Inverted potentials in two-electron processes in organic electrochemistry

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Many molecules can accept or lose electrons in two sequential one-electron steps. Normally, gain or loss of the second electron occurs less readily than the first, which gives rise to two separate one-electron processes detected by voltammetry. In this instance, the intermediate (one-electron product) is stable with respect to disproportionation. There are cases known, however, in which the gain or loss of the second electron occurs more easily than the first, leading to a single two-electron voltammetric process. Here, the standard potentials are inverted with respect to their normal order and the one-electron intermediate is unstable with respect to disproportionation. Semiempirical molecular orbital calculations (AM1) have been used to compute disproportionation energies for a variety of aromatic hydrocarbons and the results were found to be remarkably similar to those calculated for charging spheres in vacuum. Experimental values of the disproportionation Gibbs energies in solution, calculated from the difference in potential for cases which show normal ordering, have been used to develop an empirical relation for the attenuation of the disproportionation energy on going from vacuum to solution. This relationship was then used to predict and/or rationalize cases where inversion or compression of potentials has been observed for hydrocarbons in the solution phase. A similar approach was used for other classes of molecules. Here, only a single model compound with normal ordering of potentials was used to predict the effect of solvation on the disproportionation energies for structurally related species. In general, the approach is quite successful in predicting and/or rationalizing the occurrence of inversion of potentials. The reduction of 3,6-dinitrodurene was predicted to occur with inversion and this was verified by cyclic voltammetric studies.

The electrochemical reactions of neutral organic compounds frequently feature a series of one-electron steps in which electrons are sequentially added to or removed from the reactant to form a series of ions with increasing charge. An extreme example of this behaviour is found with the fullerenes, C_{60} and C_{70} , each of which is capable of accepting up to six electrons to produce, formally, the corresponding hexaanions.^{1,2} More typically, only one or two electrons can be added or removed within the range of potentials available in solution.

In the normal case, the addition or removal of the second electron is significantly more difficult than the first and the successive reversible formal potentials differ by several tenths of a volt. Thus stepwise reduction or oxidation of the molecules is observed with the singly charged radical anion or cation being a stable intermediate that tends not to disproportionate to the doubly charged ion and neutral starting material. The origin of this difference in reversible potentials is largely electrostatic in nature, *i.e.* it is more difficult to add charge to the singly charged intermediate than is required to charge the neutral compound. This normal ordering of potentials is illustrated in Fig. 1.

There are instances, however, in which the normal order is not observed and it is in fact easier to add or remove the second electron than the first.³⁻²² In the present discussion we will call this order 'inverted potentials' as also shown in Fig. 1. In cases where inverted potentials are seen in organic electrochemistry, a significant structural change is associated with one or both electron-transfer steps and it is this structural change that is the cause of the inversion. There are also numerous examples of inverted potentials in the redox reactions of inorganic and organometallic compounds²¹ but the focus of this paper will be organic systems.

We will first review and expand a semiquantitative treatment of the differences between two-electron processes in the solution and gas phases. This will be followed by a demonstration of how calculated energy differences for the species in vacuum can be used to predict potential inversion in solution and a discussion of the structural factors that cause this unusual behaviour. Finally, the voltammetry of a compound for which potential inversion is predicted will be reported.

Disproportionation in vacuum compared to solution

The discussion will be developed in terms of reduction reactions but conversion to oxidations is straightforward. A reactant A^z , bearing charge z, is reduced in two steps each with its own reversible formal potential, $E_1^{\circ'}$ and $E_2^{\circ'}$.

$$A^{z} + e^{-} = A^{z-1}; \quad E_{1}^{\circ'}$$
 (1)

$$A^{z-1} + e^{-} = A^{z-2}; E_{2}^{\circ\prime}$$
 (2)

It will be convenient to present the results in terms of the disproportionation of the intermediate A^{z-1}

$$2A^{z-1} = A^z + A^{z-2}$$
(3)

because the Gibbs energy change for the disproportionation reaction is simply related to the difference between the two



Fig. 1 Schematic representation of normal and inverted ordering of potentials for a reduction reaction. E_1° and E_2° are the formal potentials for addition of the first and second electrons, respectively.

formal potentials as given in eqn. (I)

$$\Delta_{\text{disp}} G^{\circ} = -RT \ln K_{\text{disp}} = F(E_1^{\circ\prime} - E_2^{\circ\prime}) \tag{I}$$

which shows that with normal ordering of potentials $(E_1^{\circ \prime} - E_2^{\circ \prime} > 0)$, $\Delta_{\text{disp}} G^{\circ}$ is positive and disproportionation is not favoured and the opposite is true when inverted potentials $(E_1^{\circ \prime} - E_2^{\circ \prime} < 0)$ are encountered.

