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# Solvation of Anion Radicals: Gas Phase vs Solution

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**Abstract:** Reversible half-wave potentials for 38 neutral/anion radical couples have been measured at 298 K by cyclic voltammetry in five solvents: tetrahydrofuran, *N,N*-dimethylformamide (DMF), acetonitrile, dimethyl sulfoxide, and methanol. Among the compounds are 22 substituted nitrobenzenes and nine quinones. The potentials are referenced to the cobaltocenium/cobaltocene couple. The results were combined with published values of adiabatic gas-phase electron affinities and an estimate of the potential of the reference electrode to give for each compound and each solvent a value of $\Delta\Delta G^\circ_{sol}$, the difference in free energies of transfer of gaseous neutral and anionic species to the solution phase. These values of $\Delta\Delta G^\circ_{sol}$ were compared and correlated with published free energies of association of gas-phase anion radicals with single solvent molecules, $\Delta G^\circ_{0,1}$. A generally linear relation was found for all five solvents. Like $\Delta G^\circ_{0,1}$, $\Delta\Delta G^\circ_{sol}$ for the nitrobenzenes was a relatively smooth function of the electron affinity, with low electron affinity leading to the largest $\Delta\Delta G^\circ_{sol}$. $\Delta\Delta G^\circ_{sol}$ was found to be an approximately linear function of the Gutmann acceptor number of the solvent. For DMF, it was also found that the logarithm of the previously determined electron self-exchange rate constants correlated linearly with $\Delta\Delta G^\circ_{sol}$.

One of the simple yet fundamentally important reactions that a neutral organic molecule can undergo is the gain or loss of an electron to form the corresponding anion or cation radical. In the gas phase, the electron affinity (EA) is a measure of the ability of the molecule to bind an electron to form the anion radical. In solution, the tendency to accept an electron is governed in part by the gas-phase EA, but it is also greatly affected by stabilization of the anion through interaction with solvent molecules. Solvation affects the thermodynamics and kinetics of these solution-phase radical anions, whose reactions are of such widespread importance in organic chemistry.

In recent years, advances in experimental techniques have made available for the first time the gas-phase adiabatic electron affinities of a large number of organic molecules with a variety of structures.[1] The most obvious solution-phase property to compare to the gas-phase EA is the standard electrode potential, $E^\circ$, of the neutral/radical anion couple, as determined by voltammetric techniques using nonaqueous solvents. The formal relationship between the two has long been recognized[2] and is given by

$$E^\circ = -\Delta G^\circ_a(\mathrm{B}) - (\Delta G^\circ_{sol}(\mathrm{B}^-) - \Delta G^\circ_{sol}(\mathrm{B})) + C \qquad (1)$$

where $\Delta G^\circ_a(\mathrm{B})$ is the gas-phase free energy of electron attachment of species B ($-\Delta G^\circ_a(\mathrm{B}) \simeq \mathrm{EA}(\mathrm{B})$[3]), $\Delta G^\circ_{sol}(\mathrm{B}^-)$ and $\Delta G^\circ_{sol}(\mathrm{B})$ are the free energies of transfer of gas phase $\mathrm{B}^-$ and B, respectively, to solution, and $C$ is a constant which depends on the reference electrode. The difference in free energies of solution is defined as

$$\Delta\Delta G^\circ_{sol} = \Delta G^\circ_{sol}(\mathrm{B}^-) - \Delta G^\circ_{sol}(\mathrm{B}) \qquad (2)$$

Because the free energy of transfer of gaseous B to solution is small, $\Delta\Delta G^\circ_{sol}$ is dominated by that for the anion. Clearly, if $\Delta G^\circ_{sol}(\mathrm{B}^-)$ is constant for a series of molecules, plots of $E^\circ$ vs EA will be linear with unit slope. This behavior has been confirmed for aromatic hydrocarbons,[4b,c,e,f] but in other cases an approximately linear relationship is found but with a nonunity slope, indicating that $\Delta\Delta G^\circ_{sol}$ is not constant but changes with EA.[1c,j,k] Much remains to be learned about those factors which govern solvation of radical anions.

In this connection, a noteworthy development was the publication[5] of gas-phase association constants for the bonding of the radical anions of 27 substituted nitrobenzenes and quinones with five different solvent molecules: tetrahydrofuran, dimethylformamide, acetonitrile, dimethyl sulfoxide, and methanol. The bonding depended not only on the solvent molecule but also on the EA of the radical anion parent, with larger EAs leading to weaker interactions. It would be extremely interesting to compare these results with solution-phase studies using the same five solvents. In spite of the fact that an abundance of voltammetric data exists, these compounds have never been studied under strictly identical experimental conditions in the five relevant solvents, so we set out to obtain accurate measurements of the reversible voltammetric half-wave potentials. In this paper we report the experimental results and discuss them in relation to the gas-phase values of EA and the gas-phase anion–solvent association constants.

## Experimental Section

*N,N*-Dimethylformamide (DMF) and acetonitrile (AN) were from Burdick and Jackson (spectroquality) while dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) were from Aldrich, and methanol (MeOH) was from Fisher. MeOH was distilled from magnesium and iodine.[6] THF was distilled from sodium and benzophenone directly into the cell. All of the other solvents were stored in stock bottles and passed through a 1.5 × 10 cm column of activated alumina (neutral, Brockman I, Aldrich, activated under nitrogen at 400 °C for at least 18 h) just before use. Tetra-*n*-butylammonium hexafluorophosphate (TBAHFP, Aldrich) was recrystallized three times from 95% ethanol and dried in a vacuum oven at 80 °C for at least 18 h.

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(3) Free energies of electron attachment have been evaluated for almost all of the compounds studied.[1k] They generally differ from the electron affinities by <1 kcal/mol. In this paper we have chosen EA for the numerical calculations to adhere to the practice of other analyses.[1c,j]

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All of the compounds studied were of commercial origin and were obtained from Aldrich except benzophenone, 1,4-naphthoquinone, 2,5-dimethyl-1,4-benzoquinone, 3-nitrotoluene (Eastman Kodak), nitrobenzene (Fisher), anthracene (MCB), 2-methyl-1,4-naphthoquinone (Fluka), and 4-chloronitrobenzene (Columbia Chemicals). Purity of the solids was confirmed by comparison of melting points with literature values.

The three-electrode cell for cyclic voltammetry was of a conventional design.[7] The working electrode was a platinum disk (0.50-mm radius) sealed in glass. A spiral of platinum wire served as the counter electrode and the reference electrode comprised a silver wire in contact with 0.010 M $AgNO_3$ and 0.10 M TBAHFP in the solvent being studied. The solution temperature was 25.0 ± 0.1 °C.

The electrochemical instrumentation has been described.[8] Positive feedback iR compensation[9] was used except for AN at 0.1 V/s, where the error was negligible. For reactions where the anion radical was relatively stable, a scan rate of 0.1 V/s was used and the reversible half-wave potential, $E_{1/2}$, was taken as the average of the cathodic and anodic peak potentials. These peak potentials were measured from the recorded voltammogram with image expansion on the digital oscilloscope and the calibrated cursor. The lifetime of the anion radicals was generally shorter in MeOH solvent (presumably due to protonation and subsequent reactions) and required somewhat faster scan rates. For a few compounds (1,2-dinitrobenzene, 1,3-dicyanobenzene, benzophenone, and phthalic anhydride) the lifetime was so short that scan rates in the range of 100–1000 V/s were needed. For these measurements a small electrode (mercury-film electrode deposited on a 100-$\mu$m-diameter platinum disk[10]) was used to reduce iR errors. The mercury surface offered the advantage of a more negative solvent-breakdown potential than that obtained with platinum in MeOH.

