is created (formally) on adjacent atoms. In this connection, it would be interesting to determine  $E_1^\circ - E_2^\circ$  for the  $O_2/O_2^{\cdot-}/O_2^{2-}$  sequence (dioxygen/superoxide/dioxygen dianion). We are not aware of attempts to do so.

Another data point, that of the dication of 2,5-bis(dimethylamino)-2,4-hexadiene (**5**), falls below the line with  $E_1^\circ - E_2^\circ$  determined to be only 0.18 V whereas a value of about 0.5 V is expected based on the linear

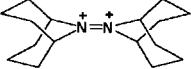
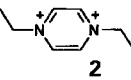
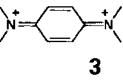
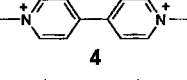
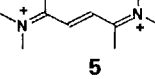
relationship found for **2-4** (see arrow in Fig. 1). This result indicates destabilization of the radical cation (or stabilization of the dication) of 0.3 V (7 kcal mol<sup>-1</sup>) compared with **2-4**. Other systems showing similar behavior will be discussed in a later section.

Similar results for some dinitro compounds are given in Table 2. Included are the well known results for the 1,ω-bis(4-nitrophenyl)alkanes where, in the compounds studied, a one-to-four carbon alkyl chain separates the two groups. As the length of the polymethylene chain increases,  $E_1^\circ - E_2^\circ$  decreases and approaches the theoretical limit of  $(RT/F) \ln 4$  (35.0 mV at 293 K).<sup>7</sup> The 35.0 mV limit pertains to the case of infinite separation of localized charges that cannot interact through the spacer. One can see that the results for the four 1,ω-bis(4-nitrophenyl)alkanes, **6-9**, fall very close to the 35 mV limit because the distance between the two nitro groups is quite large for all of them (9 to 14 Å).

The remainder of the dinitro compounds contain nitro groups that are formally conjugated with one another (Table 2). The data for four of these compounds (**11-14**) fall on a line whose slope corresponds to  $D_{\text{eff}} = 5.3$  in eqn. (7) (Fig. 1), a value quite close to that seen for the cationic nitrogen systems. The intercept, however, is not zero as predicted by eqn. (7). Rather it is -0.29 eV (6.7 kcal mol<sup>-1</sup>) suggesting that, in general, the dinitro compounds experience destabilization of the radical anions (or stabilization of the dianions) in excess of the electrostatic effects upon which eqn. (7) is based.

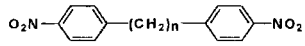
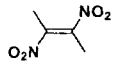
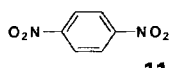
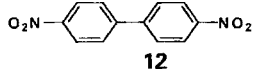
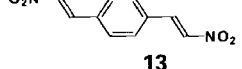
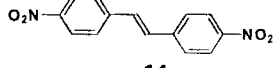
A fifth compound, (*E*)-2,3-dinitrobutene (**10**), deviates strongly with an observed  $E_1^\circ - E_2^\circ$  that is much smaller than predicted by the line constructed from the data for the other four. (The *Z* isomer is reported to behave identically).<sup>11</sup> Even though the nitro-nitro separation is the smallest in the family, the potentials are apparently

Table 1. Data for reduction of some nitrogen cationic systems.<sup>a</sup>

Compound	$\Delta E^\circ = E_1^\circ - E_2^\circ / \text{mV}$	N-N distance <sup>b</sup> /Å	Reference
	1190	1.4	4
	1060	2.8	5
	590 570	5.6	6 7
	410	7.1	8
	180	6.1	9

<sup>a</sup>Acetonitrile as solvent with tetraalkylammonium salts as supporting electrolytes.  $E_1^\circ$  corresponds to the dication/radical cation couple and  $E_2^\circ$  to the radical cation/neutral couple. <sup>b</sup>From optimized structures obtained by semiempirical molecular orbital calculations (AM1).