If species A^z is considered to be a spherical particle located in vacuum and possessing no special affinity for electrons, its Gibbs energy can be computed as the reversible work required to charge the sphere to charge z. The result is the Born expression,²³ $\Delta G^\circ = N_A(ze_0)^2/8\pi\epsilon_0 r$, where N_A is Avogadro's number, e_0 is the electronic charge, ϵ_0 is the permittivity of free space and r is the spherical radius. By combining the energies of all three species, the Gibbs energy for disproportionation of charged spheres in vacuum is found to be given by eqn. (II) which contains only physical constants and the radius. Note that the charge number z does not appear in eqn. (II), indicating that the disproportionation energy is independent of charge type. Included in Fig. 2 is a plot of eqn. (II) showing the predicted linear dependence of the Gibbs energy change on reciprocal radius.

$$\Delta_{\rm disp} \, G_{\rm Born}^{\circ}(\rm vac) = \frac{N_{\rm A} \, e_0^2}{4\pi\epsilon_0 \, r} \tag{II}$$

For spheres of molecular dimensions, the values are large and positive, reflecting the much larger energy required to form A^{z-2} and A^z compared to two A^{z-1} , e.g. $\Delta_{disp} G_{Born}^{\circ}(vac) =$ 464 kJ mol⁻¹ for r = 3 Å. This corresponds to a splitting of 4.8 V between the hypothetical vacuum formal potentials. This fact has long been recognized,^{15,24} as has the ability of solvation to reduce the splitting to the values typically seen in solution.

Another way to compute the disproportionation energy for molecular systems is to employ semiempirical molecular orbital calculations to obtain the energies of the three participants in the reactions. Previously, this was done for anthra-



Fig. 2 Gibbs energy of disproportionation as a function of reciprocal radius of reactants. For molecular species plotted, the radius is the equivalent spherical radius from the molecular volume based on the molecular weight and an assumed constant density of 1.25 g ml⁻¹. (----) $\Delta_{disp} G^{\circ}$ for charging spheres in vacuum. (\cdots -··) $\Delta_{disp} G^{\circ}$ predicted by the Born expression for solvation energies for a solvent with relative permittivity equal to that of dimethylformamide or acetonitrile. (\bigcirc) $\Delta_{disp} G^{\circ}$ calculated by AM1 for aromatic hydrocarbon reduction (neutral, radical anion, dianion) in vacuum. $\Delta_{disp} G^{\circ}$ assumed to equal $\Delta_{disp} H^{\circ}$. Compound numbers are given in Table 1 and beneath the structures. (\bigcirc) Results calculated for hydrocarbon oxidation (neutral, radical cation, dication). (\times) $\Delta_{disp} G^{\circ}$ for six aromatic hydrocarbons in dimethylformamide from ref. 28. Left to right: 9,10-diphenylanthracene, coronene, perylene, benz[a]anthracene (above), chrysene (below), anthracene. Vertical arrow illustrates the attenuation of $\Delta_{disp} G^{\circ}$ for anthracene upon going from vacuum to dimethylformamide.

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cene and its anions²⁴ giving a disproportionation energy of 430 kJ mol⁻¹. Here, we have employed the AM1 semiempirical molecular orbital method²⁵ (parametrized to produce $\Delta_f H^\circ$) to calculate disproportionation enthalpies, $\Delta_{disp} H^\circ$ (AM1), for a variety of compounds (Table 1) which will be close to the Gibbs energy change if entropy effects are small.

$$\Delta_{\text{disp}} H^{\circ}(\mathbf{A}\mathbf{M}1) = \Delta_{\text{f}} H^{\circ}(\mathbf{A}^{z}) + \Delta_{\text{f}} H^{\circ}(\mathbf{A}^{z-2}) - 2\Delta_{\text{f}} H^{\circ}(\mathbf{A}^{z-1})$$
$$\approx \Delta_{\text{disp}} G^{\circ}(\mathbf{A}\mathbf{M}1) \tag{III}$$

The results for 16 aromatic hydrocarbons (neutral, radical anion, dianion) are plotted in Fig. 2 together with calculations for neutral, radical cation, dication for four of the compounds. The value of molecular radius in the plot is the equivalent spherical radius corresponding to the molecular volume, the latter being calculated from the molecular weights and an assumed average density of 1.25 g ml^{-1} .

These AM1 calculations are surprisingly close to the Born line and the values for the largest hydrocarbons appear to be



Table 1	Heats of formation	obtained for	hydrocarbons	by	AM1	calculations
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compound (ion type)	r ^b /Å	$\Delta_{\rm f} H^{\circ}({\rm n})$	$\Delta_{\rm f} H^{\circ}({\rm ri})$	$\Delta_{\rm f} H^{\circ}({ m di})$	$\Delta_{disp} H^{\circ}(AM1)$	$\Delta E^{\circ\prime c}$	$\Delta\Delta_{\rm disp}G^{\circ}({\rm AM1}\rightarrow{\rm sol})^d$
1 (anions)	2.91	91.50	114.39	748.14	610.86		
1 (cations)	2.91	91.50	983.32	2466.26	591.12		
2 (anions)	3.44	168.82	108.83	521.12	472.29		
2 (cations)	3.44	168.82	970.94	2236.64	463.59		
3 (anions)	3.84	261.96	146.44	435.14	404.22	0.740	-332.82
3 (cations)	3.84	261.96	1008.60	2154.84	399.61		
4 (anions)	3.84	239.03	158.16	472.04	394.76		
5 (anions)	4.17	362.13	206.98	413.76	361.92		
5 (cations)	4.17	362.13	1071.52	2138.65	357.73		
6 (anions)	4.17	325.72	210.00	447.19	352.92	0.665	-288.76
7 (anions)	4.00	280.33	162.42	423.42	378.90		
7 (cations)	4.00	280.33	1030.85	2156.18	374.80		
8 (anions)	4.17	314.22	229.79	515.43	370.07		
9 (anions)	4.17	317.23	211.88	455.80	349.28	0.505	- 300.56
10 (anions)	4.31	371.92	224.89	416.31	338.44	0.615	-279.10
11 (anions)	4.45	466.01	282.04	429.11	331.04		
12 (anions)	4.70	572.04	366.73	468.19	306.77		
13 (anions)	4.93	679.48	457.98	523.63	287.15		
14 (anions)	4.57	400.62	274.81	476.64	327.65	0.640	-265.90
15 (anions)	4.70	504.46	365.93	560.82	333.42		
16 (anions)	4.71	506.89	361.20	546.85	331.33	0.675	-266.20
17 (anions)	3.21	264.76	191.96	557.23	438.06		
18 (anions)	5.06	707.01	594.00	765.25	284.26		
19 (anions)	4.72	513.42	396.43	554.51	275.06		
20 (cations)	5.24	-123.26	568.56	1493.77	233.38		

