Hydrogen-Bonding and Protonation Effects in Electrochemistry of Quinones in Aprotic Solvents

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Abstract: Hydrogen-bonding and protonation are fundamental factors controlling potentials and mechanisms in the reduction of quinones. These are studied systematically in benzonitrile, acetonitrile, and dimethylsulfoxide solutions by cyclic voltammetry of a series of quinones of increasing basicity (chloranil to duroquinone), in the presence of hydroxylic additives of increasing hydrogen-bonding power (*tert*-butyl alcohol to hexafluoro-2-propanol) or acidity (trifluoroacetic acid). Electrochemical effects are demonstrated over the complete interaction range, from hydrogen bonding of reduced dianions to protonation of unreduced quinones. With increasing concentrations of additives, three clearly different types of electrochemical behavior are observed for weakly (I), moderately (II), and strongly (III) interacting quinone-additive pairs, as follows: (I) Two well-separated reduction waves, corresponding to formation of quinone mono- and dianions, shift positively, with no loss of reversibility. The second wave is smaller, shifts more strongly, and finally merges with the first. The relative heights of the waves remain constant. (II) The positive shift is accompanied by increasing height of the first peak and broadening and irreversibility of the second wave. (III) One or even two, more positively shifted, new prior waves appear, together with a new anodic wave. In interpreting these phenomena, the role of hydrogen-bonding is clearly distinguished from protonation on the basis of pK_a values of relevant species, effects of solvent variation, magnitude of potential shifts, and the onset of irreversibility. Type I behavior is attributed to stabilization by hydrogen-bonding of mono- and dianion reduction products; the number of bonds per quinone ion and bonding equilibrium constants are estimated from the shifts in peak potentials with additive concentration. These results are supported by simulating the experimental cyclic voltammograms using these parameters. Type III behavior is assigned to initial hydrogen-bonding or protonation of the quinones. Type II is attributed to a reduction mechanism involving disproportionation of primary radicals, assisted by hydrogen-bonding or protonation of the dianion.

Introduction

Quinone−hydroquinone couples have been studied over many decades as the prototypical examples of organic redox systems.[1−3] In this regard, their electrochemical behavior, involving the kinetics and equilibria of coupled electron and proton transfer reactions, has given much information concerning the effect of molecular structure[1,2,4] and environment[5−8] on these basic processes. In addition to their intrinsic chemical interest, these studies are particularly important in view of the key biological functions of quinone-based couples as electron−proton transfer agents in oxidative phosphorylation or photosynthesis.[9−13] Thus, it is necessary to understand, as far as possible, the environmental factors which regulate the potentials and reaction pathways of the various species which appear in these quinone−hydroquinone systems, both *in vitro* and in mitochondrial or photosynthetic membranes. Among these factors, we are particularly concerned in this paper with hydrogen-bonding, which has been implicated in the biological function of the quinone systems[11] and on which surprisingly little systematic research has been done.[1,2]

In well-buffered aqueous media (including mixtures with ethanol, dioxane, etc.), quinone−hydroquinone couples provide familiar, reversible two-electron redox systems in which potentiometric or polarographic potentials vary with pH in a straightforward Nernstian manner.[3] This behavior is conveniently summarized in E−pH (Pourbaix) diagrams, showing regions of existence of various redox and protonated species and their respective pK_a values.[1,14] In the strongly basic region (pH > pK_a of QH^-) only the unprotonated forms, Q, $Q^{-\bullet}$, and Q^{2-} appear.[1,14]

Similarly, in dry, neutral, aprotic media, quinones show typically two cathodic polarographic waves, E_1 and E_2, separated by about 0.7 V, which correspond to the formation of $Q^{-\bullet}$ and Q^{2-}, respectively.[1] In these reductions, the first step is generally reversible and the second is at least quasi-reversible at customary scan speeds. The potentials of these reductions depend on the polarity of the solvent,[2,7,8] the nature of the supporting