The half-wave potentials were measured both with respect to the reference electrode and also with respect to an internal standard whose voltammetric peaks were recorded together with those of the compound under investigation. The internal standard was cobaltocenium hexafluorophosphate except when its half-wave potential was so close to that being measured that severe overlap occurred or so distant that it was not convenient to include both half-wave potentials within the range of potentials scanned. In such cases one of the other compounds was used as internal standard and the result was referred to cobaltocenium/cobaltocene with the separately determined half-wave potential of the alternate internal standard.

Reproducibility was confirmed by making measurements from replicate voltammograms. As a further test, every potential was measured at least once more with a newly prepared sample solution. Results were accepted when successive measurements agreed to within 10 mV. The error in the half-wave potentials vs cobaltocenium/cobaltocene is estimated to be 0.005 V or less.

In polarography, cyclic voltammetry, chronopotentiometry, etc., the characteristic potential that is measured for the reaction O + $ne$ = R is the half-wave potential given by[11]

$$E_{1/2} = E^{\circ\prime} + (RT/2nF)\ln(D_R/D_O) \quad (3)$$

where $E^{\circ\prime}$ is the formal potential of the couple and $D_R$ and $D_O$ are the diffusion coefficients of R and O, respectively. Thus, knowledge of the ratio of diffusion coefficients is needed to convert $E_{1/2}$ to $E^{\circ\prime}$. Diffusion coefficients of radical ions are not easily determined, but in cases where measurements have been made,[12] the ratio did not exceed 1.5, leading to a maximum difference between $E_{1/2}$ and $E^{\circ\prime}$ of 5 mV. This small difference was ignored in the present work and the measured half-wave potentials are assumed to equal the formal potentials.

The formal potential is related to the standard potential, $E^\circ$, by[11]

$$E^{\circ\prime} = E^\circ + (RT/nF)\ln(\gamma_O/\gamma_R) \quad (4)$$

where $\gamma_O$ and $\gamma_R$ are the activity coefficients of O and R, respectively. The concentrations of O and R are low and the ionic strength is governed almost entirely by the supporting electrolyte (0.10 M TBAHFP). The sizes of the various radical anions studied in this work are similar, so it is likely that the activity coefficient term is almost constant along the series.

The formation of ion pairs between the cation of the supporting electrolyte and anion radicals can affect the measured formal potentials.[13] A large cation (tetra-$n$-butylammonium ion) was selected to avoid large effects. For example, in acetonitrile, ion-pair formation between $TBA^+$ and $PF_6^-$ is not detectable.[14] Of the solvents studied, THF is likely to give the highest degree of ion pairing, so the results could be affected to an unknown extent.

It is also known that apparent formal potentials for neutral/anion radical couples are affected by residual water in the solvent,[15] inducing us to dry the solvents just before use.

## Results

Values of the reversible half-wave potentials for the neutral/anion radical couples with respect to that of cobaltocenium/cobaltocene are given in Table I. Included also are values for ferrocene/ferricinium and the aqueous saturated calomel electrode (SCE). The constant difference between the ferrocene and cobaltocenium potentials confirms that use of the latter as a reference couple[16] with the assumption that its potential is independent of the solvent is equivalent to the widely used ferrocene convention.[17] In AN a scan rate of 1.0 V/s was required to determine the reversible half-wave potential for phthalic anhydride due to a slow reaction that destroyed the radical anion. The reaction was so fast in MeOH that no oxidation peak for the anion radical was observed even at 1000 V/s, so no half-wave potential is reported. The half-wave potentials for reduction of anthracene and cobaltocene are more negative than the solvent-breakdown potential for MeOH, so they could not be measured in this solvent.

## Discussion

**Correlation of Half-Wave Potentials with Electron Affinities and Calculation of $\Delta\Delta G^\circ_{sol}$.** To aid in visualization of the results, plots of observed half-wave potential vs EA are shown in Figures 1 and 2. Certain subsets of the compounds exhibit approximately unit slope, but on the whole there is considerable scatter and the average slope is less than unity. The most striking feature is the almost constant displacement of half-wave potentials for all of the compounds on going from one solvent to the next. This is particularly true for the four nonhydroxylic solvents. There is a shift of about +130 mV on going from THF to AN and DMF (which are very similar) and another +50-mV shift to reach DMSO. The half-wave potentials for MeOH are still more positive and the gap between MeOH and DMSO increases perceptibly at low EA.

These results are reflecting changes in the solvation free energy term, $\Delta\Delta G^\circ_{sol}$, that occur with changes in structure of the solute and the identity of the solvent. What do the data reveal about $\Delta\Delta G^\circ_{sol}$? There are three levels of interpretation. First, if we restrict ourselves to a single solvent, we can evaluate relative values of $\Delta\Delta G^\circ_{sol}$, i.e., changes in $\Delta\Delta G^\circ_{sol}$ on going from one compound to another. No extrathermodynamic assumption is needed.

At the second level, relative values of $\Delta\Delta G^\circ_{sol}$ for all compounds in all the solvents can be evaluated by assuming that the potential of the reference electrode is independent of solvent. The reference couple we have used is cobaltocenium/cobaltocene, which we have shown to be equivalent to using ferricinium/ferrocene (compound **38**, Table I). This assumption means that the same value of the constant $C$ in eq 1 is used for all solvents or, equivalently, that

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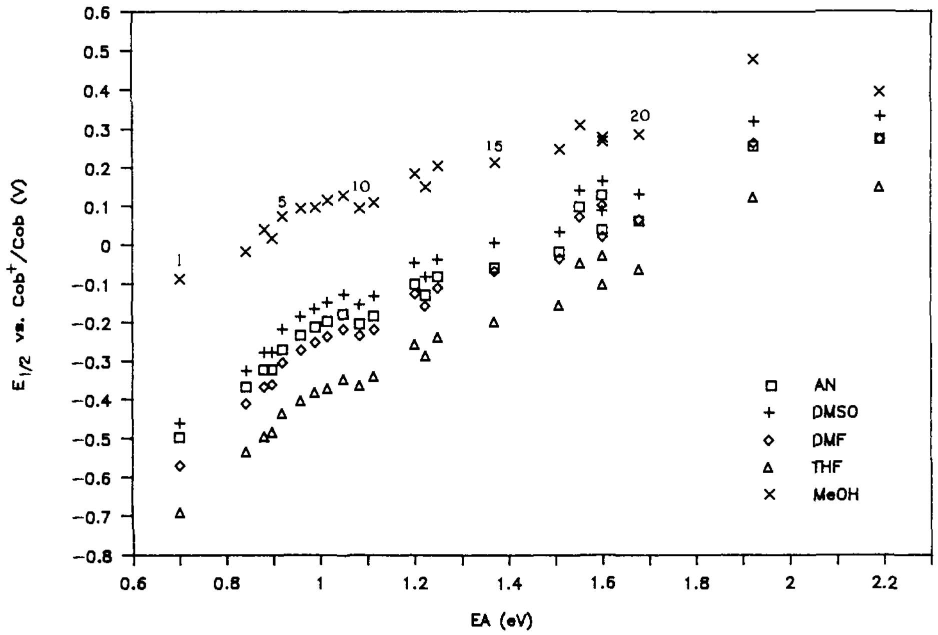

**Figure 1.** Reversible half-wave potentials for neutral/anion radical couples of 22 nitrobenzenes in five solvents. The potentials are referenced to the cobaltocenium/cobaltocene couple in the same solvent. The data and compound numbers are from Table I.