^{*a*} 1 = benzene, 2 = naphthalene, 3 = anthracene, 4 = phenanthrene. Energies expressed in kJ mol⁻¹. Enthalpy of formation labels: n = neutral; ri = radical ion; di = doubly charged ion. ^{*b*} Effective spherical radius computed from molecular volume based on an assumed constant density of 1.25 g ml⁻¹. ^{*c*} Experimental values from ref 28. 0.2 M Me₄NBr, DMF, 11 °C. $\Delta E^{\circ\prime} = E_1^{\circ\prime} - E_2^{\circ\prime}$. ^{*d*} Attenuation of vacuum Gibbs energy of disproportionation [assumed to equal $\Delta_{disp} H^{\circ}(AM1)$] by solvation.

approaching the values predicted by eqn. (II) as the molecular size increases. Reasons to be surprised include acknowledged²⁶ inaccuracies in calculation of heats of formation by AM1, the neglect of entropy changes, the fact that the molecules are far from spherical in shape and the fact that the dianions are unstable with respect to ejection of an electron, making one wonder just what AM1 is calculating for dianions. The agreement may simply reflect a fortuitous cancellation of errors, but, in any case, we can conclude that AM1-calculated disproportionation energies are fairly close to the values predicted for charging spheres that possess no chemical properties. Thus, the ca. 5 V splitting of the potentials in vacuum is calculated to be almost entirely electrostatic in origin. This fact was recognized for hydrocarbon ions in a qualitative sense several decades ago.²⁷

Of course, when the molecular species are moved from vacuum to a solution phase, the electrostatic factors leading to large values of $\Delta_{disp} H^{\circ}(AM1)$ are strongly attenuated. In fact, the Born treatment of ionic solvation²³ gives eqn. (IV) for the disproportionation energy in solution where D is the relative permittivity of the medium.

$$\Delta_{\rm disp} \, G^{\circ}_{\rm Born}({\rm sol}) = \frac{N_{\rm A} \, e_0^2}{4\pi D \varepsilon_0 \, r} \tag{IV}$$

The dotted line in Fig. 2 is eqn. (IV) for the solvent DMF and it can be seen that the Born treatment predicts that $\Delta_{disp} G^{\circ}(sol)$ never exceeds *ca*. 10 kJ mol⁻¹.

It is well known²³ that the Born equation overestimates ionic solvation energies and this is substantiated by the experimental data plotted in Fig. 2. These points were taken from $E_1^{\circ\prime} - E_2^{\circ\prime}$ values measured in DMF by Jensen and Parker²⁸ and one notes that they all are higher than the Born prediction. In fact, the difference between the AM1-calculated and solution values the experimental values. $\Delta \Delta_{disp} G^{\circ}(AM1 \rightarrow sol)$, is simply a measure of the relative solvation energies of the neutral, monoanionic and dianionic species with a possible contribution from ion-pairing energies. A very similar treatment has been used earlier to estimate solvation energies based on observed solution-phase potential differences and MO calculations.²⁹

In the treatment to be followed here, $\Delta \Delta_{disp} G^{\circ}(AM1 \rightarrow sol)$ is simply the vertical distance from the AM1-calculated point and the experimental point in Fig. 2 (illustrated by the arrow for anthracene). The values of $\Delta\Delta G_{disp} G^{\circ}(AM1 \rightarrow sol)$ for the six compounds studied by Jensen and Parker²⁸ are similar (Table 1) but vary somewhat with molecular size, being larger for the smaller molecules. By linear regression, the six experimental points from Jensen and Parker give $\Delta \Delta_{disp} G^{\circ}(AM1 \rightarrow sol)$ according to eqn. (V) (correlation coefficient = 0.96). The regression line reproduces the experimental values with an average deviation of 5.8 kJ mol⁻¹ (60 mV).

$$\Delta \Delta_{\text{disp}} G^{\circ}(\text{AM1} \rightarrow \text{sol}) = 41.3 - 1420/r; \text{ (kJ mol}^{-1}; r \text{ in Å)}$$
(V)

Eqn. (V) represents an experimental determination of the attenuation of the disproportionation Gibbs energy for aromatic hydrocarbons on going from vacuum to DMF. The Born prediction [eqn. (IV) – eqn. (II)] is $\Delta\Delta_{disp} G^{\circ}_{Born}(vac \rightarrow sol) = -1350/r$. Note that the slope of the empirical relationship is very similar to the Born slope and that the positive intercept of eqn. (V) reflects the aforementioned tendency for the Born treatment (zero intercept) to overestimate the effects of solvation. These observations have been made before, although in a slightly different context.²⁹