Table 2. Difference in formal potentials for dinitro compounds.<sup>a</sup>

Compound	$\Delta E^\circ = E_1^\circ - E_2^\circ / \text{mV}$	N-N distance <sup>b</sup> / $\text{\AA}$
	70.5	9.1
<b>6:</b> $n = 1$		
<b>7:</b> $n = 2$	46.1	11.8
<b>8:</b> $n = 3$	37.7	11.7
<b>9:</b> $n = 4$	46.1	14.1
	$< 0$ (?) <sup>c</sup>	3.9
<b>10</b>		
	212	5.8
<b>11</b>		
	20.7	10.1
<b>12</b>		
	$\approx 0$ <sup>d</sup>	10.2
<b>13</b>		
	$-46 < \Delta E^\circ < -31$	12.3
<b>14</b>		

<sup>a</sup>Ref. 7 except as noted. All results obtained in acetonitrile solvent except as noted. <sup>b</sup>From optimized structures obtained by semiempirical molecular orbital calculations (AM1) except 6–9 for which molecular mechanics (MM+) were used. <sup>c</sup>Ref. 11. 20% acetonitrile in water, pH > 7. <sup>d</sup>Ref. 12.

inverted,  $E_1^\circ - E_2^\circ$  being negative. This is again an indication that factors other than electrostatic are affecting the results as will be discussed in a separate section. Also, it is noted that three of the four compounds that adhere to the linear relationship have values of  $E_1^\circ - E_2^\circ$  that are smaller than the statistical limit of 35 mV again suggesting that other factors are at work.

The data in Table 3 are from a recent study<sup>13</sup> of bis-carbene complexes of tungsten and molybdenum that include saturated one- and two-carbon linkers, as well as an ethenyl link and an ethynyl separator. The saturated linkers show a distance dependence of  $E_1^\circ - E_2^\circ$  that

Table 3. Data for bis-carbyne complexes of tungsten and molybdenum.<sup>a</sup>

Compound	$E_1^\circ - E_2^\circ / \text{mV}$
$[\text{W}] = \text{C} - \text{CH}_2 - \text{C} \equiv [\text{W}]$	189
$[\text{W}] = \text{C} - \text{CH}_2\text{CH}_2 - \text{C} \equiv [\text{W}]$	72
$[\text{W}] = \text{C} - \text{CH} = \text{CH} - \text{C} \equiv [\text{W}]$	177
$[\text{W}] = \text{C} - \text{C} \equiv \text{C} - \text{C} \equiv [\text{W}]$	278
$[\text{Mo}] = \text{C} - \text{CH}_2 - \text{C} \equiv [\text{Mo}]$	146
$[\text{Mo}] = \text{C} - \text{CH}_2\text{CH}_2 - \text{C} \equiv [\text{Mo}]$	36
$[\text{Mo}] = \text{C} - \text{CH} = \text{CH} - \text{C} \equiv [\text{Mo}]$	126
$[\text{Mo}] = \text{C} - \text{C} \equiv \text{C} - \text{C} \equiv [\text{Mo}]$	239

<sup>a</sup> $[\text{W}] = \text{Tp}'(\text{CO})_2\text{W}$ ,  $[\text{Mo}] = \text{Tp}'(\text{CO})_2\text{Mo}$ ,  $\text{Tp}' = \text{hydridotris}(3,5\text{-dimethyl-1-pyrazolyl})\text{borate}$ .  $\text{CH}_2\text{Cl}_2$  with 0.10 M  $\text{Bu}_4\text{NPF}_6$ . Data from Ref. 13.

is reminiscent of that seen for the 1, $\omega$ -bis-(4-nitrophenyl)alkanes (Table 2). The data also provide a nice illustration of the fact that transmission of the electrostatic effect is weakest for the saturated linkages (smallest  $E_1^\circ - E_2^\circ$ ), stronger with the ethenyl bridge, and strongest of all for the ethynyl bridge (largest  $E_1^\circ - E_2^\circ$ ).

*Ion pairing.* Before discussing the factors that lead to potential inversion, we will consider briefly another factor that can influence  $E_1^\circ - E_2^\circ$ , viz., ion pair formation between the ions of the system under investigation and counter ions originating from the supporting electrolyte. For the case of a neutral/radical anion/dianion system and monovalent cations in the electrolyte, the change in  $E_1^\circ - E_2^\circ$  brought about by ion pairing,  $\Delta\Delta E^\circ$ , will be given by eqn. (8).<sup>14</sup>

$$\Delta\Delta E^\circ = E_1^\circ - E_2^\circ - (E_1^\circ - E_2^\circ)_{C_{M^+} \rightarrow 0} \\ = \frac{RT}{F} \ln \frac{(1 + K_{11} C_{M^+})^2}{1 + K_{21} C_{M^+} + K_{21} K_{22} C_{M^+}^2} \quad (8)$$