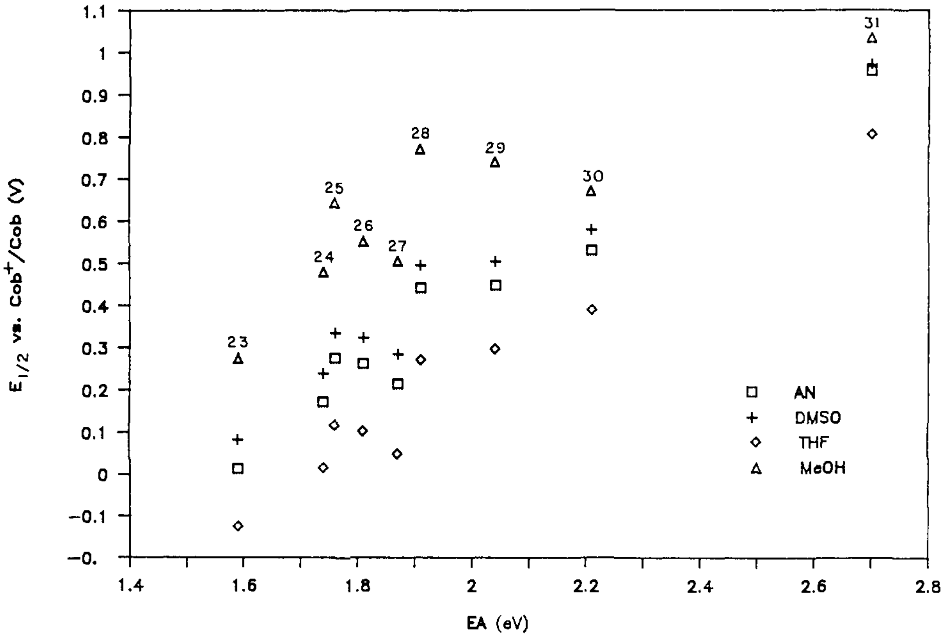

**Figure 2.** Reversible half-wave potentials for neutral/anion radical couples of nine quinones in four solvents. The data for DMF are omitted for clarity. The data and compound numbers are from Table I.

$\Delta\Delta G°_{sol}$ for ferricinium/ferrocene is the same for all the solvents. Within the error introduced by this assumption, relative values calculated from eq 1 ($\Delta\Delta G°_{sol} - C$) can be interpreted for all of the compounds in all of the solvents.

Finally, at the third level, a numerical value for $C$ can be introduced in order to calculate absolute values of $\Delta\Delta G°_{sol}$. Here we have followed the lead of Heinis et al.,[1j] who reviewed the literature and selected −4.71 V to use for the potential of the aqueous SCE. Combining this value with our determination of the potential of the aqueous SCE vs cobaltocenium/cobaltocene in acetonitrile (+0.93 V) gives $C = -3.78$ V for measurements referred to cobaltocenium/cobaltocene.

In what follows, we will calculate and discuss absolute values of $\Delta\Delta G°_{sol}$, bearing in mind that each assumption introduces an unknown level of error. Nevertheless, the magnitudes of the solvation energy term are actually quite reasonable,[1j,4b,f] and fortunately, many interesting conclusions can be reached from the relative values alone.

**Dependence of $\Delta\Delta G°_{sol}$ on Electron Affinity and Solvent.** Values of $\Delta\Delta G°_{sol}$ for the nitrobenzenes are plotted vs EA in Figure 3 and the data for the quinones are presented in Figure 4. For the substituted nitrobenzenes there is a strong correlation of $\Delta\Delta G°_{sol}$ with EA for each solvent, with larger values of EA leading to smaller solvation energies. This is strikingly similar to the gas-phase results,[5] where the association constants for the radical anions with a single solvent molecule were found to decrease with increasing EA. The qualitative interpretation of the effect is that larger values of EA are achieved by adding electron-withdrawing substituents which lead to greater delocalization of charge in the anion radical. This results in a larger effective distance between the anion and the solvent molecule and, because the bonding forces are principally electrostatic in nature, to lower free energies of binding. Interestingly, in the solution-phase data $\Delta\Delta G°_{sol}$ seems to approach a limiting value for compounds with low EA (compounds **1**–**8**). These compounds include nitrobenzene itself and seven derivatives with electron-donating substituents. We suggest

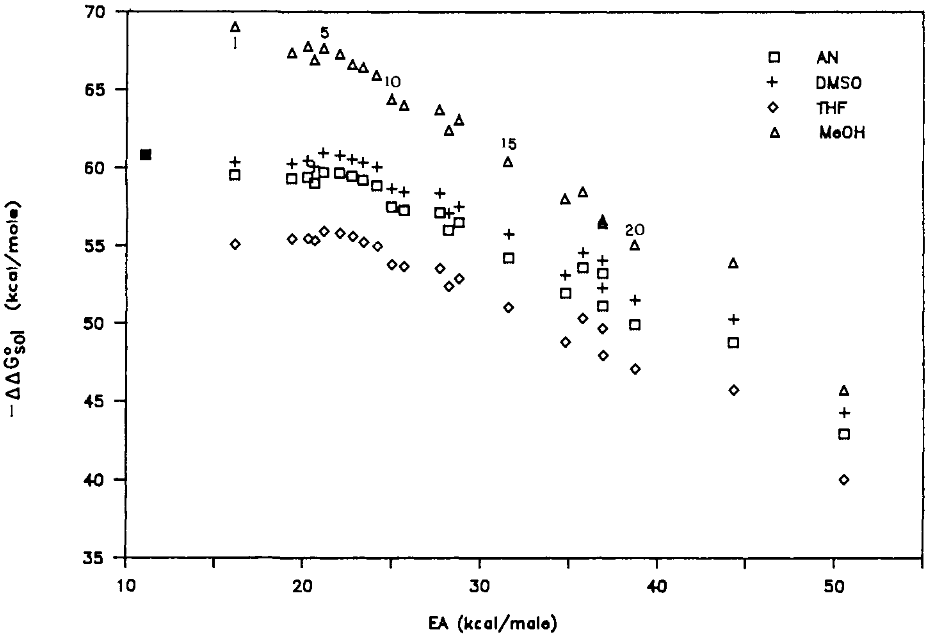

**Figure 3.** $\Delta\Delta G^\circ_{sol}$ for 22 nitrobenzenes calculated from EA and half-wave potentials for four solvents. The data for DMF are omitted for clarity. The solid square represent nitromethane in AN.