Now, for aromatic hydrocarbons, eqn. (V) can be used with the AM1-calculated disproportionation energies to predict $\Delta_{disp} G^{\circ}(sol)$ and hence $E_1^{\circ\prime} - E_2^{\circ\prime}$ for yet unstudied compounds [eqn. (VI)]. For example, for hexacene, 12, $E_1^{\circ\prime} - E_2^{\circ\prime}$ is predicted to be +0.50 V, not unlike the experimental values for other hydrocarbons.²⁸

$$965(E_1^{\circ\prime} - E_2^{\circ\prime}) = \Delta_{disp} H^{\circ}(AM1) + \Delta\Delta_{disp} G^{\circ}(AM1 \to DMF)$$
(VI)

Structural factors influencing $\Delta_{disp} H^{\circ}(AM1)$

Examination of Table 1 reveals cases where $\Delta_{disp} H^{\circ}(AM1)$ is considerably lower than calculated for aromatic hydrocarbons of comparable size. An example is tetraphenylethylene, **19**, for

which $\Delta_{disp} H^{\circ}(AM1)$ is only 275 kJ mol⁻¹ compared to 307 kJ mol⁻¹ for hexacene, 12, which has about the same effective spherical radius. This difference of 32 kJ mol⁻¹ (0.33 V) suggests that, if solvation energies for the anions of 19 and 12 are similar, the lower $\Delta_{disp} H^{\circ}(AM1)$ for 19 could lead [eqn. (VI)] to the prediction of inverted, or at least compressed, potentials.

What factors cause $\Delta_{disp} H^{\circ}(AM1)$ for 19 to be abnormally low? The causes may be traced to changes in structure which accompany introduction of electrons into neutral tetraphenylethylene. The sterically congested neutral form of 19 possesses a virtually untwisted double bond (twist angle 5°) with the phenyl groups turned out of the plane of the central alkene unit and four attached aromatic carbons. In the radical anion, AM1 calculates that the congestion is relieved by a partial twisting of the ethylene bond (30°) and in the dianion, the ethylene bond is essentially a single bond allowing free rotation. The calculations indicate that the dihedral angle between the two (Ph)₂C units is *ca.* 90° in the dianion.

In a qualitative sense, the lowering of $\Delta_{disp} H^{\circ}(AM1)$ toward values which could lead to potential inversion can be understood in terms of the effect of the structural changes on the LUMO energies as illustrated in Fig. 3 where these have been calculated for neutral 19, first in its optimized structure, and for 19 in the optimized (twisted) structure of the radical anion. The twisting that accompanies the first step of reduction results in a lowering of the LUMO energy by 0.84 eV making it energetically more favourable to add an electron than would be the case if no significant structural change occurred. Similarly, the SOMO energy for the radical anion of 19 is lowered by 1.04 eV upon going from the radical anion structure to that of the dianion. The greater lowering of the energy of the orbital receiving the electron for the second step relative to the first explains qualitatively why compression or even inversion of potentials might occur in the reduction of 19.

One should also notice that the changes in structure have the effect of raising the HOMO energies resulting in enhanced



Fig. 3 Orbital energies for the neutral and radical anion forms of tetraphenylethylene, 19, each in two different structures. Note the lowering of the LUMO energy of the neutral when it is converted to the structure of the radical anion and also the lowering of the SOMO energy of the radical anion as it adopts the structure of the dianion.

removal of the second electron compared to the first in oxidation of 19. Indeed, potential compression and inversion have been observed for the oxidation of a variety of derivatives of tetraphenylethylene.^{11,13,15,17}

Another way of depicting the factors that bring about a lowering of $\Delta_{disp} H^{\circ}(AM1)$ is to concentrate on the AM1-computed system energies rather than the orbital energies. What is discovered is that the structural changes that accompany the reduction bring about a reduction in $\Delta_{disp} H^{\circ}(AM1)$ compared to the value that would have accrued had no structural change occurred. In Table 2, the results for reduction of a normal aromatic hydrocarbon, anthracene, are contrasted with those for 19. For anthracene, the structural changes are so minor that the values of $\Delta_r H^{\circ}$ for the radical anion and dianion calculated in the structure of neutral anthracene are only slightly greater than the values for the energy-optimized structures and the resulting $\Delta_{disp} H^{\circ}(AM1)$ is only 17 kJ mol⁻¹ greater than when the optimized structures are used.

By contrast, the substantial structural changes that accompany reduction of 19 cause the energies of the radical anion and dianion to soar when these species are forced to adopt the neutral structure. The result is that $\Delta_{disp} H^{\circ}(AM1)$ is 87 kJ mol⁻¹ greater when the neutral structure is used than when optimized versions of each species are computed. So, it can be seen that the structural changes accompanying reduction of 19, predicted by AM1, allow a lowering of the $\Delta_f H^{\circ}$ of the radical anion and dianion that result in a depression of $\Delta_{disp} H^{\circ}(AM1)$ and the noticeable compression of the potentials observed in the solution phase (see below).

Using calibrated values of $\Delta \Delta_{disp} G^{\circ}(AM1 \rightarrow sol)$ to interpret data for hydrocarbons

Assuming that the correlation for polycyclic aromatic hydrocarbons embodied in eqn. (V) can be used to predict $\Delta\Delta_{disp} G^{\circ}(AM1 \rightarrow sol)$ for other hydrocarbons, we can now discuss previously studied examples of potential compression or inversion and make predictions for yet unstudied systems. The AM1 disproportionation energy for tetraphenylethylene, **19**, is 275.06 kJ mol⁻¹ (Table 1) and the value of $\Delta\Delta_{disp} G^{\circ}(AM1 \rightarrow sol)$ from eqn. (V) is -257.48 which gives +18 kJ mol⁻¹ for $\Delta_{disp} G^{\circ}(DMF)$. This corresponds to $E_1^{\circ\prime} - E_2^{\circ\prime} = 0.18$ V compared to the experimental value of 0.035 V³⁰.

