K indicates that the proton-transfer reaction dominates as the source of the water.

Higher oxygen predoses do lead to formate. If a larger oxygen dose (0.2 ML) was preadsorbed, and the crystal heated to 205 K and rapidly cooled to quench the surface reaction, the vibrational spectrum showed losses characteristic of monodentate DCOO on silver[18] (see Figure 4 and Table I). The absolute values and the separation of the ν(OCO) frequencies are almost the same as for the HCOO formed from formic acid. However, in the case of DCOO the π(CD) modes are no longer obscured by the stronger OCO stretch, and the π(CD) mode is clearly observed at 1025 cm^{-1}. We conclude that at these higher oxygen coverages the aldehyde is nucleophilicly attacked by surface oxygen even at 80 K.

The preadsorption of oxygen not only leads to nucleophilic attack on adsorbed formaldehyde, but it also appears to lead to a more ordered overlayer. No low-energy electron-diffraction studies were performed; however, the much stronger elastic peak in the loss spectrum obtained with oxygen precoverage compared to the elastic peak observed for monolayer coverage of the aldehyde on the clean surface is indicative of a more ordered overlayer in the presence of adsorbed oxygen. Adsorbed oxygen forms islands on Pd(100).[23] The islands may force the adsorbed formaldehyde to assume a more ordered configuration. Oxygen clearly reacts with formaldehyde, although at low θ_O the formate appears to be a transitory intermediate due to the nearly coincident temperatures for formaldehyde oxidation and formate decomposition. At higher θ_O the reaction to formate occurs at $\approx$200 K. This strong shift in reaction temperature with an $\approx$20% change in θ_O indicates that excess oxygen aids the nucleophilic attack. A similar process in which methylene dioxide is a transient intermediate between formaldehyde and formate has been proposed for the oxidation of formaldehyde on Cu.[13]

The comparative reaction temperatures of the formic acid and formaldehyde oxidations give information on the relative activation energies of the the two paths to formate. The acid–base reaction for formic acid runs to completion at 80 K, while the nucleophilic attack occurs at $\approx$200 K or higher. The acid–base reaction is that of a very strong base with a strong acid. The driving force is obviously large, but the activation barrier need not be a priori small. However, the complete reaction at 80 K indicates that at least for formic acid the activation energy is less than 5 kcal/mol. By comparison, the activation energy for the nucleophilic attack leading to the same product, formate, has an activation energy of approximately 12 kcal/mol, based on the reaction temperature. Despite some uncertainty in these values, it is reasonable to infer that the activation energy of the acid–base reaction (H transfer) is significantly lower than the nucleophilic reaction (O incorporation) on this surface.

Conclusions

The formate group forms on Pd(100) as a result of both acid–base chemistry in the oxidation of formic acid and nucleophilic attack in the oxidation of formaldehyde. Formate adopts a monodentate form with the molecule tilted in a plane perpendicular to the surface. The formate is stable up to 265 K where is decomposes to CO_2 and hydrogen. The proton-transfer reaction in formic acid oxidation occurs via a direct path at 80 K while the nucleophilic attack in formaldehyde oxidation occurs at or above 200 K.

On Pd, as on silver, oxygen can act as both a nucleophile and a strong Brønsted base. Acids as weak as water, methanol, and presumably other alcohols react with oxygen in an acid–base fashion. Additionally, the nucleophilic reactivity of adsorbed oxygen, previously well documented on group IB metals, has also been demonstrated on Pd(100).

Electron Affinities of Benzo-, Naphtho-, and Anthraquinones Determined from Gas-Phase Equilibria Measurements

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Abstract: The equilibrium constant K_{et} for gas-phase electron transfer equilibria A$^-$ + B = A + B$^-$ between compounds A with known electron attachment energies and some 21 benzo-, naphtho-, and anthraquinones = B were determined. These lead to electron attachment free energies $\Delta G_a°$(B) for the following process: e + B = B$^-$. Determination of the temperature dependence of K_{et} leads to $\Delta H_a°$(B) and $\Delta S_a°$(B). The electron affinities EA(B) correspond to $-\Delta H_a$(B). The substituent effects on the electron affinities of the quinones are examined. Available half-wave reduction potentials for the quinones in water, dimethylformamide, and acetonitrile are used in order to evaluate the solvation free energies of the quinone radical anions in these solvents. The substituent effects on the solvation energies are examined. In general it is found that the exothermicity of the solvation free energy decreases as the electron affinity of the quinones increases.

The quinones are an extremely important group of compounds. In biological systems quinones attached to proteins are the prosthetic group involved in electron and hydrogen transfers.[1-3] The one- or two-electron reduction of quinone (quinone–hydroquinone) is reversible and represents one of the most important examples of organic electrochemistry.

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Quantitative information on the stability of the radical anions resulting after single electron capture in solution can be obtained from the reduction potentials of quinones. The data that are generally available are polarographic half-wave potentials measured in different solvents. The corresponding quantity in the gas phase is the electron affinity and the related enthalpy $\Delta H_a°$ and free energy $\Delta G_a°$ of electron attachment shown in eq 1, where

$$e + B = B^- \qquad (1)$$

$$\Delta H_1° = \Delta H_a°(B), \ \Delta G_1° = \Delta G_a°(B), \ -\Delta H_a°(B) \approx EA(B)$$

B is a molecule with electron affinity.

Table I. Data[a] Obtained from van't Hoff Plots of Electron Transfer Equilibrium Constants K_{et}

	A	B[b]	$-\Delta G^{\circ}{}_{et}$ (150 °C)	$-\Delta H^{\circ}{}_{et}$	$\Delta S^{\circ}{}_{et}$
1	4-CN-NB	2,3-di-MeO-dimethoxy-6-Me-1,4-BQ	2.1	3.2	-2.9
2	di-MeO-6-Me-2,4-BQ	BQ	1.6	1.2	1.2
3	duroquinone	4-CN-NB	2.7	2.1	1.3
4	2-CN-NB	duroquinone	0.2	0.2	0.9
5	4-NO₂-NB	2-Ph-BQ	0.8	0.9	-0.7
6	4-CN-NB	2-Me-5-*i*-Pr-BQ	1.3	1.7	-0.6
7	4-CN-NB	2,6-diMeO-BQ	0.4	0.1	0.8
8	2,3-di-*t*-Bu-BQ	4-NO₂-NB	3.1	2.6	1.1
9	2-CN-NB	2,6-di-*t*-Bu-BQ	5.6	5.7	-0.7
10	4-CN-NB	2,6-di-*t*-Bu-BQ	2.8	3.9	-2.7
11	AnQ	2-CN-NB	0.4	0.4	-0.3
12[c]	NpQ	4-NO₂-NB	4.1	4.4	-0.6
13[c]	4-CN-NB	NpQ	1.5	2.2	-1.5
14[c]	3,5-di-NO₂-BN	2,3-di-Cl-NpQ	0.9	0.9	-0.2
15[c]	4-NO₂-NB	2,3-di-Cl-NpQ	5.0	4.6	1.0