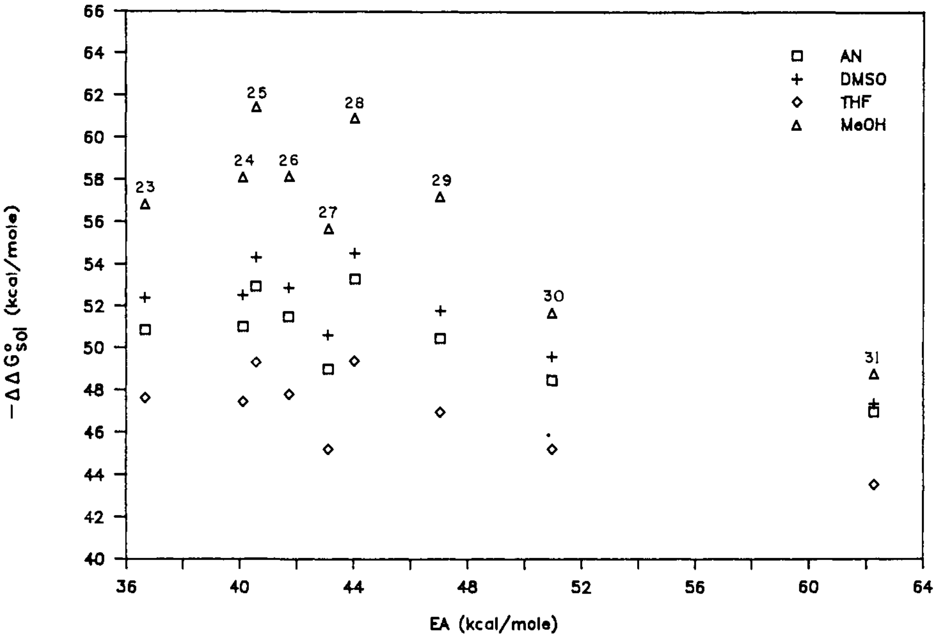

**Figure 4.** $\Delta\Delta G^\circ_{sol}$ for nine quinones calculated from EA and half-wave potentials for four solvents. The data for DMF are omitted for clarity.

that most of the charge in the anion radicals of these compounds is located on the nitro group, causing the solvation energy term to be roughly constant. Supporting this view is the fact that $\Delta\Delta G^\circ_{sol}$ for nitromethane in acetonitrile, calculated from its EA[1k] and published half-wave potential,[18] is only slightly higher (Figure 3) than those of compounds **1**–**8**. The negative charge on the anion radical of a nitroalkane is almost wholly on the nitro group.

Figure 3 also demonstrates vividly the almost constant difference in $\Delta\Delta G^\circ_{sol}$ on going from one solvent to another for every compound. As one's eye moves from left to right through the figure, increases or decreases in $\Delta\Delta G^\circ_{sol}$ (even small changes) are almost equal in all solvents. Calculations of $(\Delta\Delta G^\circ_{sol})_S - (\Delta\Delta G^\circ_{sol})_{THF}$ give average values (standard deviations) of −2.9 (0.1) kcal/mol for S = DMF, −3.6 (0.4) kcal/mol for S = AN, and −4.8 (0.3) kcal/mol for S = DMSO. The standard deviations scarcely exceed the uncertainty in the measurement of the half-wave potentials. MeOH is an exception. Here the values of $\Delta\Delta G^\circ_{sol}$ deviate further from the other four solvents as EA decreases.

These differences in $\Delta\Delta G^\circ_{sol}$ are approximately equal to the free energies of transfer of $B^-$ from THF to the other solvents because the free energy of transfer of B is small.[19] Ionic free energies of transfer involving THF do not appear to have been reported previously, but taking DMF as reference, the average $\Delta\Delta G^\circ_{sol}$ values give free energies of transfer of the anion radicals of the nitrobenzenes of −0.7 kcal/mol from DMF to AN and −1.9 kcal/mol from DMF to DMSO. Examination of individual compounds reveals a weak dependence on structure, with those of low EA giving slightly larger values and those of high EA giving slightly lower values of the free energy of transfer. The average values are identical with those for thiocyanate and similar to those

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(19) (a) Free energies of transfer among DMF, AN, and DMSO for a variety of compounds are typically 0.0–0.4 kcal/mol.[19b] (b) Alexander, R.; Ko, E. C. F.; Parker, A. J.; Broxton, T. J. *J. Am. Chem. Soc.* **1968**, *90*, 5049–5069.

**Table I.** Half-Wave Potentials of Various Compounds[a]

| compound | EA, eV[b] | $E_{1/2}$, V vs cobaltocenium/cobaltocene THF | DMF | AN | DMSO | MeOH |
|---|---|---|---|---|---|---|
| | | Nitrobenzenes | | | | |
| (**1**) 2,4,6-trimethylnitrobenzene | 0.70 | −0.691 | −0.569 | −0.497 | −0.461 | −0.087 |
| (**2**) 2,3-dimethylnitrobenzene | 0.84 | −0.533 | −0.411 | −0.366 | −0.325 | −0.016 |
| (**3**) 4-methoxynitrobenzene | 0.88 | −0.494 | −0.367 | −0.322 | −0.276 | 0.041 |
| (**4**) 2-methylnitrobenzene | 0.90 | −0.483 | −0.360 | −0.322 | −0.276 | 0.019 |
| (**5**) 4-methylnitrobenzene | 0.92 | −0.434 | −0.304 | −0.270 | −0.216 | 0.074 |
| (**6**) 3-methylnitrobenzene | 0.96 | −0.401 | −0.271 | −0.232 | −0.183 | 0.097 |
| (**7**) nitrobenzene | 0.99 | −0.380 | −0.250 | −0.211 | −0.163 | 0.099 |
| (**8**) 3-methoxynitrobenzene | 1.02 | −0.370 | −0.235 | −0.196 | −0.146 | 0.116 |
| (**9**) 2-fluoronitrobenzene | 1.05 | −0.345 | −0.216 | −0.176 | −0.125 | 0.130 |
| (**10**) 4-fluoronitrobenzene | 1.08 | −0.362 | −0.233 | −0.202 | −0.152 | 0.097 |
| (**11**) 2-chloronitrobenzene | 1.11 | −0.338 | −0.217 | −0.181 | −0.131 | 0.111 |
| (**12**) 3-fluoronitrobenzene | 1.20 | −0.256 | −0.125 | −0.100 | −0.046 | 0.185 |
| (**13**) 4-chloronitrobenzene | 1.22 | −0.285 | −0.157 | −0.128 | −0.081 | 0.151 |
| (**14**) 3-chloronitrobenzene | 1.25 | −0.238 | −0.110 | −0.080 | −0.036 | 0.205 |
| (**15**) 3-(trifluoromethyl)nitrobenzene | 1.37 | −0.197 | −0.068 | −0.058 | 0.007 | 0.212 |
| (**16**) 3-cyanonitrobenzene | 1.51 | −0.155 | −0.035 | −0.017 | 0.034 | 0.248 |
| (**17**) 2-cyanonitrobenzene | 1.55 | −0.045 | 0.072 | 0.098 | 0.141 | 0.310 |
| (**18**) 1,3-dinitrobenzene | 1.60 | −0.101 | 0.022 | 0.039 | 0.088 | 0.269 |
| (**19**) 1,2-dinitrobenzene | 1.60 | −0.026 | 0.102 | 0.129 | 0.167 | 0.279 |
| (**20**) 4-cyanonitrobenzene | 1.68 | −0.061 | 0.066 | 0.063 | 0.131 | 0.288 |
| (**21**) 1,4-dinitrobenzene | 1.92 | 0.124 | 0.265 | 0.257 | 0.321 | 0.480 |
| (**22**) 3,5-dinitrobenzonitrile | 2.19 | 0.147 | 0.272 | 0.273 | 0.331 | 0.394 |
| | | Quinones | | | | |
| (**23**) 9,10-anthraquinone | 1.59 | −0.125 | 0.023 | 0.015 | 0.082 | 0.275 |
| (**24**) 2-methyl-1,4-naphthoquinone | 1.74 | 0.017 | 0.169 | 0.172 | 0.239 | 0.481 |
| (**25**) 2,5-dimethyl-1,4-benzoquinone | 1.76 | 0.118 | 0.269 | 0.276 | 0.336 | 0.645 |
| (**26**) 1,4-naphthoquinone | 1.81 | 0.103 | 0.254 | 0.263 | 0.323 | 0.553 |
| (**27**) 2,6-di-*tert*-butyl-1,4-benzoquinone | 1.87 | 0.050 | 0.224 | 0.215 | 0.285 | 0.506 |
| (**28**) 1,4-benzoquinone | 1.91 | 0.272 | 0.428 | 0.443 | 0.496 | 0.773 |
| (**29**) phenyl-1,4-benzoquinone | 2.04 | 0.297 | 0.441 | 0.449 | 0.505 | 0.742 |
| (**30**) 2,3-dichloro-1,4-naphthoquinone | 2.21 | 0.390 | 0.529 | 0.532 | 0.581 | 0.672 |
| (**31**) tetrafluoro-1,4-benzoquinone | 2.70 | 0.807 | 0.934 | 0.957 | 0.973 | 1.036 |
| | | Others | | | | |
| (**32**) anthracene | 0.57 | −1.172 | −1.072 | −1.075 | −1.014 | |
| (**33**) benzophenone | 0.62 | −0.989 | −0.893 | −0.890 | −0.817 | −0.431 |
| (**34**) 1,3-dicyanobenzene | 0.91 | −1.057 | −0.919 | −0.912 | −0.882 | −0.825 |
| (**35**) 1,2-dicyanobenzene | 0.95 | −0.886 | −0.756 | −0.774 | −0.697 | −0.714 |
| (**36**) 1,4-dicyanobenzene | 1.10 | −0.813 | −0.675 | −0.701 | −0.621 | −0.637 |
| (**37**) phthalic anhydride | 1.21 | −0.493 | −0.353 | −0.351 | −0.291 | |
| (**38**) ferrocene | | 1.332 | 1.330 | 1.329 | 1.329 | 1.324 |
| (**39**) cobaltocene/cobaltocenate | | −1.123 | −0.956 | −0.979 | −0.903 | |
| (**40**) aqueous SCE | | | | 0.93 | | |