Another example is cyclooctatetraene, 17, in which the tubshaped neutral becomes planar on the addition of an electron to form the radical anion. The dianion is also planar. AM1 finds a disproportionation energy of 438.06 kJ mol⁻¹, $\Delta\Delta_{\text{disp}} G^{\circ}(\text{AM1} \rightarrow \text{sol})$ from eqn. (V) gives -398.65 kcal mol⁻¹, leaving $\Delta_{\text{disp}} G^{\circ}(\text{DMF}) = 39$ kcal mol⁻¹ or $E_{1}^{\circ \circ}$ $-E_{2}^{\circ \circ} = 0.41$ V compared to 0.28 V found.³¹ Thus, in these two instances the treatment is successful, within *ca.* 150 mV, in predicting the observed compression of $E_{1}^{\circ \circ} - E_{2}^{\circ \circ}$ to smaller than typical values.

1,3,5,7-Tetraphenylcyclooctatetraene, 18, in contrast, is known¹² to have inverted potentials in acetonitrile. That is, $E_1^{\circ\prime} - E_2^{\circ\prime}$ is negative. The enthalpy of disproportionation found by AM1 is 284.26 kJ mol⁻¹ and eqn. (V) gives $\Delta \Delta_{\text{disp}} G^{\circ}(AM1 \rightarrow \text{sol})$ of $-237.65 \text{ kJ mol}^{-1}$ which is much too

Table 2 Effect of structural change on $\Delta_f H^{\circ}$ (kJ mol⁻¹) for neutral, radical anion and dianion of anthracene and tetraphenylethylene, 19

compound	structure ^a	$\Delta_{\rm f} H^{\circ}({ m n})$	$\Delta_{\rm f} H^{\circ}({\rm ri})$	$\Delta_{\rm f} H^{\circ}({ m di})$	$\Delta_{disp} H^{\circ}(AM1)$
anthracene, 3	optimized	261.96	146.44	435.14	404.22
anthracene, 3	as neutral	261.96	155.39	470.11	421.29
tetraphenylethylene, 19	optimized	513.42	396.43	554.51	275.06
tetraphenylethylene, 19	as neutral	513.42	449.03	746.47	361.83

^a Optimized: the enthalpy of formation of each species was calculated in its energy-optimized structure. As neutral: the enthalpy of formation of each species was calculated in the optimized structure of the neutral species.

small to cause inversion. In this case, the source of the discrepancy may be the fact that the charge distribution in the anions of **18** may be much more localized than with the polycyclic aromatic hydrocarbons. According to AM1, the electron density in the two nearly degenerate HOMOs of the dianion of **18** is situated almost entirely on the cyclooctatetraene ring, so these ions may behave as though they are considerably smaller than the total ion size would indicate. This would increase the calculated $\Delta \Delta_{\text{disp}} G^{\circ}(AM1 \rightarrow \text{sol})$ and possibly rationalize the observed inversion of potential. It is worth emphasizing that the AM1 calculations provide an immediate hint that inversion may occur as $\Delta_{\text{disp}} H^{\circ}(AM1)$ is 154 kJ mol⁻¹ smaller for **18** than for cyclooctatetraene itself.

Another type of fused ring aromatic hydrocarbon is illustrated by dibenzo[g,p]chrysene, 15, which is a non-planar molecule owing to severe steric interactions of the hydrogen atoms (shown in the structure) as planarity is approached. AM1 confirms the non-planarity, showing each phenanthrene unit turned with respect to the other about the linking C—C group. The molecule actually exists as two diastereoisomers, a *meso* and an enantiomeric pair.²⁶ AM1 calculates (for the enantiomeric pair) an enthalpy of disproportionation (333.42 kJ mol⁻¹) which, with eqn. (V), predicts normal ordering of potentials, $E_1^{o'} - E_2^{o'} = +0.77$ V. Investigation of the electrochemical behaviour of 15 would be an interesting test of the present treatment.

One of the most thoroughly studied cases of near inversion of potentials is tetrakis-*p*-methoxyphenylethylene, **20**. Oxidation to the radical cation and dication occurs at nearly identical potentials and $E_1^{\circ'} - E_2^{\circ'}$ for acetonitrile solvent has been reported to be -3, 4.5 or 8 mV depending upon the methods employed.^{13,16} AM1 gives $\Delta_{disp} H^{\circ}(AM1)$ of 233.38 kJ mol⁻¹ and eqn. (V) indicates $\Delta \Delta_{disp} G^{\circ}(AM1 \rightarrow sol) = -228.32$ kJ mol⁻¹. Here the aromatic hydrocarbon calibration equation was used, as no suitable model compounds were available (see below). Combining these quantities as in eqn. (VI) gives $E_1^{\circ'} - E_2^{\circ'} = +0.05$ V indicating that our treatment accommodates the experimental results for **20** quite well.

Summarizing the discussion to this point, it appears that an empirical correlation such as eqn. (V) is fairly successful in predicting the attenuation in the disproportionation energy upon moving from vacuum to solution phase, at least when applied to molecules similar to those used to establish the correlation. However, when we considered other types of compounds, it was soon clear that the calibration obtained from aromatic hydrocarbons [eqn. (V)] was much less successful. Presumably, a separate calibration relationship would be needed for each class of compound. Unfortunately, in most cases the available data on related compounds are insufficient to establish a correlation so an alternative procedure must be sought.