[a] van't Hoff plots shown in Figure 2. Equilibrium constants for electron transfer reaction: A⁻ + B = A + B⁻. Numbers coincide with those used in Figure 2. [b] ΔH° and ΔG° in kcal mol⁻¹, ΔS° in cal mol⁻¹ deg⁻¹. Abbreviations used: BN (benzonitrile), NB (nitrobenzene), BQ (1,4-benzoquinone), NpQ (1,4-naphthoquinone), AnQ (9,10-anthraquinone). [c] From Chowdhury.[4]

The electron affinity corresponds to the energy difference between B and B⁻ when both species are in their ground vibrational and rotational states. However, because of the similarity of the vibrational and rotational levels in B and B⁻, generally $-\Delta H_a{}^{\circ}(B)$ ≈ EA(B) within less than 1 kcal/mol at ordinary temperatures.[4]

Even though the EA's are fundamental quantities and many methods for their determination have been used,[5,6] until recently, electron affinities for many compounds of interest were not available, and the data for compounds that had been studied were often in disagreement. For example, gas-phase EA determinations for only a few quinones were available,[5] and for 1,4-benzoquinone values ranging from 0.4 to 2.1 eV have been determined.[5]

Recently we reported a large number of EA determinations[4,7-13] which were based on measurements of the gas-phase electron transfer equilibria, ETE, eq 2, with a pulsed electron high-pressure

$$A^- + B = A + B^- \qquad (2)$$

$$\Delta G_2{}^{\circ} = \Delta G_{et}{}^{\circ}$$

mass spectrometer,[14] PHPMS. These included the electron affinities of seven quinones. The present work extends the quinone determinations to a total of 21. The data are of interest not only in experimental situations where gas-phase negative ions of the quinones are encountered such as negative ion analytical mass spectrometry (NICI, FAB, MS–MS, Thermospray, etc.) and negative ion electron capture detector in gas chromatography, but also to theoretical computational work on the properties of the radical anions. Comparison of the EA's and $\Delta G_a{}^{\circ}$ with available reduction potential data in solution permit one to establish whether the polarographic half-wave potentials correlate with the gas-phase data and thus correspond to reversible potentials. Furthermore, when reliable reversible potentials are available, solvation energies
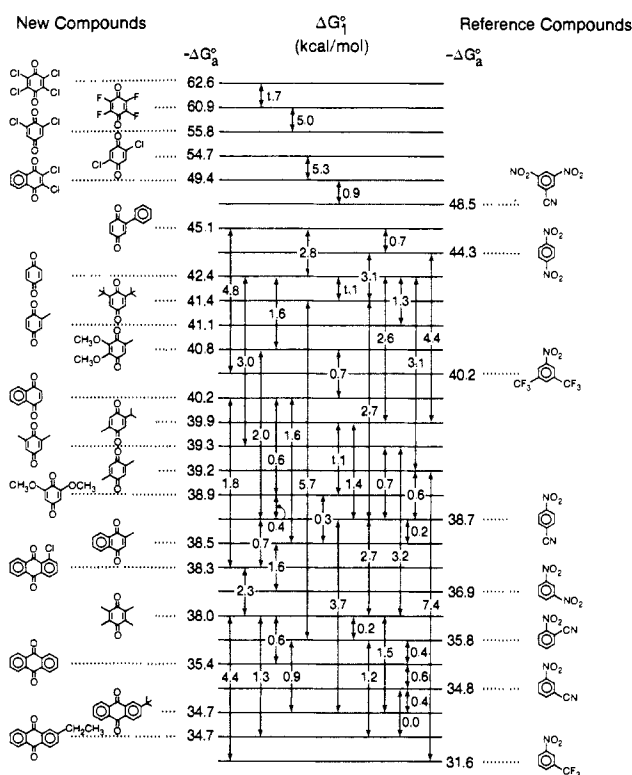
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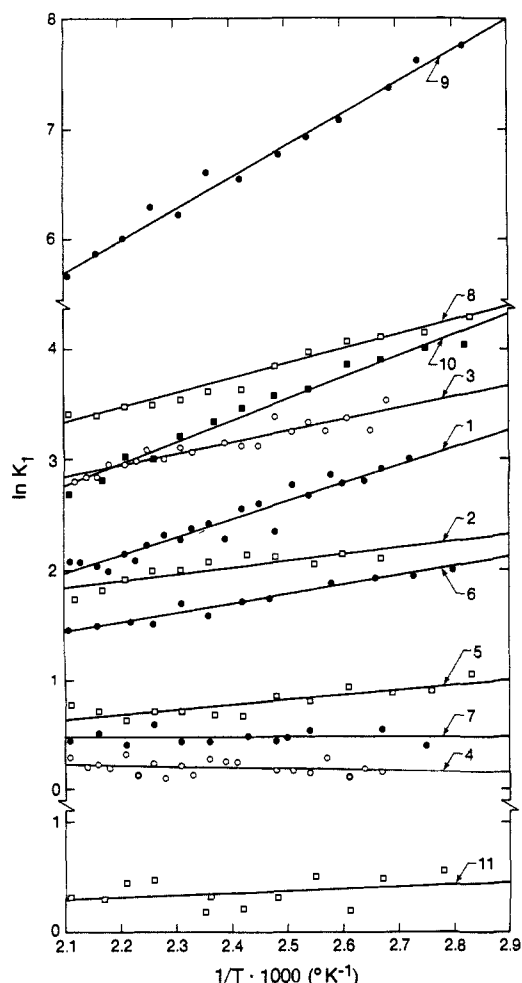

Figure 1. Free energies $\Delta G_1{}^{\circ} = \Delta G_{et}{}^{\circ}$ for gas-phase electron transfer reactions, A⁻ + B = A + B⁻ involving quinones. ΔG_a is the free energy for the capture of a stationary electron by the given compound. Values for 423 K but because of weak temperature dependence also approximately valid for 298 K.

of the radical anions in the respective solvents can be derived from a combination of the gas-phase and solution data.

Results and Discussion

a. Results for the Electron Transfer Equilibria and Electron Attachment Energies. Determinations of the ETE were performed with the pulsed electron high-pressure mass spectrometer[14] using techniques that have been fully described in earlier work.[4,7-14] The equilibrium constants $K_2 = K_{et}$ obtained from the measured equilibria are used to evaluate the electron transfer free energy change, eq 3.

$$\Delta G_{et}{}^{\circ} = -RT \ln K_{et} \qquad (3)$$

The quinone determinations are summarized in Figure 1. The $\Delta G_{et}{}^{\circ}$ were determined at 423 K (150 °C), a temperature at which formation of dimers $A_2{}^-$, AB^-, and $B_2{}^-$ is minor and does not affect measurement of the transfer equilibria.[13] The electron attachment

Figure 2. van't Hoff plots of equilibrium constants $K_1 = K_{et}$ for electron transfer reactions $A^- + B = A + B^-$ involving quinones. Numbers identify reactions shown in Table I.