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electrolyte[1,5,15−17] and the presence of acidic additives, reflecting respectively nonspecific solvation energies, ion-pairing, and protonation equilibria. With regard to the last factor, numerous studies of the effect of acid strength (extending into very strongly acidic media), concentration, and quinone basicity[1,2,6,18−23] have been interpreted on the basis of the full 3 × 3 array[6,24] of redox and protonated species and reaction pathways in the $Q-QH_2$ systems. For our purpose, we are concerned now mainly with the effects of *weak* proton donors on the above two simple reduction waves, E_1 and E_2. Two situations can be clearly distinguished, depending on whether the donor can protonate $Q^{-\bullet}$ or only Q^{2-}. As typified, for example, by reduction of anthraquinone (AQ) in dimethylformamide (DMF),[2,25,26] addition of increasing concentrations of a weak acid (phenol), reacting only with Q^{2-}, leads to a progressive positive displacement of E_2, due to protonation of the dianion,[25] until this wave merges with E_1. A stronger donor (benzoic acid) causes the first wave, E_1, to increase at the expense of E_2. This is generally attributed to the well-known sequence, fast protonation of $Q^{-\bullet}$, and reduction of the more easily reduced $QH^{\bullet}$ radical at the same potential.[25,27] The polarographic effect of adding increasing concentrations of water or acid to DMF or dimethylsulfoxide (DMSO) quinone solutions has been interpreted in the same way.[25,28,29]

However, quite similar polarograms are obtained in quinone systems containing hydroxylic additives in which proton-coupled reductions do *not* occur. For example, reversible waves of AQ in DMF shift smoothly toward less-negative values upon addition of ethanol (but not acetone).[29a] Nevertheless, at the same time, the presence of unprotonated mono- and dianion reduction products is directly demonstrated by their optical spectra which also exhibit characteristic hydrogen-bonding effects.[29b] Moreover, addition of water to DMF doubles the height of the reversible E_1 wave of AQ, at the expense of E_2, but ESR measurements establish the stability of the unprotonated anion radical in the mixtures.[30] The increase in wave height in this case is explained by dismutation of $AQ^{-\bullet}$ regenerating AQ, which is favored by hydrogen-bonding of the AQ^{2-} dianion. Smooth shifts in quasi-reversible waves of *p*-benzoquinone, caused by small increments of water in aprotic solvents, are also found by Wilford and Archer, who state that these effects "are not consistent simply with protonation of $Q^{-\bullet}$ and Q^{2-}".[7] The role of hydrogen-bonding in modifying the redox behavior of quinones has been particularly emphasized by Peover.[2] He points out that in a series of methyl- and chloro-substituted *p*-benzoquinones, the one-electron reduction potentials in strongly alkaline aqueous ethanol are much more positive than in aprotic solvents and that this discrepancy increases with the basicity of $Q^{-\bullet}$.[2,31] Accordingly, he has attributed this difference to stabilization of anions by hydrogen-bonding in the aqueous medium and has even estimated bonding equilibrium constants as high as 10^{10}, to account for the observed effects.[2a] In indirect support of this is the positive shift in reduction potential of 9,10-anthraquinones associated with α-OH substitution[32,33] and the interpretation of solvent-dependent ESR spectra of semiquinone radical ions in terms of hydrogen-bonding.[34,35]

It is thus clear that neither a positive shift in potential nor a change in wave height necessarily indicates involvement of protonation by hydroxylic agents. Both these effects may result from stabilization by hydrogen-bonding of the anionic products, either of primary reduction or secondary disproportionation. Work on this problem in the quinone system to date has been rather scattered, involving few systems and over limited concentration ranges. Indeed, references to the role of hydrogen-bonding in quinone redox chemistry are remarkably sparse,[36] in view of the enormous literature on the subject. To further clarify the situation, we present here cyclic voltammetric studies of quinone reduction in aprotic solvents, in which we systematically vary the acidity and hydrogen-bonding power of added hydroxylic reagents (increasing from *tert*-butyl alcohol to hexafluoro-2-propanol (HFIP)) as well as the basicity of substituted *p*-benzoquinones (from chloranil to duroquinone). The onset of irreversibility and the effect of solvent and an unambiguous protonating agent (trifluoroacetic acid) are used to help distinguish protonation from hydrogen-bonding. We show that hydrogen-bonding interactions produce large positive shifts in reduction potentials, particularly of the second reduction step. From these shifts, we estimate the number of hydrogen bonds per quinone anion and dianion in these various pairs and their respective equilibrium constants.