[a] Determined at 25 °C in 0.10 M TBAHFP; referred to the half-wave potential of cobaltocenium/cobaltocene in the same solvent and electrolyte. [b] Adiabatic electron affinities for nitrobenzenes from ref 5; all others from ref 1*l*.

of iodide (−1.0 kcal/mol for DMF to AN and −2.2 kcal/mol for DMF to DMSO) and bromide (−0.7 and −1.7 kcal/mol, respectively).[20] Thus the free energies of transfer of the anion radicals of these 22 nitrobenzenes are almost independent of the identity of the substituents and are similar in magnitude to small inorganic anions in accord with the notion that most of the solvation interaction occurs at the nitro group.

The pattern of $\Delta\Delta G^\circ_{sol}$ for the quinones (Figure 4) bears similarity to the nitrobenzenes. The compounds have been studied earlier by Heinis et al.,[1j] who used literature values of half-wave potentials in AN and DMF to calculate $\Delta\Delta G^\circ_{sol}$. For the six compounds examined in both papers, $\Delta\Delta G^\circ_{sol}$ for AN agree to within 1 kcal/mol. For DMF (nine compounds) our values average 4 kcal/mol lower, which may be traced to a different reference electrode. Heinis et al. used half-wave potentials referred directly to aqueous SCE whereas ours are referred through the ferrocene assumption to AN and thence to aqueous SCE. In any case, the differences serve to emphasize the caveat expressed elsewhere[1j] that the absolute values of $\Delta\Delta G^\circ_{sol}$ are uncertain to perhaps 5 kcal/mol.

As with the nitrobenzenes, the parallelism between $\Delta\Delta G^\circ_{sol}$ for different solvents is striking for the nonhalogenated quinones (compounds **23–29**, Figure 4). The values are roughly constant for the seven compounds and positive and negative "deviations" have been interpreted in terms of steric effects on solvation and small differences in $\Delta G^\circ_{sol}(B)$.[1j] The anion radicals of the two halogenated quinones (compounds **30** and **31**, Figure 4) are more weakly solvated and the differences among the five solvents are smaller. This is thought to reflect greater charge delocalization in these anions.[1j]

**Table II.** Solvent Properties and Average $\Delta\Delta G^\circ_{sol}$ for Substituted Nitrobenzenes

| solvent | $(1 - 1/\epsilon)$ | $\mu$, D | acceptor number[a] | $-(\Delta\Delta G^\circ_{sol})_{av}$, kcal/mol[b] |
|---|---|---|---|---|
| THF | 0.868 | 1.8 | 8.0 | 52.1 |
| DMF | 0.973 | 3.9 | 16.0 | 55.0 |
| AN | 0.973 | 3.4 | 19.3 | 55.7 |
| DMSO | 0.979 | 3.9 | 19.3 | 56.8 |
| MeOH | 0.967 | 2.9 | 41.3 | 62.2 |

[a] Gutmann acceptor number.[21] [b] Average of the values for 22 compounds.

**Correlation of $\Delta\Delta G^\circ_{sol}$ with the Gutmann Acceptor Number of the Solvents.** In the gas phase, the bonding of single solvent molecules by anion radicals can be interpreted in a semiquantitative manner in terms of the dipole moment of the solvent molecule and the effective distance between the ion and the dipole.[5]

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(20) Parker, A. J.; Mayer, U.; Schmid, R.; Gutmann, V. *J. Org. Chem.* **1978**, *43*, 1843–1854.

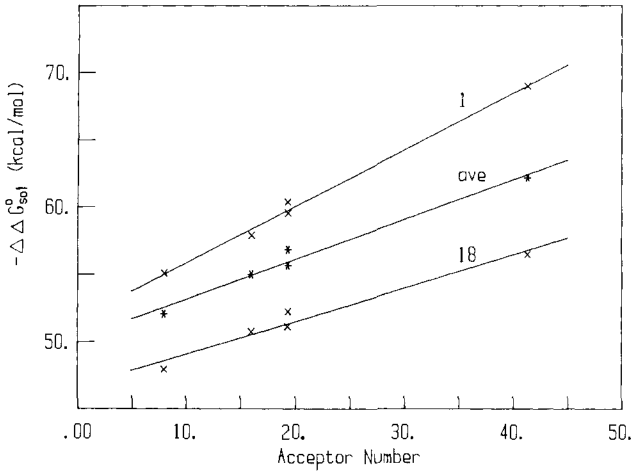

**Figure 5.** $\Delta\Delta G^{\circ}_{sol}$ for nitromesitylene (compound **1**), 1,3-dinitrobenzene (compound **18**), and the average of all 22 nitrobenzenes as a function of the Gutmann acceptor number of the five solvents.