Table II. Thermochemical Data[a] for Electron Attachment Reaction: B + $e^- \to B^-$

compound B	ΔG°_a (423 K) (kcal/mol)	$\Delta S_a^{\circ c}$ (cal deg⁻¹) mol⁻¹	$-\Delta H_a^\circ$ (kcal/ mol)	EA (eV)	lit. (eV)
tetra-Cl-BQ[b]	62.6 (62.3)[d]	(-3.5)[c]	(64.0)[c]	2.78	2.76[e]
tetra-Fl-BQ[b]	60.9	(-3.5)	(62.3)	2.70	2.92[e]
2,6-di-Cl-BQ[b]	55.8 (56.1)[d]	(-3.5)	(57.2)	2.48	
2,5-di-Cl-BQ	54.7	(-3.5)	(56.2)	2.44	
2,3-di-Cl-NQ[b]	49.4	-3.5	50.9	2.21	
2-Ph-BQ	45.1	-5.2	47.1	2.04	
BQ[b]	42.4 (43.0)[d]	-4.0	44.1	1.91	1.89[e]
2,6-di-t-Bu-BQ	41.4	-4.9	43.0	1.87	
3,5-di-t-Bu-1,2-BQ[f]	~40.0[f]			~1.73[f]	
2-Me-BQ	41.1 (41.3)[d]	(-4.0)	(42.7)	1.85	
2,3-di-MeO-6-Me-BQ	40.8	-5.4	42.8	1.86	
NpQ[b]	40.2 (40.1)[d]	-4.0	41.8	1.81	
2-Me-5-i-Pr-BQ	39.9	-3.3	40.5	1.76	
2,6-di-Me-BQ	39.3	(-3.3)	(40.7)	1.77	
2,5-di-Me-BQ	39.2 (39.4)[d]	(-3.3)	(40.6)	1.76	
2,6-di-MeO-BQ	38.9 (39.4)[d]	-1.9	39.6	1.72	
2-Me-NpQ	38.5 (38.7)[d]	(-4.0)	(40.0)	1.74	
1-Cl-AnQ	38.3	(-2.4)	(39.5)	1.71	
duroquinone	36.0 (35.9)[d]	-3.2	37.4	1.62	
AnQ	35.4	-2.9	36.7	1.59	
2-t-Bu-AnQ	34.7	(-2.9)	(35.9)	1.56	
2-Et-AnQ	34.7	(-2.9)	(35.9)	1.56	

[a] Energies given are for attachment of a stationary electron; i.e., stationary electron convention has been used.[4] Abbreviations used: BQ (1,4-benzoquinone), NpQ (1,4-naphthoquinone), AnQ (9,10-anthraquinone). Estimated error: ΔG_a° ±0.5 kcal/mol, ΔH_a° ±1 kcal/mol, EA ±0.06 eV, ΔS_a° ±3 cal mol⁻¹ deg⁻¹. [b] From previous work, this laboratory.[4] [c] Entropy shown in parentheses was estimated by assuming entropy equalities: tetrachloro BQ = tetrafluoro BQ = 2,6-dichloro BQ = 2,3-dichloro NpQ; 2-methyl BQ = BQ; 2,6-dimethyl BQ, 2,5-dimethyl BQ = 2-methyl-5-isopropyl BQ; 1-Cl-AnQ, 2-tert-butyl AnQ, 2-ethyl AnQ = AnQ. ΔH° shown in parentheses based on ΔS° shown in parentheses. [d] ΔG_a° based on ΔG_{et}°: Fukuda and McIver.[15] The electron transfer results were anchored in the present work to the known $\Delta G_a^\circ(SO_2)$ = -16.7 kcal/mol, the primary anchor used for the PHPMS data.[4,13] [e] Copper et al.[16] [f] Fully consistent ETE measurements could not be obtained with 3,5-di-tert-butyl-1,2-benzoquinone. ETE measurements involving benzoquinone, 4-cyanonitrobenzene, and 1,4-dinitrobenzene led to value given in table within ±0.3 kcal/mol.

energies ΔG_a° of the reference compounds shown in Figure 1 were determined previously.[4,13] Combination of the measured ΔG_{et}° with the known ΔG_a° of the reference compounds leads to ΔG_a° for the quinones.

The temperature dependence of 11 equilibria involving quinones was determined. The corresponding van't Hoff plots are shown in Figure 2. The resulting enthalpy, entropy, and free energy changes are shown in Table I which also contains data from four van't Hoff plots involving quinones, obtained in earlier work.[4] The ΔH_{et}° and ΔS_{et}° from Table I were combined with the known[4,13] ΔH_a° and ΔS_a° of the reference compounds to evaluate electron attachment enthalpies and entropies ΔH_a° and ΔS_a° for the quinones involved in the measurements.

Examination of the ΔS_{et}° in Table I shows that these are generally quite small such that $T\Delta S_{et}^\circ$ is generally less than 0.5 kcal/mol, which means that ΔG_{et}° is within 0.5 kcal/mol of ΔH_{et}°. The electron attachment entropies ΔS_a° are also relatively small and this led to ΔH_a° being within ~1 kcal/mol of ΔG_a°. It should be pointed out that the stationary electron convention was used in which the translational entropy of the electron is neglected such that $\Delta S_a^\circ(B) = S^\circ(B^-) - S^\circ(B)$.

The accuracy of the entropy changes obtained from van't Hoff plots of exchange reactions is generally in the ±2 to ±3 cal deg⁻¹ mol⁻¹ range;[4,13] therefore, not too much should be made from measured ΔS_{et}° values that differ by 1 or 2 cal deg⁻¹ mol⁻¹. All the ΔS_a° results for the quinones fall in the -3 to -4 cal deg⁻¹ mol⁻¹ range. These results indicate a loss of freedom in the radical anion relative to the neutral quinone. Since the aromatic character is increased on formation of the quinone radical anion, this change could be reflecting stiffening of skeletal and C–C–O bending vibrations. The compounds, 2-phenyl-, 2,3-methoxy-, and 2,6-

tert-butylbenzoquinone have a somewhat higher $-\Delta S_a^\circ$ of around 5 cal deg⁻¹ mol⁻¹. A possible cause for this change would be a stiffening of the torsional oscillations involving the substituents in the 2 position due to increased interactions of the substituents with the negative oxygen in position 1.
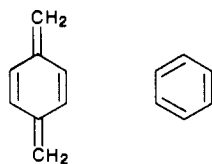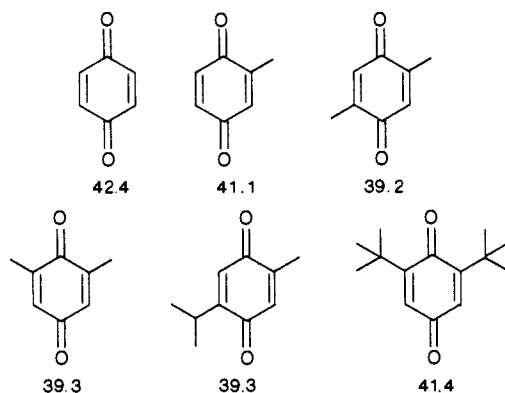
Several ΔS_a° values of quinones were estimated as shown in Table II in order to obtain a complete set of ΔH_a° and thus also EA $\approx -\Delta H_a$.