Here  $C_{M^+}$  is the electrolyte concentration,  $K_{11}$  is the ion pair formation constant for the radical anion and the cation of the electrolyte,  $K_{21}$  is the formation constant for the dianion with one cation and  $K_{22}$  is the formation constant for forming the ion triplet (one dianion and two cations) from the ion pair of the dianion with one cation. In some cases, all three formation constants have been evaluated<sup>15</sup> but typically only one (usually  $K_{21}$ ) can be extracted from the data.<sup>16</sup>

Most frequently the effects of ion pairing are explored only for the first step of reduction or oxidation. However, in a number of cases the effect on  $E_1^\circ - E_2^\circ$  has been assessed, an example being the reduction of benzil where  $E_1^\circ - E_2^\circ$  decreases from about 1 V in the presence of tetraalkylammonium ions to 82 mV in 0.10 M  $\text{NaClO}_4$  in acetonitrile.<sup>17</sup> Most investigations have centered on ion pairing between group IA metal ions and anion radicals and dianions<sup>14,15,18–22</sup> but reports of similar studies with group IIA and first-row transition and post-transition metals have also appeared.<sup>23–29</sup> There has been at least one report on the effect of anions on  $E_1^\circ - E_2^\circ$  for the cation radicals and dications of 10-phenylphenothiazine, 9,10-diphenylanthracene, and thi-anthrene.<sup>30</sup> Finally, in an organometallic example,  $E_1^\circ - E_2^\circ$  for  $\text{Rh}_2(\text{TM}_4)_4^{2+}$  ( $\text{TM}_4 = 2,5\text{-diisocyano-2,5-dimethylhexane}$ ) was found to be  $> 0.6$  (comproportionation favored), 0.12, 0.063,  $-0.036$ ,  $-0.074$ ,  $< -0.36$  V (disproportionation favored) for  $\text{TFPB}^-$ ,  $\text{SbF}_6^-$ ,  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$  and  $\text{Cl}^-$ , respectively { $\text{TFPB}^- = \text{tetrakis}[3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}] \text{-borate}$ , a noncoordinating ion developed in this work}.<sup>31</sup> The solvent was dichloromethane in which ion association is expected to be strong but it is nonetheless surprising to see, for example, that interaction of  $\text{ClO}_4^-$  with these cations is so strong as to cause potential inversion. Coordination between the anions and the metal centers was invoked to explain the results.

Normally, it is implicitly assumed that tetraalkylammonium ions do not form ion pairs with anions in the more polar solvents such as *N,N*-dimethylformamide, acetonitrile and dimethyl sulfoxide that are commonly used in organic electrochemistry. An exception is the work of Rüssel and Jaenicke,<sup>16</sup> who studied the reduction of 1,4-benzoquinone in acetonitrile and dimethylformamide and concluded that significant ion pairing occurred between the dianion and tetraalkylammonium ions [ $K_{21}$  in eqn. (8)] for tetramethyl-, tetraethyl- and tetrabutyl-ammonium cations in acetonitrile, but not in *N,N*-dimethylformamide. No indication of ion pair formation between the radical anion of benzoquinone and tetraalkylammonium ions was found.

Such ion pair formation constants are known to be small. In a careful study that included activity effects, Chauhan *et al.*<sup>32</sup> reported barely detectable  $K_{11}$  for tetraethylammonium ions and the radical anion of nitro-mesitylene, around  $30 \text{ M}^{-1}$  in acetonitrile and *N,N*-dimethylformamide. Recently a value of  $K_{11}$  of  $200 \text{ M}^{-1}$  has been reported for tetrabutylammonium ions and  $\text{Co}^{\text{I}}(\text{salen})^-$  [salen = bis(salicylidene)ethylenediamine] in *N,N*-dimethylformamide.<sup>33</sup> However, this result may have been affected by migration which is known<sup>34</sup> to influence measured half-wave potentials at the low support ratios [ratio of supporting electrolyte concentration to  $\text{Co}^{\text{II}}(\text{salen})$  concentration] that were used.