Extension to other families of compounds

Consider the compounds 21-35 (also Table 3). These have been chosen because a number of them have, or might be expected to have, inverted potentials. In all cases, the charge distribution in the ions will be far from uniform suggesting that family-specific solvation interactions may exist requiring a new means of calibration for the estimation of $\Delta \Delta_{\operatorname{disp}} G^{\circ}(AM1 \rightarrow \operatorname{sol})$. We decided to attempt a single-point calibration. This was accomplished by computing [eqn. (VI)] the $\Delta \Delta_{\text{disp}} G^{\circ}(AM1 \rightarrow \text{sol})$ for a single model compound for each class using $\Delta_{disp} H^{\circ}(AM1)$ and the experimental value of $E_1^{\circ\prime} - E_2^{\circ\prime}$ obtained for that compound in DMF or acetonitrile (which have identical relative permittivities, 36³²). As noted above, the experimental correlation for aromatic hydrocarbons gave a slope that was very close to the Born slope. Thus, a single model compound can be used to develop an equation for $\Delta \Delta_{disp} G^{\circ}(AM1 \rightarrow sol)$ as a function of 1/r if we assume that the Born slope, 1350 Å kJ mol⁻¹, holds for each family. Table 4 gives the resulting equations for each family together with the model compound which was used.

The single-compound calibrations in Table 4 allow the prediction of $\Delta \Delta_{\text{disp}} G^{\circ}(AM1 \rightarrow \text{sol})$ for the other members of each compound class and, together with the AM1-calculated disproportionation energies, the prediction of $\Delta_{disp} G^{\circ}(sol)$ as shown in Table 5. The examples shown in Table 5 represent a single type of structural change that accompanies the electron transfer reactions, i.e. formation of a boat form in the central ring with folding of the molecule. This is nicely illustrated for the dication of 23, Fig. 4, as computed by AM1. The neutral form of 23 can retain a planar durene ring because the steric interactions between the dimethylamino methyls and ring methyls can be relieved by twisting the dimethylamino groups out of the plane of the ring. In the dication, double bonds connect the nitrogen atoms to the ring which prevents the aforementioned twisting of the dimethylamino groups. The steric strain is relieved in the dication by formation of the boat form which folds the ring methyl groups away from the dimethylamino groups. AM1 also finds the boat form of the radical cation of 23 to be more stable than the twisted form.

The neutral form of 25 has also been shown to adopt the folded boat-type of structure in the solid phase as shown by

 Table 3
 Heats of formation and disproportionation (kJ mol⁻¹) obtained for 21-35 by AM1 calculations

compound (ion type)	r ^a ∕Å	$\Delta_{\rm f} H^{\circ}({\rm n})$	$\Delta_{\rm f} H^{\circ}({\rm ri})$	$\Delta_{\rm f} H^{\circ}({\rm di})$	$\Delta_{disp} H^{\circ}(AM1)$
21 (cations)	3.73	167.82	818.77	1890.88	421.16
22 (cations)	4.38	387.44 (T)	1007.26 (B)	1924.47 (B)	297.40
23 (cations)	4.12	101.92 (T)	775.17 (B)	1759.29 (B)	310.87
24 (anions)	4.02	792.95	454.09	485.76	370.54
25 (anions)	4.59	927.59 (B)	666.59 (B)	686.22 (T)	280.62
26 (anions)	4.35	724.46 (B)	435.47 (B)	430.78 (T)	284.30
27 (anions)	3.76	138.49	-122.51	59.33	442.83
28 (anions)	4.40	359.53 (T)	71.25 (B)	129.29 (B)	346.31
29 (anions)	4.14	59.74 (T)	-167.65 (T)	1.13 (B)	396.18
30 (cations)	4.24	271.54	942.49	1917.11	303.67
31 (cations)	4.76	460.62 (T)	1139.89 (T)	2023.09 (B)	203.93
32 (anions)	3.88	78.07	-205.81	-123.72	365.97
33 (anions)	4.96	362.50 (T)	79.04 (T)	87.86 (T)	292.28 (T)
, , , , , , , , , , , , , , , , , , ,		311.50 (B)	117.15 (B)	215.22 (B)	292.42 (B)
34 (anions)	4.55	-51.17 (T)	-357.44 (T)	-328.61 (T)	335.10 (T)
. ,		-95.60 (B)	-298.44 (B)	-176.98 (B)	324.30 (B)
35 (cations)	5.36	- 1231.04	- 560.70	348.02	238.38

Structure types: T is twisted; B is boat form, folded. Lowest energy structures reported except for 33 and 34 for which energies for both structures have been tabulated.

^a Equivalent spherical radius computed from molecular volume based on an assumed constant density of 1.25 g ml⁻¹.