Fukuda and McIver[15] have reported results from ETE quinone measurements with an ion cyclotron resonance (ICR) mass spectrometer. Since these authors did not convert their relative values to absolute values with use of an external standard, we have, in order to facilitate comparison, given the McIver results in Table II as absolute values (ΔG_a°) by calibrating to the primary standard SO_2, used in the PHPMS determinations,[4,13] $\Delta G_a^\circ(SO_2)$ = -16.7 kcal/mol. Examination of the ΔG_a° in Table II shows that the agreement between the present and McIver's results is very good, generally within less than 0.5 kcal/mol.

Cooper et al.[16,17] have measured the EA of 2,4-benzoquinone, and the tetra-substituted 1,4-benzoquinones: fluoranil, chloranil,

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Scheme I

Scheme II[a]

42.4   41.1   39.2

39.3   39.3   41.4

[a] Values in kcal/mol.

Figure 3. Substituent effects on the electron affinity of 1,4-benzoquinone.

Scheme III

and bromanil. The technique used (collisional ionization) consists of determining the kinetic energy threshold for the ionizing collision: Cs + B = Cs⁺ + B⁻, where the Cs atoms are in a beam of known kinetic energy. Cooper's[16] result of 1.89 eV for 2,4-benzoquinone is very close to the present 1.91 eV, and the results for the choranil are also very close, 2.76 vs. 2.78. For fluoranil, Cooper[16] gets 2.92 eV, a value that is higher than that for chloranil, while the present result, 2.70 eV, is lower. Since it is generally observed that the electron affinity increases more for chloro vs. fluoro substitution on sp²-hybridized carbon (see Kebarle[13]), one may conclude that Cooper's fluoranil result is probably too high by ~0.2 eV.

b. General Discussion of Electron Affinities of Quinones. The extra electron enters the LUMO of the quinones which is a π*-type orbital. The lower the LUMO, the higher is the expected electron affinity. Quinodimethane (Scheme I) has a substantial delocalization energy (1.924β)) which is similar to that of benzene (2β). However, benzene in the gas phase does not form a stable negative ion; i.e., it has a negative electron affinity of ~(-26 kcal/mol),[18] and one would expect a similar value also for quinodimethane. The very large positive electron affinity of 1,4-benzoquinone of +44.1 kcal/mol is thus a consequence of the very large electronegativity of the two oxygen atoms replacing the two CH₂ groups in quinodimethane. On this simple basis it becomes clear that while the electron is in the molecular π* LUMO of quinone, the negative charge must be largely located on the two oxygens; i.e., the singly occupied electron molecular orbital, SOMO, is concentrated on the oxygens.

Introduction of electron-withdrawing groups increases the electron affinity of benzoquinone, an effect generally observed for the electron affinities of substituted aromatic compounds.[13] On the other hand, methyl substitution or generally alkyl substitution leads to a decrease of electron affinity.[13] The destabilization of anions by methyl substitution on sp²-hybridized carbon is a general effect observed also for even electron anions and manifest in the acidities of acetylenes,[19] carboxylic acids,[20] and phenols.[21] The effect of multiple methyl substitution on the electron affinity of quinone is shown in Figure 3. It is interesting to note that the decrease of EA per methyl substituent is essentially constant and equal to 1.7 kcal/mol per substituent. Isopropyl
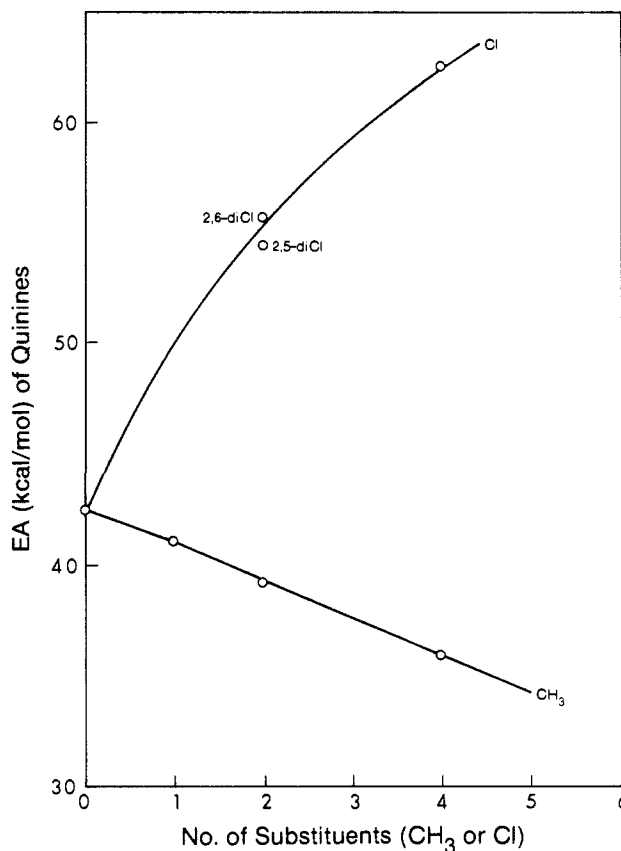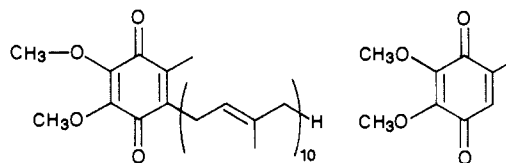
substitution is slightly less destabilizing than methyl, and tert-butyl substitution is the least destabilizing, as illustrated by the ΔG_a° values given in Scheme II.

The effect of multiple chlorine substitution on the electron affinity of benzoquinone is illustrated in Figure 3. The increase with each Cl substituent is quite large. There is indication that the effect decreases somewhat with increased Cl substitution. Four Cl substituents (chloranil) increase the electron affinity by a whole 20 kcal/mol (see Figure 3 and Table II).