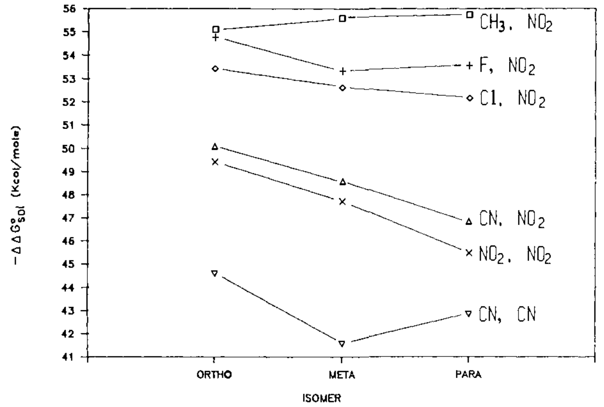

**Figure 6.** $\Delta\Delta G^{\circ}_{sol}$ for six sets of ortho, meta, and para isomers in THF solvent.

In Table II, values of various solvent parameters are given along with the average $\Delta\Delta G^{\circ}_{sol}$ for the 22 substituted nitrobenzenes. Though the absolute magnitude of $\Delta\Delta G^{\circ}_{sol}$ is subject to the error introduced through selection of constant $C$ in eq 1, the relative values are probably more accurate, as they rely on the less stringent requirement that the ferrocene assumption is valid for the five solvents used. Clearly, $\Delta\Delta G^{\circ}_{sol}$ does not correlate with the molecular dipole moment nor with the dielectric constant (i.e., $(1 - 1/\epsilon)$, as would be expected for the Born energy). However, a good correlation is found between $\Delta\Delta G^{\circ}_{sol}$ and the empirical solvent parameter, the Gutmann acceptor number[21] (Figure 5). The success of this correlation undoubtedly arises from the fact that both $\Delta\Delta G^{\circ}_{sol}$ and the acceptor number are measures of the ability of the solvent to accept electron density from a solute, the anion radicals in the first case and a reference Lewis base for the acceptor number. (The scale of acceptor numbers is based on $^{31}$P NMR chemical shifts of the solute triethylphosphine oxide in the various solvents.) MeOH is the solvent with the greatest ability to accept electron density from the radical anions, leading to the largest values of $\Delta\Delta G^{\circ}_{sol}$.

**Variation of $\Delta\Delta G^{\circ}_{sol}$ with Position of Substitution.** Included in the data are four sets of 2-, 3-, and 4-substituted nitrobenzenes as well as *o*-, *m*-, and *p*-dinitrobenzene and *o*-, *m*-, and *p*-dicyanobenzene (the phthalonitriles). Values of $\Delta\Delta G^{\circ}_{sol}$ for these 18 compounds in THF are displayed in Figure 6. Very similar trends are seen for all of the other solvents. As noted above, $\Delta\Delta G^{\circ}_{sol}$ is large and almost independent of solute structure for low EA compounds such as the three methyl derivatives. For the fluoro and chloro derivatives, $\Delta\Delta G^{\circ}_{sol}$ is lower but independent of the position of substitution within experimental error. On the other hand, the strongly electron withdrawing cyano and nitro substituents show a distinct trend with $\Delta\Delta G^{\circ}_{sol}$ of ortho > meta > para. This same trend was seen in the gas phase for the free energies of association of these radical anions with a nonhydroxylic solvent molecule.[5] The trend was explained by an increase in the effective distance between the solvent molecule (located near the nitro group) and the ionic charge as the second electron-withdrawing substituent is moved farther away on going from 2- to 4-substitution. Apparently the same factor is affecting the free energy of solvation of these anions.

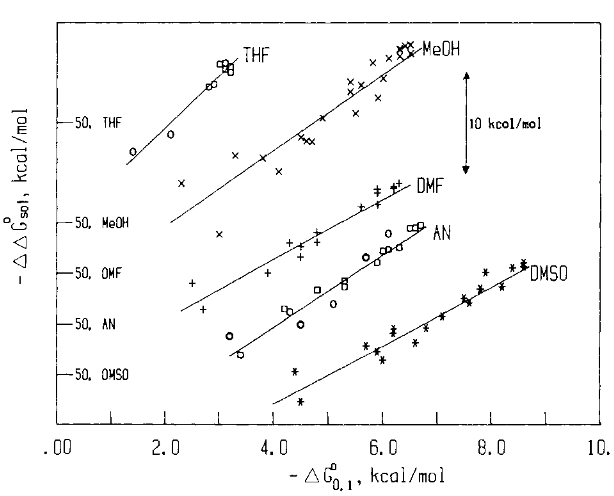

**Figure 7.** $\Delta\Delta G^{\circ}_{sol}$ as a function of the free energy of binding of radical anions and a solvent molecule in the gas phase[5] at 70 °C. Ordinates are referenced to 50 kcal/mol for each solvent as shown. The least-squares lines shown have slopes of 5.2 for THF, 3.8 for MeOH, 3.0 for DMF, 3.5 for AN, and 2.9 for DMSO.

The above discussion pertains to relative values of $\Delta\Delta G^{\circ}_{sol}$ in a single solvent which, as pointed out earlier, do not depend on any extrathermodynamic assumptions. Throughout the discussion, we have been assuming that $\Delta\Delta G^{\circ}_{sol} \simeq \Delta G^{\circ}_{sol}(B^{-})$, i.e., the free energy of transfer of gaseous B to solution is negligible. However, as we are interpreting small changes in $\Delta\Delta G^{\circ}_{sol}$ (4–5 kcal/mol for the cyano and nitro substituents in Figure 6), it is important to determine how much $\Delta G^{\circ}_{sol}(B)$ varies among these derivatives. Very little data is available, so we resorted to the approximate calculation adopted by Heinis et al.,[1j] by which $\Delta G^{\circ}_{sol}(B)$ can be obtained from the vapor pressure and solubility of B. For methanol, we find $\Delta G^{\circ}_{sol}(B) = -6.2$, $-6.9$, and $-4.9$ kcal/mol for *o*-, *m*-, and *p*-dinitrobenzene, respectively. Clearly, the variation in $\Delta G^{\circ}_{sol}(B)$ among the three isomers is insufficient to account for the trend in $\Delta\Delta G^{\circ}_{sol}$ seen for MeOH, THF (Figure 6), and the other solvents.

Though the EA of the dicyanobenzenes (phthalonitriles) is near that of the nitrotoluenes, the solvation energies are 10–15 kcal/mol lower (Figure 6). The anion radicals of the dicyanobenzenes have solvation energies closer to that of anthracene anion radical (−47.0 kcal/mol in THF), suggesting that for these ions there is considerably more charge delocalization than in the anion radicals of nitrobenzenes and quinones, in which a large fraction of the charge resides on the oxygen atoms.

**Relationship between $\Delta\Delta G^{\circ}_{sol}$ and the Free Energy of Binding of Gas-Phase Anion Radicals with Single Solvent Molecules.** We have referred earlier to similarities between $\Delta\Delta G^{\circ}_{sol}$ measured in our solution-phase studies and the free energy of association of an anion radical and one solvent molecule in the gas phase, $\Delta G^{\circ}_{0,1}$.[5] For example, in each case the energies increase with decreasing EA. How are these two quantitites related? In Figure 7 values of $\Delta\Delta G^{\circ}_{sol}$ derived from the data in Table I are plotted vs $\Delta G^{\circ}_{0,1}$ for 20 substituted nitrobenzenes and three quinones.[5] To avoid crowding the figure, the points have not been labeled with the corresponding solute names, but their identities can be deduced from the data in Table I, ref 5.