So the question remains whether and to what extent ion pairing between tetraalkylammonium ions and radical anions and dianions will affect  $E_1^\circ - E_2^\circ$ . In an attempt to answer this question for one system, Lehmann and Evans<sup>35</sup> studied the reduction of 7,7,8,8-tetracyanoquinodimethane, TCNQ, in acetonitrile at ionic strengths (the electrolyte was  $\text{Me}_4\text{NPF}_6$ ) ranging from 0.001 to 0.070 M. The support ratio was maintained at 10 so as nearly to eliminate migration effects. Values of  $E_1^\circ - E_2^\circ$  were found to decrease about 30 mV over this range of ionic strengths in the direction expected if  $\text{Me}_4\text{N}^+$  ions were forming ion pairs with the anions of TCNQ. However, it was found that this change of 30 mV could be accounted for by changes in activity coefficients of the anion radical and dianion of TCNQ as the ionic strength was increased. The Debye-Hückel equation accounted for the observations quantitatively. In other words, no ion pairing occurred between  $\text{Me}_4\text{N}^+$  and the anion radical or dianion of TCNQ. Also, no ion pairing was detected at 10 mM  $\text{CsClO}_4$  or 5 mM  $\text{RbClO}_4$  or  $\text{KClO}_4$ . In accord with earlier results,<sup>19,20</sup> evidence was found for ion pair formation between  $\text{Li}^+$  (10 mM) and the dianion of TCNQ.

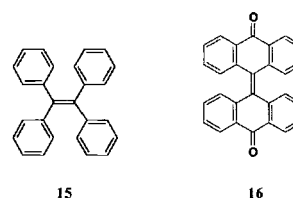
Thus, for this particular case, ion pairing by tetraalkylammonium ions is not influencing  $E_1^\circ - E_2^\circ$ . This, of course, is not a general result but it suggests caution in interpreting small changes in  $E_1^\circ - E_2^\circ$  as being due to ion pairing.

#### Factors affecting the difference in formal potentials: inversion of potentials

*Linear, unsaturated carbon-chain separators.* Earlier, we defined potential inversion as the case where  $E_1^\circ - E_2^\circ$  was

negative, i.e., insertion or removal of the second electron occurs with greater ease than the first. It was also pointed out that for two identical and non-interacting electroactive groups, the statistical limit for  $E_1^\circ - E_2^\circ$  was  $(RT/F) \ln 4$ , 35.6 mV for 298 K. As this is the lower limit when electrostatic factors have vanished, it is perhaps more valid to say that potential inversion has occurred whenever  $E_1^\circ - E_2^\circ$  falls below about 35 mV because that signifies that other factors must be considered.

In Table 2, it may be seen that four of the dinitro compounds fall in this category, **10** and **12–14**. Three of the four have unsaturated linker(s) between the nitro groups augmented by one (**13**) or two (**12**, **14**) benzene rings. It was in this class of compounds that potential inversion was first recognized. An early example is that of the oxidation of derivatives of tetraphenylethylene (**15**), some of which show potential inversion.<sup>36–40</sup> It was

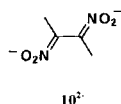


recognized that the potential inversion was caused in some way by electronic and steric factors associated with turning about the C-phenyl and the C-C (ethylene) bonds. A qualitative molecular orbital argument was offered that showed that these changes in torsional angles can raise the energy level of the HOMO making the removal of the second electron occur more easily than the first.<sup>38</sup> Similar qualitative arguments were invoked for the reactions of compounds in the bianthrone (**16**) series wherein twisting about the formal double bond connecting the two anthrone moieties will cause a raising of the HOMO and lowering of the LUMO making twisted conformations both more readily oxidized and more readily reduced than untwisted counterparts.<sup>41</sup>

In these interpretations, emphasis was placed upon the steric interactions being the cause of the structural adjustments that in turn led to modification of the HOMO or LUMO level. However, it should be noted that in the dinitro series, potential inversion occurs even in the absence of appreciable steric interactions. For example, uncrowded planar versions of **10** and **12–14** can exist for the neutral, radical anion and dianion so there is no steric reason for structural change to occur. Rather, as will be seen, electronic factors bring about the structural change and associated inversion of potentials.

Consider (*E*)-2,3-dinitro-2-butene, **10**. Semiempirical molecular orbital calculations (AM1) on **10** show that its HOMO is principally a  $\pi$ -bonding orbital at the C=C bond whereas the LUMO is strongly  $\pi$ -antibonding in the same region. Thus, addition of an electron to form the radical anion of **10** will weaken the olefin pi bond and possibly cause twisting. Optimization of the structure of the radical anion indicates that twisting occurs with

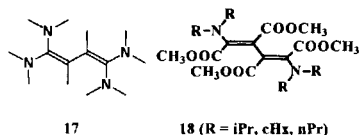
the N-C-C-N torsional angle decreasing from 180° in the neutral to 158° in the radical anion. This twisting continues in the conversion into the dianion whose N-C-C-N torsional angle is 125° according to AM1. Thus the dianion has much of the character of two independent nitronate units as in **10**<sup>2-</sup>.