As mentioned in the preceding section, fluorine substitution increases the electron affinity somewhat less than Cl substitution, an effect observed also in the electron affinities of substituted nitrobenzenes[13] and operating also in even electron anions like the phenoxides and benzoate anions.[21] The more strongly ion stabilizing effect of Cl should be due to its higher polarizability, an effect much more important in stabilizing the ion in the gas phase than in solution and to the much lesser ability of Cl relative to F for π-donation, an effect that destabilizes the negative ion.

Substitution with methoxy decreases slightly the electron affinity of benzoquinone. A similar effect is observed also for the electron affinities of substituted benzenes.[13] Methoxy substitution in the 4 position reduces slightly the acidities of phenols and benzoic acids,[21] an effect attributed to significant destabilization of the anions due to π-donation from the oxygen. The stabilizing field effect of the methoxy dipole conteracts the above so that only a slight destabilization results.

Ubiquinone (Scheme III) bound to proteins plays a multiple role in the electron transfer and photochemical events of bacterial photosynthesis. The electron affinity of ubiquinone was not determined because the compound is not available commericially

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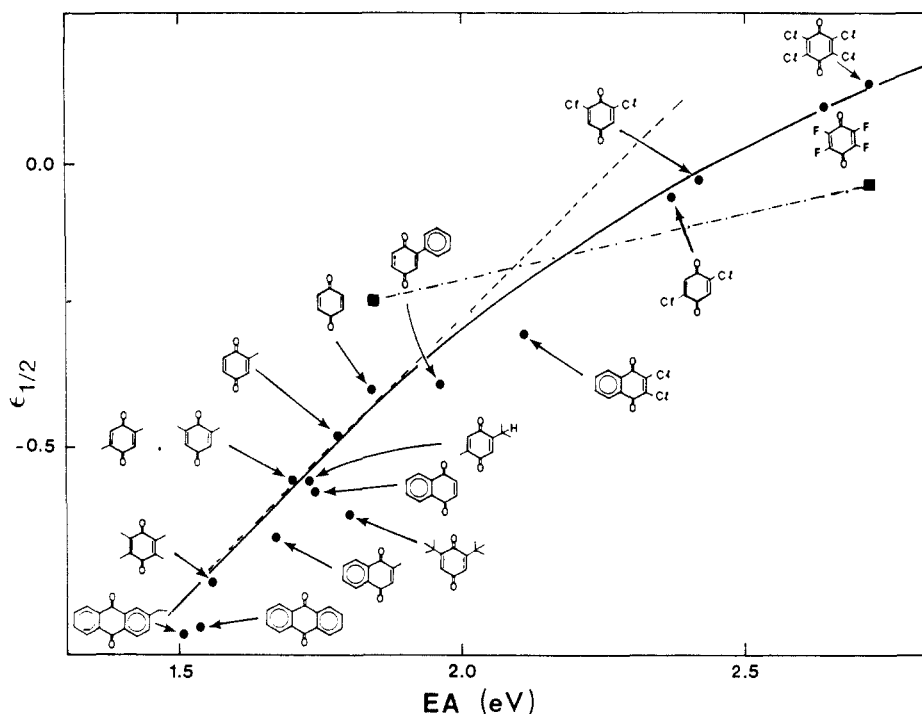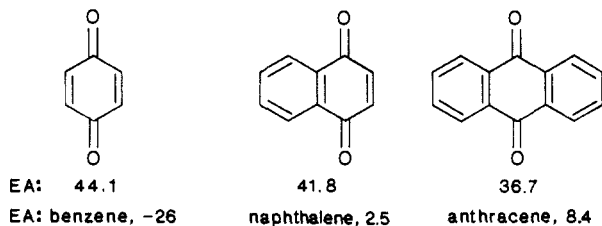
Figure 4. Plot of electron affinities of substituted quinones vs. polarographic half-wave potentials of Price[30] in dimethylformamide (DMF).

Scheme IV[a]

EA: 44.1   41.8   36.7

EA: benzene, −26   naphthalene, 2.5   anthracene, 8.4

[a] Values in kcal/mol.

and also probably would not have been sufficiently volatile for the gas-phase PHPMS method. However, on the basis of the substituent effects discussed above and the measured EA = 1.77 eV of 1-methyl-4,5-dimethoxyquinone (Scheme III), the EA of ubiquinone can be estimated to be close to 1.70 eV.

Expansion of the π system from benzoquinone to naphthoquinone to anthraquinone leads to a decrease of electron affinities (see Figure 1 and Table II), as shown in Scheme IV. On the other hand, the electron affinities of benzene, naphthalene, and anthracene increase rapidly in this order,[18] (see Scheme IV). These opposing trends are predicted from theory. Thus, the Hückel MO energies of the π^* LUMO's increase for the benzoquinones in the order benzo, naphtho, and anthra, while they decrease for benzene, naphthalene, and anthracene. In fact, the changes in the Hückel MO energies are close to proportional to the changes of electron affinities for the two series.[22,23] A simple qualititative consideration based on delocalization energies (Hückel MO) or resonance (VB) predicts the above opposing trends (Streitwieser,[23] pp 251–253). STO-3G calculated LUMO's of the quinones[24] also increase in energy in the order benzo, naphtho, anthraquinone and thus predict the observed electron affinity trend.

From the above considerations it follows that while for the radical anions of benzene, naphthalene, and anthracene the

negative charge is spread out over the whole molecule and thus the charge dispersal increases rapidly in the above series, for benzo-, naphtho-, and anthraquinone the negative charge will be largely concentrated on the oxygens and only very minor changes of the negative charge distribution will occur for the above series. This result finds application in the next section.

c. Stabilities and Solvation Energes of the Quinone Radical Anions in Solution. The half-wave reduction potentials, $\epsilon_{1/2}$, obtained by polarographic measurements represent a very useful source of data on the stabilities of radical anions in solution.[25–30] The reversible reduction $\epsilon_{1/2}$ values can be related to the electron affinity and the solvation energies of the radical anion and the neutral. $\epsilon_{1/2}(B)$ obeys[25–28] the approximate equality shown in eq 4, where $\epsilon^\circ(B)$ is the reduction potential of B and $\epsilon^\circ(\text{ref})$ is the

$$\epsilon_{1/2}(B) = \epsilon^\circ(B) - \epsilon^\circ(\text{ref}) \qquad (4)$$

reduction potential of the reference electrode used in the polarographic determination. The *absolute* reduction potential of B can be expressed with use of a simple Born cycle[25] by eq 5 or

$$F\epsilon^\circ(B) = -\phi(\text{Hg}) - \Delta G_a(B) - (\Delta G_{\text{sol}}^\circ(B^-) - \Delta G_{\text{sol}}^\circ(B)) \qquad (5)$$

6. $\phi(\text{Hg})$ is the mercury work function, F is Faraday's constant,

$$F\epsilon^\circ(B) \approx -\phi(\text{Hg}) + \text{EA}(B) - (\Delta G_{\text{sol}}^\circ(B^-) - \Delta G_{\text{sol}}^\circ(B)) \qquad (6)$$

and $\Delta G_{\text{sol}}^\circ(B)$ and $\Delta G_{\text{sol}}^\circ(B^-)$ correspond to the free energies of transfer of gaseous B and B⁻, respectively, to solution. Since electron attachment free energies $\Delta G_a^\circ(B)$ were not available, earlier workers[25–28] used eq 6, which makes use of the approximate equality $-\Delta G_a^\circ(B) \approx \text{EA}(B)$.