Though there is considerable scatter, a generally linear relationship is evident, and the lines obtained by least-squares analysis

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[21] Gutmann, V. *Electrochim. Acta* **1976**, *21*, 661–670.

have been included in Figure 7. The slopes fall in the range of about 3–4 except for THF which is near 5. The slopes should be quantitatively significant because determination of changes in $\Delta\Delta G°_{sol}$ does not require any extrathermodynamic assumptions. The intercepts are 39, 39, 36, 36, and 42 kcal/mol for THF, DMF, AN, DMSO, and MeOH, respectively. Their similarity is not too surprising in view of the fact that the values of $\Delta\Delta G°_{sol}$ fall in the fairly narrow range of 48–68 kcal/mol.

The values of $\Delta G°_{0,1}$ do not exceed 9 kcal/mol for these relatively large anions, considerably smaller than observed[22] for small anions such as $Cl^-$ or $O_2^-$. Yet these relatively small energies are associated with somewhat larger changes in $\Delta\Delta G°_{sol}$, as manifested by the slopes of 3–4 seen in Figure 7. A simple model for the relationship between $\Delta G°_{0,1}$ and $\Delta\Delta G°_{sol}$ can be constructed with a thermodynamic cycle.[23] With the free ion, $B^-$, in the gas phase, $i$ molecules of solvent, S, are evaporated and allowed to form a shell around $B^-$ in the gas phase. The free energy change for this process is $\Delta G°_{0,i} + i\Delta G°_{vap}$, where $\Delta G°_{0,i}$ is the total free energy of binding of $i$ molecules of S to $B^-$ in the gas phase (of which $\Delta G°_{0,1}$ is the component for binding the first molecule) and $\Delta G°_{vap}$ is the free energy of vaporization of the solvent. It is then imagined that a cavity of a size appropriate for ion $B^-$ and its solvent cluster is created in the liquid solvent requiring $\Delta G°_{cav}$. The ion and its cluster shell are then transported from the gas phase to the solvent cavity releasing the Born energy, $\Delta G°_{Born}$, and finally, the solvent molecules in the cluster are allowed to interact with solvent molecules forming the wall of the cavity, giving a free energy term, $\Delta G°_{inter}$. The combination of these gives

$$\Delta G°_{sol}(B^-) = \Delta G°_{0,i} + i\Delta G°_{vap} + \Delta G°_{cav} + \Delta G°_{Born} + \Delta G°_{inter} \quad (5)$$

The definition of $\Delta\Delta G°_{sol}$ from eq 2 can be combined with eq 5 and rearranged to give

$$\Delta\Delta G°_{sol} = \left[\frac{\Delta G°_{0,i} - \Delta G°_{sol}(B)}{\Delta G°_{0,1}}\right]\Delta G_{0,1} + i\Delta G°_{vap} + \Delta G°_{cav} + \Delta G°_{Born} + \Delta G°_{inter} \quad (6)$$

For a given solvent and a series of $B^-$ of similar size, it is reasonable to consider the last four terms in eq 6 to be roughly constant. The two free energy terms which should depend on the nature of B are combined to give a predicted slope of the plot of $\Delta\Delta G°_{sol}$ vs $\Delta G°_{0,1}$. If $\Delta G°_{sol}(B)/\Delta G°_{0,1}$ is negligible, this slope will be $\Delta G°_{0,i}/\Delta G°_{0,1}$, i.e., the ratio of the total free energy for surrounding the ion with its solvent shell to that for binding the first solvent molecule in the gas phase. For small ions such as halides, this ratio can be 2–3 for $i$ = 3–5,[22] but binding of more than one solvent to the large anions studied here was not reported,[5] suggesting that, to the extent this simple model is valid, the slopes of 3–4 found[24] in Figure 7 are affected by significant values of $\Delta G°_{sol}(B)/\Delta G°_{0,1}$, i.e., the solvation energies of neutral B are correlated to the gas-phase binding energies.

**Discussion of Electron-Transfer Kinetics.** In terms of the Marcus theory of electron transfer,[25] the principal factor governing the rates of the electron-transfer reactions of the aromatic compounds studied here is the solvent (outer) reorganization energy, the energy required to reorient solvent molecules from their configuration as they surround the neutral molecule to the arrangement which exists around the ion. This solvent-reorganization energy is related to $\Delta\Delta G°_{sol}$ as determined in this paper. One would expect that large values of $\Delta\Delta G°_{sol}$ should be associated with large solvent-reorganization energies and hence with large free energies of activation for electron-transfer reactions.

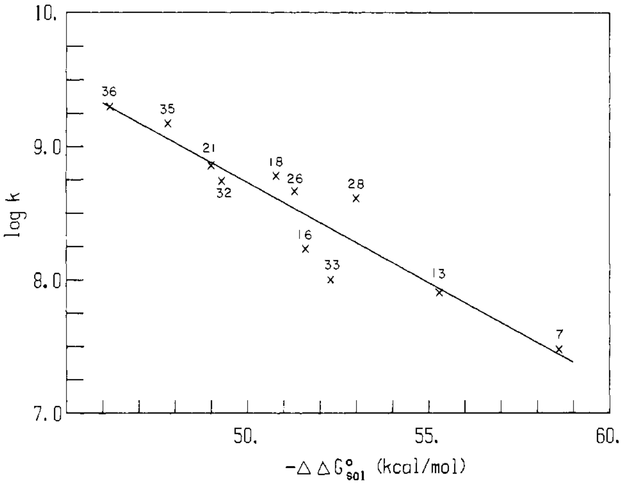

**Figure 8.** Rate constants ($M^{-1}$ $s^{-1}$) for neutral/anion radical electron exchange reaction as a function of $\Delta\Delta G°_{sol}$ for DMF. The data for compounds **35** and **36** are from ref 29; the others are from ref 28.

Electron exchange rate constants (self-exchange) for a number of the neutral/anion radical couples studied here have been determined in DMF solvent.[27,28] The diffusional contribution to the rate constants was eliminated[29] and the logarithm of the corrected rate constants was plotted vs $\Delta\Delta G°_{sol}$ for DMF (Figure 8). A remarkably linear relationship exists, with large values of $\Delta\Delta G°_{sol}$ leading to small rate constants. This is a satisfying correlation considering the variety of compound types included in the 11 entries (an aromatic hydrocarbon, two quinones, two aromatic nitriles, an aromatic ketone, and five nitrobenzenes). The rate constants range from close to diffusion-controlled (compounds **35** and **36**) to about 2 orders of magnitude lower (compound **7**, nitrobenzene).

Having established a relationship between the electron exchange rate constants and $\Delta\Delta G°_{sol}$, we can examine its implications. Clearly, compounds with $\Delta\Delta G°_{sol}$ lower than the phthalonitriles (compounds **35** and **36**), anthracene (**32**), or 1,4-dinitrobenzene (**21**) will have self-exchange reactions whose rates approach the diffusion-controlled limit and are therefore difficult to characterize. At the other extreme, among the nitrobenzenes the $\Delta\Delta G°_{sol}$ of nitrobenzene in DMF (−58.6 kcal/mol) is at the limiting value (−58 to −59 kcal/mol) for the low EA compounds (compounds **1–7**, Figure 3). Thus, if the solvent reorganization energy is the dominant contributor to the activation energy, we cannot expect the electron transfer rate constants of compounds **1–6** to be much lower than that of nitrobenzene itself.