The inversion in potentials seen for **10** can be rationalized in the following way. If we focus on the change in the twist angle at the olefin unit, we see that a 22° change occurs upon conversion of the neutral into the radical anion. This twisting of the C-C double bond lowers the LUMO facilitating introduction of the electron. The reduction of the LUMO energy is 0.59 eV according to AM1. Conversion of the radical anion into the dianion involves a larger change, 33°. Thus, it is reasonable to expect that introduction of the second electron will be even more favored than the first. AM1 predicts that this change in angle is associated with a 0.94 eV lowering of the SOMO energy, much larger than the lowering predicted for introduction of the first electron. Of course, this argument is highly simplified. Nevertheless, it may help to understand how inversion can occur even in systems where steric factors are unimportant.

Similar calculations on neutral (*E*)-4,4'-dinitrostilbene (**14**) again show a HOMO with strong  $\pi$ -bonding character in the olefinic bridge and strong  $\pi$ -antibonding character in the LUMO suggesting that similar factors are at work here (see Table 2).

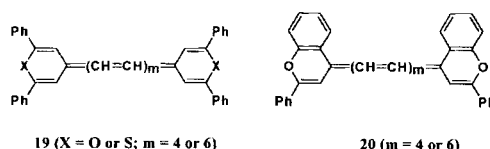
In other cases, potential inversion is seen where more than one olefin unit separates the electroactive groups as in butadienes **17**<sup>9</sup> and **18**.<sup>42</sup> It is generally difficult to



evaluate the extent of potential inversion. For **17**,  $E_1^\circ - E_2^\circ$  was estimated to be equal or more negative than -0.24 V based on failure to detect an ESR signal in mixtures of **17** and its dication. Evans and Hu<sup>42</sup> estimated  $E_1^\circ - E_2^\circ$  for **18** (R = *i*Pr) to be in the range -0.16 to -0.30 based on fits of simulations to experimental voltammograms.

Potential inversion was also seen for several members of families **19** and **20**.<sup>43</sup> All six compounds indicated showed potential inversion for their stepwise oxidation to dications and spectroscopic evidence was presented indicating that  $E_1^\circ - E_2^\circ$  was -80 mV for **19** (X = S; *m* = 4). Interestingly, in these cases shorter unsaturated linkages (*m* = 1, 2 or 3) showed normal ordering of potentials.

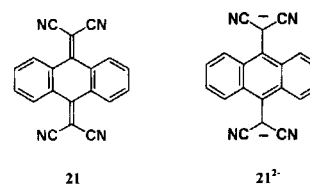
Potential inversion has also been observed in some 2,5-disubstituted furans where the substituents contain



ethene or butadiene units terminated (usually) with a malononitrilidene [=C(CN)<sub>2</sub>] group.<sup>44</sup> The two electroactive centers for reduction may be considered to be the =C(CN)<sub>2</sub> groups that are separated by unsaturated bridges and are conjugated with one another through the furan ring. The authors used a spectroelectrochemical (UV-VIS-near IR) technique to measure the disproportionation equilibrium constants from which  $E_1^\circ - E_2^\circ$  ranging from -280 to -23 mV was calculated. Again, no inversion was seen when the =C(CN)<sub>2</sub> groups were connected to furan (or thiophene) by short linkers, e.g., only one carbon atom.

The infrared region of the spectrum is very useful for determining disproportionation equilibrium constants for certain organometallic complexes. For example, in the neutral/anion/dianion series for W<sub>2</sub>(SBz)<sub>2</sub>(CO)<sub>8</sub> (Bz = benzyl), the absorption bands in the carbonyl region afford quantitative determination of the small amount of anion present in equimolar mixtures of neutral and dianion and hence the equilibrium constant.<sup>45</sup> The value obtained for 0.10 Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> was  $K_{\text{disp}} = 7500 \pm 4000$  giving  $E_1^\circ - E_2^\circ = -0.229 \pm 0.022$  V.