Combining eq 4 with eq 5 one obtains:

$$F\epsilon_{1/2}(B) =$$
$$-\phi(\text{Hg}) - \Delta G_a^\circ(B) - (\Delta G_{\text{sol}}^\circ(B^-) - \Delta G_{\text{sol}}^\circ(B)) - F\epsilon^\circ(\text{ref}) \qquad (7)$$

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$$\Delta G_{sol}{}^\circ(B^-) - \Delta G_{sol}{}^\circ(B) =$$
$$-\phi(Hg) - F\epsilon^\circ(ref) - F\epsilon_{1/2}(B) - \Delta G_a{}^\circ(B) \quad (8)$$

$$(\Delta G_{sol}{}^\circ(B^-) - \Delta G_{sol}{}^\circ(B)) \; (kcal/mol) =$$
$$C - 23.06 \; \epsilon_{1/2}(B) \; (V) - \Delta G_a{}^\circ(B) \quad (9)$$

where

$$C = -\phi(Hg) - F\epsilon^\circ(ref)$$

$$C = -115.6 \; kcal/mol \; (LPS^{32} \; and \; Gomer^{34})$$

$$C = -108.6 \; kcal/mol \; (Randles^{33,35})$$

and

$$\Delta\Delta G_{sol}{}^\circ = \Delta G_{sol}{}^\circ(b^-) - \Delta G_{sol}{}^\circ(B)$$

$\epsilon^\circ(ref)$ in eq 7 corresponds to the *absolute* reduction potential of the reference electrode.

Before abundant electron affinities became available, due to ETE measurements, eq 7 was used for evaluation of electron affinities on the basis of experimentally available half-wave reduction potentials.[25-29] For a series of $\epsilon_{1/2}(B)$ of related compounds B, determined under the same experimental conditions and the same reference electrode, eq 7 predicts a linear unit slope relationship between $\epsilon_{1/2}(B)$ and $EA(B) \approx -\Delta G_a{}^\circ(B)$, if one assumes that the solvation energy differences, $\Delta\Delta G_{sol}{}^\circ = \Delta G_{sol}{}^\circ(B^-) - \Delta G_{sol}{}^\circ(B)$ does not change. Calibration to a known EA value in the series led to the determination of the remaining electrode affinities.[25-29]

A previous examination[8,13] of this procedure on the basis of EA values from ETE measurements showed that while an approximate straight line was obtained in plots of $\epsilon_{1/2}(B)$ vs. $EA(B)$, the slope of the line was not equal to unity as required by eq 7 but was less than unity and was solvent dependent. It was concluded that this behavior reflected the neglect of the change in the $\Delta\Delta G_{sol}{}^\circ$. The systems examined were mosly substituted benzenes, and for these compounds higher electron affinity corresponds to radical anions with more extensive charge delocalization. The solvation energy difference, $\Delta G_{sol}{}^\circ(B^-) - \Delta G_{sol}{}^\circ(B)$, is dominated by the much larger solvation energy of the radical anion. It is well known that the ion solvation energy decreases with increasing charge delocalization. Thus less than unit slopes are expected and reflected the expected decreasing solvation energy of the ion B^- with increasing electron affinity of B.[8,13]

A plot of the $\epsilon_{1/2}(B)$ vs. the $EA(B)$ for the quinones is shown in Figure 4. The reduction potentials used are from Price et al.,[30] who used dimethylformamide (DMF) as solvent and the saturated calomel electrode as reference electrode. The correlation of the $\epsilon_{1/2}$ and EA in Figure 4 is only fair. A curved line was drawn through the data, but a straight line with a slope which is less than unity could have been fitted also.

The $\epsilon_{1/2}(B)$ of benzoquinone and tetrachlorobenzoquinone measured in 75% ethanol by Peover[27] are also shown in Figure 4. Since these values were obtained under somewhat different conditions, only the observed slope of the line is significant. The much lower slope for the protic ethanol vs. that for the dipolar aprotic DMF is typical. Protic solvents engage in significant specific, hydrogen-bonding, solvation of the negative oxygen groups. The strong hydrogen-bonding interactions are expected to decrease very rapidly with the decrease of negative charge density on the oxygens in the radical anions which is expected to occur for the change from quinone to tetrachloroquinone.[27] The situation is very similar to that observed for the acidities of phenols in the gas phase and in protic and dipolar aprotic solvents.[21]

Now that gas-phase electron affinities are available, one can use them to evaluate the solvation energies $\Delta\Delta G_{sol}{}^\circ$, (see eq 8), which is a rearranged form of eq 7. Substitution of $\phi(Hg)$ and $\epsilon^\circ(ref)$ for the absolute value of the aqueous saturated calomel cell leads to the numerical constants C shown in eq 9. The numerical constants[31-34] are given in kcal/mol and require that
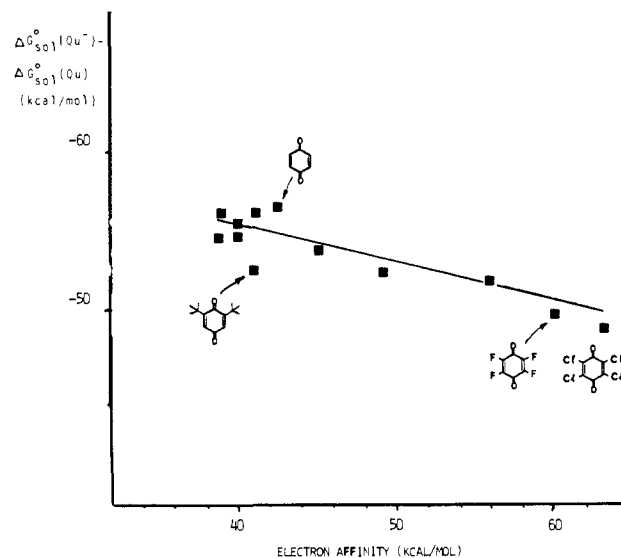

Figure 5. Plot of solvation free energies of the quinones in DMF, from Table III, vs. the electron affinities, $EA \approx -\Delta G_a{}^\circ$, of the quinones.

the other energy terms be also substituted in kcal/mol. Two values are given. $C = -115.6$ kcal/mol is based on determinations of Latimer, Pitzer, Slansky,[32] and Gomer.[34] The value $C = -108.6$ kcal/mol is due to Randles[33a] and is supported by the most recent work.[35]

Solvation energies $\Delta\Delta G_{sol}{}^\circ$ for the quinones evaluated from eq 9 with literature $\epsilon_{1/2}(B)$, $C = -108.6$ kcal/mol (Randles[31]), and $\Delta G_a{}^\circ(B)$ from the present measurements are shown in Table III.