Though few data for self-exchange reactions exist, Peover and Powell[30] determined the standard heterogeneous electron transfer rate constants of several nitrobenzenes and nitroalkanes at a mercury electrode in DMF. For 2- and 4-methylnitrobenzene (compounds **4** and **5**), they found large and similar values (1.6 and 2.7 cm/s, respectively) which are also near that of nitrobenzene itself (2.2 cm/s).[29] As pointed out above, the $\Delta\Delta G°_{sol}$ for these three compounds is constant within experimental error. However, for nitromesitylene (compound **1**), Peover and Powell

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(22) Keesee, R. G.; Castleman, A. W. *J. Phys. Chem. Ref. Data*, **1986**, *15*, 1011–1071.

(23) Magnera, T. F.; Caldwell, G.; Sunner, J.; Ikuta, S.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 6140–6146.

(24) The values of $\Delta G°_{0,1}$ were determined[5] at 70 °C. Because $\Delta S°$ is quite similar for the 10 cases where measurements were made, $\Delta G°_{0,1}$ at 25 °C is likely to be offset from the value at 70 °C by a constant amount for all compounds. To the extent that this generalization is correct, there would be no effect on the slope of the plots in Figure 7 if $\Delta G°_{0,1}$ at 25 °C were used.

(25) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966–978. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322.

(26) Though conceptually similar, the solvent- (outer) reorganization energy and $\Delta\Delta G°_{sol}$ are not identical. The former is the energy required to change the orientation of solvent molecules around the ion to that which exists around the neutral species (and vice versa). It is usually estimated from dielectric continuum theory.[25] On the other hand, $\Delta\Delta G°_{sol}$ is the difference in the free energies of transfer from gas phase to solution of the ion and the neutral species. It is not surprising that large values of $\Delta\Delta G°_{sol}$ are associated with large solvent-reorganization energies and hence small self-exchange rate constants.

(27) (a) Malachesky, P. A.; Miller, T. A.; Layloff, T.; Adams, R. N. *Exch. React., Proc. Symp.* **1965**, 157–171. (b) Layloff, T.; Miller, T.; Adams, R. N.; Fäh, H.; Horsfield, A.; Proctor, W. *Nature* **1965**, *205*, 382–383.

(28) Kowert, B. A.; Marcoux, L.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 5538–5550.

(29) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317–6324.

(30) Peover, M. E.; Powell, J. S. *J. Electroanal. Chem.* **1969**, *20*, 427–433.

found the rate constant to be about 1 order of magnitude lower (0.28 cm/s) though $\Delta\Delta G^\circ_{sol}$ for nitromesitylene is the same as the other three within experimental error.

Bulky ortho substituents force the nitro group to be turned out of the plane of the ring and ESR measurements show that this is accompanied by an increase in spin density on the nitro group in the anion radical.[30] Peover and Powell suggested that the charge density, like the spin density, was also larger on the nitro group for radical anions, like that of nitromesitylene, where the nitro group is turned out of the plane due to the ortho methyl substituents. This more localized charge should lead to a larger solvent-reorganization energy and, hence, a lower rate constant. However, our measurements cast doubt on this interpretation because $\Delta\Delta G^\circ_{sol}$ for nitromesitylene does not differ significantly from that of nitrobenzenes with large rate constants such as 4, 5, and 7.

Other factors must be responsible for the lower rate constants seen for 2,6-dialkylnitrobenzenes.[18,30-34] The most likely would appear to be an increase in the inner reorganization energy associated with resistance to turning of the nitro group toward the plane of the ring upon going from the neutral species to the anion radical. The allowable change in angle is small due to steric crowding, but only a relatively modest increase in activation energy is needed to bring about the observed factor of 10 reduction in the rate constant.

Recently, electron-transfer reactions among nitroaromatic radical anions and neutral species have been investigated in aqueous solution,[35] and it was found that reactions involving 2,6-dimethylnitrobenzene were much slower than for compounds with no or only one ortho substituent. The self-exchange rate constant for 2,6-dimethylnitrobenzene was estimated to be only 0.01–0.1 $M^{-1}\ s^{-1}$! The effect was again attributed to increased solvation energy due to greater charge on the nitro group. Though we did not determine $\Delta\Delta G^\circ_{sol}$ in aqueous solution, the results for MeOH (Figure 3) suggest that $\Delta\Delta G^\circ_{sol}$ for nitromesitylene (which is structurally similar to 2,6-dimethylnitrobenzene) would not be very much larger than for compounds that are not 2,6-substituted, so the large diminution in the electron exchange rate constant is likely to be caused by factors other than solvent-reorganization energy. As suggested earlier, increases in the inner reorganization energy may be responsible. Theoretical studies of the small structural changes accompanying electron transfer to substituted nitrobenzenes are likely to be illuminating and helpful.

**Acknowledgment.** This research was supported by the National Science Foundation (Grant CHE-8722764).

**Registry No. 1**, 603-71-4; **2**, 83-41-0; **3**, 100-17-4; **4**, 88-72-2; **5**, 99-99-0; **6**, 99-08-1; **7**, 98-95-3; **8**, 555-03-3; **9**, 1493-27-2; **10**, 350-46-9; **11**, 88-73-3; **12**, 402-67-5; **13**, 100-00-5; **14**, 121-73-3; **15**, 98-46-4; **16**, 619-24-9; **17**, 612-24-8; **18**, 99-65-0; **19**, 528-29-0; **20**, 619-72-7; **21**, 100-25-4; **22**, 4110-35-4; **23**, 84-65-1; **24**, 58-27-5; **25**, 137-18-8; **26**, 130-15-4; **27**, 719-22-2; **28**, 106-51-4; **29**, 363-03-1; **30**, 117-80-6; **31**, 527-21-9; **32**, 120-12-7; **33**, 119-61-9; **34**, 626-17-5; **35**, 91-15-6; **36**, 623-26-7; **37**, 85-44-9; **38**, 102-54-5.

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# Kinetics and Mechanism of the Exo Cyclizations of ω-Formylalkyl Radicals

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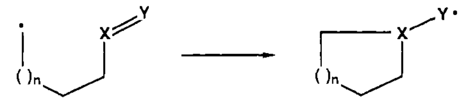
**Abstract:** Kinetic analysis of the reactions of 5-bromopentanal (**1**) and 6-bromohexanal (**7**) indicates that both the formylbutyl radical (**2**) and the formylpentyl radical (**8**) undergo fast exo cyclization. In each case the reaction is reversible and the equilibrium lies in favor of the open-chain form. The reactions are complicated by the propensity of aldehydes to undergo abstraction of formyl hydrogen atoms. Rate constants were measured by competition against reactions of the formylalkyl radicals, **2** and **8**, and the cycloalkoxy radicals, **3** and **9**, with tributylstannane. Values obtained at 80 °C include $8.7 \times 10^5\ s^{-1}$ and $1.0 \times 10^6\ s^{-1}$ for cyclization of **2** and **8**, respectively, and $4.7 \times 10^8\ s^{-1}$ and $1.1 \times 10^7\ s^{-1}$ for the reverse reactions. The Arrhenius parameters for cyclization of **2** and its alkenyl analogue, 5-hexenyl radical, are very similar, but the activation energy for cyclization of **8** is unexpectedly low. Molecular orbital (AM1) and molecular mechanics (MM2) calculations of transition structure strain energies are consistent with these observations.

Intramolecular radical cyclizations (Scheme I) have generated considerable interest, both synthetically[1] and mechanistically.[2] Although radicals derived from species containing a variety of X=Y functional groups have been investigated, among them alkenes, alkynes, and nitriles, only recently have ketones[3] and aldehydes[4,5] received much attention. In what follows, we will focus on cyclizations of species containing the aldehyde function,

**Scheme I**



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