*Unsaturated carbocyclic separators.* One of the most striking examples of potential inversion was found in the reduction of 11,11,12,12-tetracyano-9,10-anthraquinodimethane, **21**.<sup>46</sup> This compound is reduced in a single



two-electron step when studied by cyclic voltammetry in acetonitrile. The process is reversible and the separation between the cathodic and anodic peaks is 30 mV, very close to the limiting value of 29 mV for a reversible, two-electron process with a large, negative value of  $E_1^\circ - E_2^\circ$ . This result was chosen as an introduction to this section because definitive structural data exist on neutral **21** that will allow us to rationalize the potential inversion that is seen. In Fig. 2 the solid state structure<sup>47</sup> of **21** is presented. The bonding pattern in **21** suggests a preferred planar geometry but such a structure would cause strong steric interaction between the cyano groups and ring hydrogens. As is evident in Fig. 2, the molecule adapts to this steric interaction by folding the anthracene ring system in such a way that the two benzo groups and the two dicyanomethylene units are folded in opposite directions. It is logical to assume that this structure persists

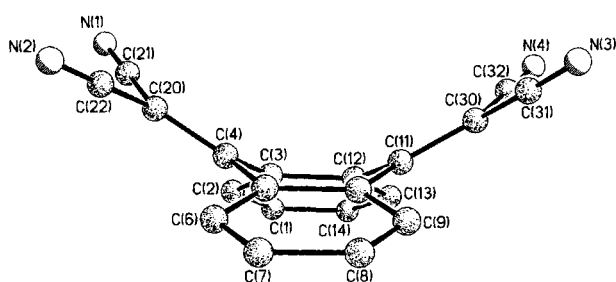


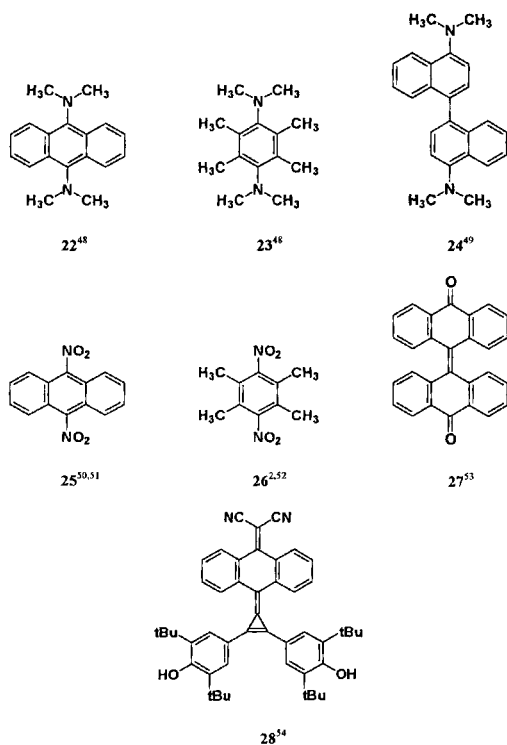
Fig. 2. Structure of 11,11,12,12-tetracyano-9,10-anthraquinodimethane, **21**. Structure created from data in Ref. 47.

in solution. Upon reduction to the dianion, the bonds from the dicyanomethylene groups to the ring become essentially single bonds (see  $\mathbf{21}^{2-}$ ) and the steric interactions can be relieved by twisting the dicyanomethylene groups out of the plane of the anthracene unit which can now enjoy a planar geometry.

These structural changes associated with the reduction of **21** are expected to alter the LUMO energy in a manner analogous to that discussed above and to bring about the observed inversion in potentials. AM1 calculations find the structure shown in Fig. 2 as the optimized structure for neutral **21** and a very similar structure for the radical anion. As expected, the optimized structure of  $\mathbf{21}^{2-}$  features a planar anthracene unit with the dicyanomethylene groups turned out of the plane.

As mentioned above, **21** will serve as a structural analogy to rationalize potential inversion that has been seen in a number of other systems, most of which lack the structural information available for **21** (see **22–28**).

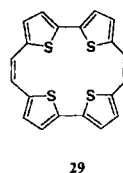
In the bis(dimethylamino) compounds **22–24**, the



dication/radical cation couple corresponds to  $E_1^\circ$  and the radical cation/neutral couple to  $E_2^\circ$ . All of the remainder involve neutral/radical anion/dianion couples. In each case, folded structures like that shown for **21** are thought to be involved. For **22–24** it is the dication that is thought to be folded. In **24** and **27** the structures of the dication and neutral, respectively, are doubly folded, with the direction of folding being opposite in the two connected ring systems. This structure is particularly well established for bianthrone, **27**, for which the potentials are not quite reversed but which does show the type of structural change discussed here.