The solvation energies in dimethylformamide (DMF) from Table III are plotted in Figure 5. The decrease of solvation exothermicity of the radical anion with increasing electron affinity is clearly expressed by these results. A smooth decrease is not expected and the "deviations" from the curve, which express

(31) The evaluation of an absolute value of the electrochemical potential of a galvanic half-cell is intimately related with the "real" or "single" ion solvation free energy, i.e., the molar solvation energy of a given positive or negative ion rather than the joint solvation of the positive and negative counterion, the latter being directly accessible through Born cycles. The first evaluation of the single ion solvation energy of alkali ions and of halide ions by Latimer, Pitzer, and Slansky[32] (LPS) led to a calculated value of the calomel electrode absolute potential $\epsilon^\circ_{red} = 0.49$ V using $\phi(Hg) = 4.52$ eV. The LPS result was based on the extrathermodynamic assumption that the Born equation can be used to describe the ion solvation energies if the "correct" ion radius can be established. Determination of the volta potential between electrolyte solution and a metal (Hg) separated from the solution by inert gas, by Randles,[33a] led to a different set of single ion solvation energies. These were accepted in the literature: Desnoyer,[33b] Noyes.[33c] More recently, Gomer et al.,[34] from experimental measurements of the electrostatic potential between the surface of a metal in contact with electrolyte solution and the solution, obtained single ion solvation energies which were essentially identical with those of LPS.[32] However, more recent work[35] provides results in agreement with the Randles' data. The reasons for the discrepancy between Gomer and Randles' results has not been discovered yet. The Randles' values, giving a relatively higher exothermicity of solvation to the positive ions, are more consistent with free energies: $\Delta G^\circ_{0,n}(M^+)$ and $\Delta G^\circ_{0,n}(X^-)$ corresponding to the gas-phase reactions: $M^+ + nH_2O = M^+(H_2O)_n$ and $X^- + nH_2O = X^-(H_2O)_n$, measured in this laboratory.[36,37] However, the gas-phase $(0,n)$ measurements do not extend to sufficiently high n to be decisive regarding the Randles–Gomer controversy.

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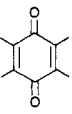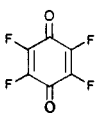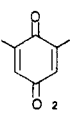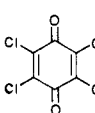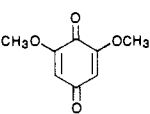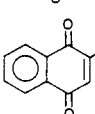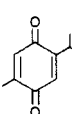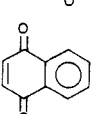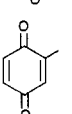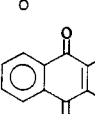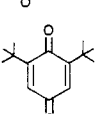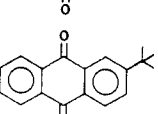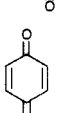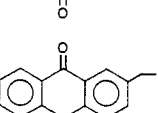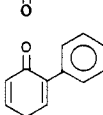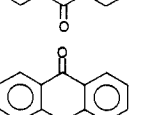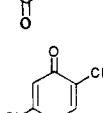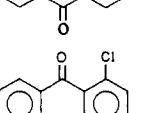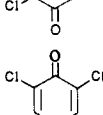
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Table III. Solvation Energies of Quinone Radical Anions

B	$-\Delta G_a°(B)^a$ kcal/mol	$[-\Delta G_{sol}°(B^-) - \Delta G_{sol}°(B)]^b$, kcal/mol			B	$-\Delta G_a°(B)^a$ kcal/mol	$[-\Delta G_{sol}°(B^-) - \Delta G_{sol}°(B)]^b$, kcal/mol		
		acetonitrile^c	DMF^d	water^e			acetonitrile^c	DMF^d	water^e
(tetramethyl-1,4-benzoquinone)	36.0		55.6	61.1	(tetrafluoro-1,4-benzoquinone)	60.9		50.0	
(dimethyl-1,4-benzoquinone) 1. 39.2 2. 39.3		54.5	56.6		(tetrachloro-1,4-benzoquinone)	62.6	48.2	49.2	
(2,6-dimethoxy-1,4-benzoquinone, CH3O…OCH3)	39.2		54.9		(2-methyl-1,4-naphthoquinone)	38.5	54.9	57.9	59.9
(isopropyl-methyl-1,4-benzoquinone)	39.9		55.8		(1,4-naphthoquinone)	40.2	52.0	55.0	
(methyl-1,4-benzoquinone)	41.1	54.1	56.5	62.0	(dichloro-1,4-naphthoquinone)	49.4	49.2	52.3	
(di-tert-butyl-1,4-benzoquinone)	41.4		53.0		(tert-butyl-9,10-anthraquinone)	34.7		54.7	
(1,4-benzoquinone)	42.4	54.4	57.0	63.0	(ethyl-9,10-anthraquinone)	34.7		54.8	
(phenyl-1,4-benzoquinone)	45.1		54.5		(9,10-anthraquinone)	35.4	51.5	54.4	
(2,5-dichloro-1,4-benzoquinone)	54.7	49.7	52.4		(1-chloro-9,10-anthraquinone)	38.3		–	
(2,6-dichloro-1,4-benzoquinone)	55.8	48.6	52.1						

^{a} Electron attachment free energies to B. See Table II. ^{b} Evaluated with eq 9 and $C = -108.6$ kcal/mol (Randles[33,35]). Only the absolute values for water have quantitative significance; the absolute values for acetonitrile and DMF are not corrected for liquid junction potentials which may be significant since the reference electrode was *aqueous* saturated calomel. ^{c} From halfwave reduction potentials in acetonitrile and saturated calomel electrode determined by Peover,[38a] and Chatterjee.[38b] ^{d} Half-wave reduction potentials, DMF. Price.[30] ^{e} Standard reduction potentials in water.[35,40]

average behavior, are physically significant. It is interesting to note that the largest negative "deviation" occurs for 1,6-di(*tert*-butyl)quinone. There can be little doublt that this effect is due to the steric hindrance introduced by the butyl groups for the approach of solvent molecules to one of the negative charge centers, i.e., one of the oxygens. The quinone with the largest positive "deviation" is the totally unsubstituted quinone (see Figure 5) for which the steric hindrance for specific solvation must be the smallest. The presence of methyl in position 2 reduces $-\Delta\Delta G_{sol}°$ by less than $\sim$0.5 kcal/mol relative to the unsubstituted compound, while phenyl leads to a somewhat larger but still rather small decrease of 1.5 kcal/mol (see Table III).