Table 4 Estimation of the attenuation in disproportionation Gibbs energy on moving from vacuum to solution phase, $\Delta \Delta_{disp} G^{\circ}(AM1 \rightarrow sol)$, as a function of molecular size using solution-phase values of ΔE° for a single model compound for each compound class^a

model compound	ion type	$\Delta E^{\circ\prime}/{ m V}$	ref.	$r^{-1}/Å^{-1}$	$\Delta\Delta_{disp}G^{\circ}(AM1 \rightarrow sol)/kJ \text{ mol}^{-1}$
N, N, N', N'-tetramethyl-1,4-phenylenediamine, 21	cations	0.60	22	0.268	-13.8-1350/r
tetracyanoquinodimethane, 24	anions	0.54	33	0.249	+18.1-1350/r
1,4-dinitrobenzene, 27	anions	0.20	34	0.266	-64.5-1350/r
N, N, N', N'-tetramethylbenzidine, 30	cations	0.195	36	0.236	+33.9-1350/r
4,4'-diphenoquinone, 32	anions	0.295	35	0.258	+10.8-1350/r

 ${}^{a}\Delta E^{\circ\prime} = E_{1}^{\circ\prime} - E_{2}^{\circ\prime}$ with the reaction sequence considered for reductons in all cases. For example, for N, N, N', N'-tetramethyl-1,4-phenylenediamine, $E_{1}^{\circ\prime}$ refers to the dication/radical cation couple and $E_{2}^{\circ\prime}$ to the radical cation/neutral couple.

X-ray crystallography.³⁸ Upon reduction, the dicyanomethylidene units in 25 can rotate freely allowing the anthracene core to become planar. The biaryl-type systems such as bianthrone, 33, also adopt similar structures. The more stable form of 33 features doubly folded anthracenes with each half folded away from the other.³⁷ In reduced forms of bianthrone, the two anthranol units can become planar with twisting about the connecting bond.

For the results reported in Tables 3 and 5, the lower energy form of each oxidation state is reported as B (boat or folded form) or T (twisted). In two cases, results for both forms are reported.

Now turning to the discussion of the predicted $\Delta E^{\circ\prime}$ values reported in Table 5, we first note that inverted potentials are indicated for 22 and 23, just as observed experimentally.²²



Fig. 4 AM1-optimized structure of the dication of 3,6-bis(dimethylamino)durene, 23, showing the characteristic boat form adopted by many of the species being discussed

This is also true for 35, even though it is less closely related to the model compound than are 22 and 23.²¹ Experimentally, it is usually only possible to confirm that inversion has occurred. It is much more difficult to establish the extent of inversion once $\Delta E^{\circ\prime}$ is more negative than *ca.* -0.1 to -0.2 V. Clearly, the treatment is quite successful in rationalizing the behaviour of 22, 23 and 35.

The reduction of 25 is predicted to show $\Delta E^{\circ \circ}$ near zero, just as observed,⁶ and the unknown substance 26 is predicted to have mildly inverted potentials. Reduction of dinitroanthracene 28 has been shown qualitatively to feature inversion of potentials^{10,14} and the present treatment makes the same prediction. Dinitrodurene, 29, is indicated to have $\Delta E^{\circ \circ}$ near zero. The single mention of its reductive electrochemistry suggests that this prediction may be borne out in practice²⁰ but the paucity of data in the literature prompted us to investigate 29 in this work (see below).

Compound 31 has been carefully studied by cyclic voltammetry and the shape of the current-voltage curve is in precise agreement with potential inversion, $\Delta E^{\circ\prime}$ estimated to be equal to or more negative than -180 mV.^5 Our treatment, which predicts an even stronger inversion, is fully consistent with the experimental observations. For bianthrone, 33, $\Delta E^{\circ\prime}$ is well accounted for by the reduction reactions of the twisted forms. However, the sequence indicated by $B \rightarrow T^- \rightarrow T^{2-}$ is predicted to be strongly inverted whereas $\Delta E^{\circ\prime}$ is found experimentally to be +0.10 V, a value based on combination of a thermochromic equilibrium constant with a measured $E^{\circ\prime,37}$

Finally, we note the interesting case of diduroquinone, 34. The neutral quinone is unknown but AM1 calculates its stablest form to be doubly folded (B) as in bianthrone. The radical anion prefers to be twisted as does the dianion. The $\Delta E^{\circ\prime}$ for the $B \rightarrow T^- \rightarrow T^{2-}$ sequence is predicted to be near zero. Experimentally, it is possible to start with the dianion

Table 5 Use of calibrated values of $\Delta \Delta_{disp} G^{\circ}(AM1 \rightarrow sol)$ to obtain predicted values of $\Delta_{disp} G^{\circ}(sol)$ and $\Delta E^{\circ \prime}$ from AM1-calculated vacuum enthalpies of disproportionation

							$\Delta E^{\circ\prime}/\mathrm{V}$	
compound (ion type)	model	$r^{-1}/Å^{-1}$	$\Delta_{disp} H^{\circ}(AM1)$	$\Delta \Delta_{\operatorname{disp}} G^{\circ}(\operatorname{AM1} \to \operatorname{sol})^a$	$\Delta_{\operatorname{disp}} G^{\circ}(\operatorname{sol})$	calc.	exp(solv.) ^b	ref.
22 (cations) 23 (cations) 35 (cations)	21 21 21	0.228 0.243 0.187	297.40 310.87 238.36	- 310.12 - 329.49 - 253.68	- 12.72 - 18.62 - 15.32	-0.13 -0.19 -0.16	inv(AN) inv(AN) inv(AN)	22 22 21
25 (anions) 26 (anions)	24 24	0.218 0.230	280.62 284.30	- 276.52 - 292.29	4.10 - 7.99	$0.04 \\ -0.08$	ca. 0(AN)	6
28 (anions)	27	0.227	346.31	- 371.75	-25.44	-0.26	inv(DMF) inv(PhCN)	14 10
29 (anions)	21	0.241	390.18	- 390.00	5.52	0.06	inv(AN) ² inv(AN)	20 this work
31 (cations)	30	0.210	203.93	- 249.91	-45.98	-0.48	inv(AN)	5
33 (anions), T/T ⁻ /T ²⁻ 33 (anions), B/T ⁻ /T ²⁻ 34 (anions), T/T ⁻ /T ²⁻ 34 (anions), B/T ⁻ /T ²⁻	32 32 32 32	0.202 0.202 0.220 0.220	292.29 241.28 335.10 290.66	- 261.75 - 261.75 - 286.44 - 286.44	30.54 - 20.47 48.66 4.22	0.32 -0.21 0.50 0.04	0.30(DMF) 0.10(DMF) c	37 37