So, a common theme of structural changes involving folded ring systems has evolved in the literature to explain potential inversions in structures like the above.

*Other systems showing potential inversion.* The reduction of cyclooctatetraene involves conversion of the tub-shaped 8  $\pi$ -electron neutral to a more planar radical anion and finally a perfectly planar 10 electron dianion is formed. These changes result in a compression in potential difference so that  $E_1^\circ - E_2^\circ$  is smaller than for aromatic hydrocarbons of similar size. The compression was well accounted for by the empirical procedures developed by Hu and Evans.<sup>2</sup> The cause of the compression can be traced to the added stability afforded the dianion by virtue of its possessing the Hückel-favored ( $4n+2$ ;  $n=2$ ) 10  $\pi$ -electrons. By contrast, 1,3,5,7-tetra-phenylcyclooctatetraene<sup>55</sup> shows potential inversion, a result not predicted by Hu and Evans. In this derivative, stabilization of the dianion is apparently stronger for reasons that are not understood. In a related case, the fourfold sulfur-bridged [20]annulene **29** shows two-electron



tron reversible reduction to the Hückel-favored ( $4n+2$ ;  $n=5$ ) 22  $\pi$ -electron system and the potentials are inverted.<sup>57</sup> The neutral compound features puckered thiophene units whereas the dianion is probably planar. The associated structural changes may underlie the observed potential inversion.

Inverted potentials are also encountered in organometallic electrochemistry. Representative examples have been cited in Ref. 42.

### The effects of disproportionation/comproportionation

*Other chemical reactions.* As mentioned in the introduction, the disproportionation/comproportionation reaction [reaction (3)] can have no effect in any voltammetric experiment provided that diffusion is the only means of

mass transfer, the diffusion coefficients of all species are equal, the electrode reactions are reversible and there are no other chemical reactions. Many chemical systems do not comply with the last of these restrictions and this type of deviation has been frequently reported. Early examples included conformational changes or isomerizations that occur for one of the species in the scheme that can lead to unusual effects in cyclic voltammetry including curve crossing and autocatalysis.<sup>57-59</sup> The effects are so many and varied that it does not seem profitable to provide a more complete discussion. Suffice it to say that the occurrence of other chemical reactions is one of the most frequent ways by which disproportionation/comproportionation in an EE system is allowed to exert its effect.

*Less-than-reversible electron-transfer reactions.* Generalized treatments of EE mechanisms in voltammetry always include the possibility of quasireversible electrode reactions.<sup>60-62</sup> One example of the effect of comproportionation is found when normal ordering of potentials is observed and the second electron transfer is quasireversible. The result is that the second wave (as observed in dc polarography or steady-state microelectrode voltammetry) is distinctly asymmetric, rising more sharply near its base than it does near the crest. This result, which is predicted by the early theoretical work of Ruzic and Smith,<sup>63</sup> has recently been observed experimentally for reduction of 7,7,8,8-tetracyanoquinodimethane in acetonitrile at platinum electrodes where the second electron-transfer reaction is less than fully reversible.<sup>64</sup> It has been shown theoretically that in the limit of a totally irreversible second electrode reaction and infinitely rapid comproportionation, the second wave should rise abruptly from the plateau current from the first electrode reaction. Such abrupt changes are not seen in experiments but the asymmetry is nonetheless striking.

A related observation was made by Heinze *et al.*<sup>65</sup> for the reduction of cyclooctatetraene at a platinum electrode in tetrahydrofuran. Here the first electron-transfer reaction is less reversible than the second. With a 'passivated' platinum electrode the difference in  $k_s$ -values becomes large and the effect of comproportionation is very much like autocatalysis. That is, the first reduction peak grows at the expense of the second while at the same time becoming sharper (higher slope on rising portion), similar to the behavior cited above. In earlier work<sup>66</sup> it was found that simulations of voltammograms for reduction of cyclooctatetraene at mercury electrodes required inclusion of the comproportionation reaction in order to obtain acceptable agreement with the data but the overall effects were much less dramatic than reported by Heinze *et al.*<sup>65</sup> Similar effects of comproportionation have been predicted for chronoamperometry.<sup>67</sup> An experimental study of the reduction of tetraphenylethylene using Fourier-transform faradaic admittance measurements required the inclusion of comproportionation because of

the quasireversible nature of the second electron-transfer reaction.<sup>68</sup>