The decreases of $-\Delta\Delta G_{sol}°$ for the change 1,4-benzoquinone to 1,4-naphthoquinone and to 9,10-anthraquinone are 2 and 2.7 kcal/mol, which are quite small considering the big changes of size. These results are consistent with the rather small change of electron density on the oxygens for the isolated radical anions expected for the ring expansions, as discussed in the preceding

section.

The large decreases of $\Delta\Delta G_{sol}°$ with tetrafluoro and tetrachloro substitution of 7 and 7.8 kcal/mol thus clearly must be largely attributed to charge delocalization from the oxygens, with steric hindrance by the substituents to solvation of the oxygens being only a secondary effect.

Values for $\Delta\Delta G_{sol}°$ in acetonitrile and water are also given in Table III. The acetonitrile data are based on half-wave potentials of Peover[38a] and Chattergee,[38b] while the aqueous results are based on standard reduction potentials quoted by Swallow.[39,40]

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Table IV. Solvation Energies $\Delta G_{sol}°(Qu)$ for Some Quinones

compound	solvent	$p°(298°)$ (atm)	solubility (298°) (mol/L)	$-\Delta G_{sol}°(Qu)^a$ (kcal/mol)
1,4-benzoquinone[b]	H$_2$O	1.9×10^{-4}	6.2×10^{-2}	3.4
1,4-benzoquinone[b]	DMF	1.9×10^{-4}	2.7	5.7
9,10-anthraquinone[c]	DMF	4.3×10^{-9}	5.1×10^{-3}	8.3

[a] Evaluated from ref 41. $\Delta G_{sol}°(Qu) = RT \ln (p°/C_s)$, where $p°$ is saturation vapor pressure in atm and C_s in solubility in mol/L. both at 298 K. [b] $p°$ from: Kruif. C. g.; Smit. E. J.; Gorens, A. J. *J. Chem. Phys.* **1981**, *74*, 5838; solubility, approximate value, this laboratory. [c] $p°$ from: Stull, D. R. *Ind. Eng. Chem.* **1947**, *34*, 517; solubility. this laboratory.

The $-\Delta\Delta G_{sol}° = 63$ kcal/mol in aqueous solution for 1,4-benzoquinone (see Table III) can be compared with the solvation free energies of other ions in water. The solvation energy of the neutral quinone, $\Delta G_{sol}°(Qu)$, is -3.4 kcal/mol[41] (see Table IV), so that $\Delta G_{sol}°(Qu^{·-}) \approx -66.4$ kcal/mol in aqueous solution. Solvation free energies for the halide ions, $\Delta G_{sol}°(X^-)$, on the Randles scale are: (F$^-$) = -103.8, (Cl$^-$) = -75.8, (I$^-$) = -61.4 kcal/mol.[33b] Thus, the exothermicity of the hydration of benzoquinone is somewhat larger than that for I$^-$. Thus result may appear surprising since the quinone radical anion is a much larger species than I$^-$. However, as pointed out in the preceding discussion, most of the negative charge is on the much smaller oxygens, and there is evidence for strong, hydrogen-bonding, solvation of the oxygens (see ethanol results in Figure 4). When this is taken into account, the quinones' radical ion hydration energy appears to be in the right range.

The decrease of hydration energy on methyl substitution is small (~ 1 kcal/mol) but still a bit larger than the ~ 0.3-kcal/mol change in DMF. Similarly, ring expansion in the change from benzo- to naphtoquinone leads to a hydration energy decrease of 2.1 kcal/mol, while for DMF the change is only ~ 1.6 kcal/mol (see Me-substituted compounds, Table III).

The changes of $\Delta\Delta G_{sol}°$ in acetonitrile (AN) are very similar but slightly smaller than those in DMF. The decreasing changes which occur in the order H$_2$O > DMF > AN are typical for these solvents. Changes in solvation energies for the halide ions from Cl$^-$ to I$^-$ decrease in the same order for the above solvents.[42]

While the *absolute* values of $\Delta\Delta G_{sol}°$ given in Table III for water are quantitatively meaningful, the data for DMF and AN are not. This is due to the neglect of the junction potentials between the nonaqueous electrolyte solution and the aqueous

calomel electrode. When the two electrodes utilize the same solvent, the junction potential can be minimized by proper choice of the electrolyte in the bridge. However, use of different solvents leads to junction potential terms involving the solvation energy differences of the bridge electrolyte anion and cation. For systems like the quinone radical anions, whose solvation energies are relatively small, neglect of the solvation transfer energy differences may lead to significant error.

Case and Parsons[42] have provided solvation free energies for a number of ions and solvents including water and acetonitrile. The transfer free energies, i.e., $\Delta G_{sol}°(X^-)_{AN} - \Delta G°(X^-)_{H_2O}$, for Cl$^-$, Br$^-$, and I$^-$ are 20.0, 10.7, and 7.7 kcal/mol. The endothermicity of transfer to the aprotic solvent is seen to decrease rapidly with increasing radius of the anion, a typical feature of dipolar aprotic solvents in which the solvation is much less sensitive to the increase of the radius of the ion.[21,37,43] Comparing the above transfer energies with the corresponding difference for 1,4-benzoquinone from Table III, $(\Delta\Delta G°_{sol,AN} - \Delta\Delta G°_{sol,H_2O}) = 6$ kcal/mol, one finds that the sign is the same and the value is of the expected order of magnitude. This suggests that while the absolute $\Delta\Delta G_{sol}°$ values for AN and DMF are not correct, they predict the right trend and are probably within 4 to 5 kcal/mol of the true values.

The $-\Delta G_{sol}°$ in DMF of 1,4-benzoquinone and 9,10-anthraquinone are 5.7 and 8.3 kcal/mol (see Table IV). The small increase of solvation exothermicity should be due to increasing London-type forces between the quinones and the solvent molecules. Similar values may be expected also for DMF. The data in Tables III and IV illustrate the relative magnitudes of $\Delta G_{sol}°(B^-)$ and $\Delta G_{sol}°(B)$ for the three solvents DMF, AN, and water.

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(41) The free energies of solvation $\Delta G_{sol}°(B)$ for the quinones do not seem to be available in the literature. Rough estimates can be obtained from the relationship: $\Delta G°(B) \approx RT \ln (P_B/C_B)$. where P_B is the saturation pressure over the pure solid or liquid and C_B is the solubility of B in the particular solvent. The relationship is obtained from a consideration of the equilibrium between the pure solid (liquid) B with its vapor and with B in solution.

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