^a From equations given in Table 4. ^b 'Inv' indicates that inversion of potentials was observed. Solvents: AN = acetonitrile; DMF = dimethylformamide; PhCN = benzonitrile. ^c Unknown. ^d The potentials are probably inverted or nearly so but there is insufficient information for a definite conclusion.



(formed *in situ* by deprotonation of bidurenol with tetra-*n*butylammonium hydroxide). Preliminary results indicate a complex reaction pathway and confirm that the neutral quinone form is exceedingly reactive. It rapidly abstracts hydrogen atoms from the surroundings to reform bidurenol.

Reduction of 3,6-dinitrodurene, 29

As indicated earlier, the available evidence suggests that potential compression or inversion occurs in the reduction of **29** but a definite conclusion cannot be reached. Thus, this compound was reinvestigated. Fig. 5 shows an experimental voltammogram for reduction of 2.00 mM **29** in acetonitrile at a glassy carbon electrode at 2.00 V s^{-1} . Also included is a digital simulation with the parameters given in the figure caption.

It is obvious qualitatively that potential inversion has occurred. Only a single reduction peak is found on the forward scan and a single oxidation peak on the return scan.



Fig. 5 Cyclic voltammogram of 2.00 mM 3,6-dinitrodurene, **29**, obtained at a 3 mm diameter glassy carbon electrode in acetonitrile containing 0.10 M Bu₄NPF₆ at 295 K. 2.00 V s⁻¹. Points: data. Curve: digital simulation. Simulation parameters: $E_1^{\circ\prime} = -1.61$ V, $\alpha_1 = 0.5$, $k_{s1} = 0.2$ cm s⁻¹, $E_2^{\circ\prime} = -1.44$ V, $\alpha_2 = 0.5$, $k_{s2} = 0.01$ cm s⁻¹, $k_{disp} = 2 \times 10^7$ mol dm⁻¹ s⁻¹ (k_{disp} is the rate constant for disproportionation of the radical anion) and diffusion coefficients of all species = 1.4×10^{-5} cm² s⁻¹.

Furthermore, the height of the reduction peak is well accounted for by an overall two-electron process using diffusion coefficients that are close to those of species of similar size in this medium.²² If one were to suppose that the single reduction peak is due to the one-electron reduction of **29** (with the second step occurring at potentials too negative to detect), then the diffusion coefficient required to match the experimental reduction currents would be impossibly large.

In addition, the value of $\Delta E^{\circ \prime}$ used in the simulation in Fig. 5, -170 mV, is able to provide good agreement with the experimental voltammogram, not only at 2.00 V s⁻¹ but also for a series of voltammograms from 0.05 to 50 V s⁻¹. One of the features of the voltammogram is the large difference between cathodic and anodic peak potentials which is caused by sluggish electron-transfer reactions as reflected by the small value of the standard heterogeneous electron-transfer rate constant for the second step, k_{s2} , which is only 0.01 cm s⁻¹, compared to a more normal value of 0.20 cm s^{-1} for the first step. Interestingly, AM1 indicates that the most stable forms of neutral 29 and its radical anion are twisted and only in the dianion is a folded B form indicated. Thus the larger structural change is associated with the second electron transfer, consistent with the smaller rate constant indicated for the second step.

As stated earlier, it is very difficult to obtain an accurate determination of $\Delta E^{\circ\prime}$ when it is quite negative. It was found that some variation about -170 mV could be made and still obtain reasonable agreement between simulation and experiment. Nevertheless, the permissible range is limited (about ± 50 mV) and it is very clear that potential inversion occurs in the reduction of **29**, in qualitative agreement with the results presented in Table 5.

In summary, it has been shown that AM1 calculations can be combined with an empirical calibration of the attenuation of disproportionation Gibbs energy on going from vacuum to solution to rationalize and/or predict the occurrence of potential compression or inversion in two-electron processes in organic electrochemistry. The study has also shed light upon the crucial role that structural change plays to bring about potential inversion.

Experimental

The electrochemical apparatus and procedures for cyclic voltammetry were as described.²² 3,6-Dinitrodurene was prepared by nitration of durene (2.7 g) using 0.1 mol concentrated sulfuric acid, 0.05 mol fuming nitric acid in 20 ml chloroform. Reaction for 1 h below 10 °C, followed by extraction with chloroform, evaporation of the solvent and recrystallization from ethanol gave 4.1 g (90%) 3,6-dinitrodurene, mp 206–208 °C.

AM1 calculations were performed using the HyperChem software package (Autodesk, Inc.) in which calculations for open-shell species use Dewar's half-electron method. Digital simulations were carried out using the program DigiSim (Bioanalytical Systems) under conditions described previously.²¹

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