*Unequal diffusion coefficients.* When the diffusion coefficients of the three species in the EE scheme are not identical, the comproportionation reaction can affect the voltammetric response. However, the effects are relatively subtle. Zhou and Evans<sup>69</sup> intentionally sought out a system in which the diffusion coefficients differed enough to produce measurable changes. In this work, it was shown for chronoamperometry that no effects will be observed if the diffusion coefficients of reactant and intermediate are identical, regardless of the value of the diffusion coefficient of the final product. These workers found for 7,7,8,8-tetracyanoquinodimethane (TCNQ) that the diffusion coefficients in acetonitrile at 293 K were 1.44, 1.35 and  $0.91 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for the neutral, radical anion and dianion forms of TCNQ. Thus, no measurable effects were anticipated upon sequential reduction of the neutral to the radical anion and dianion because the diffusion coefficients of starting material and intermediate are so similar. However, a significant effect was seen upon stepwise oxidation of the dianion. In normal pulse voltammetry, the second oxidation step was predicted to be 9% larger than the first and an 8% enhancement was observed. Similar effects were seen in cyclic voltammetry of the dianion and these were successfully accounted for by digital simulation. These effects are predicted to be absent if the comproportionation reaction is slow.

Because the three species in the EE scheme are structurally similar, it is unusual to find significant differences (say greater than 30-40%) among their diffusion coefficients so behavior like that seen by Zhou and Evans will be rarely encountered.

*Other modes of mass transport.* One of the most interesting effects of the comproportionation reaction on the voltammetric response is encountered when the ratio of supporting electrolyte concentration to substrate concentration (support ratio) becomes small enough that mass transport by electrical migration comes into play. By lifting this mass transport restriction, the comproportionation reaction can begin to affect the electrochemical behavior. The effect has been studied mainly by steady-state microelectrode voltammetry because this technique is amenable to solutions of high electrical resistance.

The effect was first noted in the reduction of TCNQ in acetonitrile at microelectrodes. At high support ratios, the steady-state voltammogram features two plateau currents for the first and second stages of reduction and the magnitudes of the two limiting currents are equal (except for the small effect of unequal diffusion coefficients cited in the previous section). However at a support ratio near unity, the second limiting current is only about one-fourth the first, a result originally interpreted as being due to an ECE reaction scheme.<sup>70</sup>

In independent work, Norton *et al.*<sup>71</sup> made the same



experimental observations but pointed out that the effect could be quantitatively accounted for by assuming that a fast comproportionation reaction occurs between the dianion and neutral of TCNQ. Since the anions of TCNQ are participating in the transport of negative charge away from the cathode at the low support ratios studied, this migrational transport can suppress the second limiting current. An analogous effect was seen upon oxidation of tetrathiafulvalene and in each case the lower limit for the rate constant for comproportionation was found to be  $10^6 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>71</sup> In another project, reduction of methyl viologen (a dication/radical cation/neutral EE system) was studied and the results were fully consistent with the observations made with TCNQ and tetrathiafulvalene.<sup>72</sup>

Later Amatore *et al.*<sup>73</sup> presented a general theoretical treatment of the effect of electrical migration on the second wave of EE systems. The results pertain to reactants of any charge type from +3 to -3 and two systems, the reduction of dicyano(fluoren-9-ylidene)-methane (reactant charge 0) and methyl viologen (reactant charge +2), were found to behave in accordance with the theoretical predictions. The results at low support ratios can deviate markedly from those seen at high support ratios. For the reduction of methyl viologen, the second limiting current was three times as large as the first at a support ratio of 0.001. The treatment has been extended to an arbitrary number of one-electron reactions and results for the ratio of limiting currents for various charge types at vanishingly small support ratios have been given for the first four steps.<sup>74</sup> The theoretical predictions were tested by studies of the three-step reduction of ruthenium trisbipyridine,  $\text{Ru}(\text{bpy})_3^{2+}$ .

In another instance, it was shown that unusual phenomena at the second reduction step of an EE system at low support ratios were *not* caused by comproportionation.<sup>75</sup> In this study, very concentrated solutions of nitrobenzene (3.9–8.7 M) in toluene were studied and the second limiting current was severely depressed at the higher concentrations. The effect was attributed to migration of negative charge away from the cathode by an 'electron hopping' mechanism mediated by the self-exchange reaction of  $\text{A}^{\cdot-} + \text{A} = \text{A} + \text{A}^{\cdot-}$ , a process that can compete with comproportionation when very high concentrations of reactant are employed.

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