Experimental Section

Materials. 1,4-Benzoquinones (BQs) were of the best available grade (>97%) from Sigma, Aldrich, or Eastman and substituted as follows: tetrachloro (TCBQ, chloranil); 2,5-dichloro (DCBQ); 2,5-diphenyl (DPBQ); 2,5-dimethoxy (DMOBQ); 2,5-dimethyl (DMBQ); tetramethyl (TMBQ, duroquinone). Benzonitrile (PhCN) (99.9%, Sigma−Aldrich), acetonitrile (CH_3CN) (HPLC reagent, J. T. Baker, Inc.), and DMSO (99.9%, Sigma−Aldrich) were stored over molecular sieves (4A, 8−12 mesh, Aldrich) preheated to 400 °C for 12 h, prior to use. 1,1,1,3,3,3-Hexafluoro-2-propanol (99+%) (HFIP), 2,2,2-trifluoroethanol (99.5+%) (TFE), trifluoroacetic acid (99+%) (TFA), 2-methyl-2-propanol (*tert*-butyl alcohol), and tetrabutylammonium hexafluorophosphate (98%) ($TBAPF_6$) were from Aldrich. Pure ferrocene was kindly provided by Prof. M. Rosenblum. All chemicals were used as received without further purification unless specified.

Procedure. Cyclic voltammetry experiments were done using a conventional three-electrode cell, with glassy carbon working electrode, platinum wire counter electrode, and Ag/AgCl (containing aqueous solution of 3 M NaCl and saturated with AgCl; EG&G) reference electrode, separated from the solution by a Vycor plug. The supporting electrolyte was 0.1 M $TBAPF_6$ in all experiments. All potentials were measured using ferrocene as internal reference and converted to aqueous SCE taking $E_{1/2}^{(Fc^+/Fc)}$ to be 0.56 V vs SCE. This value of $E_{1/2}^{(Fc^+/Fc)}$ was determined with respect to known C_{60} ($E_{1/2}^{(C_{60}/C_{60}^{-\bullet})} = -0.45$ V vs

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Table 1. pK_a Values and Hydrogen-Bonding Equilibrium Constants of Alcohols and Acids

alcohols/acids	pK_a (H_2O)[a]	pK_a (DMSO)[b]	log K[c]
tert-butyl alcohol	19.0	32.2	0.78
2-propanol	17.1	30.3	0.91
ethanol	15.9	29.8[d]	1.21
water	15.7[b]	32[e]	
TFE	12.4	23.6	2.0
HFIP	9.3	17.85[f]	2.83
TFA	0.52	3.45	3.55

[a] Reference 39. [b] Reference 58. [c] Hydrogen-bonding equilibrium constant toward the common acceptor *N*-methylpyrrolidinone in 1,1,1-trichloroethane.[39] [d] Reference 59 [e] The high pK_a of water in basic polar solvents should be kept in mind in interpreting the role of traces of moisture in these systems. [f] Bordwell, F. G., private communication.

SCE)[37] in the same solvent-supporting electrolyte system, since the $E_{1/2}^{(Fc^+/Fc)}$ in this system is not available in the literature. Voltammograms were run using an EG&G-PAR Versastat potentiostat, coupled to a PC and EG&G M270 electrochemical software to record and analyze the data. Solutions were purged with argon to remove oxygen, and argon was passed over the solution during the measurement. Quinone concentrations were in the range of 2−3 mM, and hydroxylic reagents were added incrementally to the solution using a microsyringe. To improve precision, shifts in potentials (ΔE) following each addition were read from a large-scale screen projection of the voltammogram. Values of $E_{1/2}$ were taken at 0.029 V, positive with respect to the peak potential. (The calculations of hydrogen-bonding constants (Table 2, below) involve only ΔE values.) Sweeps were initiated in the cathodic direction. All experiments were done at room temperature (25 °C). Simulation of the cyclic voltammograms was done using the Bioanalytical System's *Digisim, version 2.1* electrochemical simulation program.[38]

For later reference, Table 1 gives pK_a values in water and DMSO for the six hydroxylic reagents used in this study, as well as equilibrium constants for hydrogen-bond formation, referred to a common acceptor, *N*-methylpyrrolidinone in 1,1,1-trichloroethane.[39] In this series, hydrogen-bonding power parallels acidity, although over a much smaller range of variation.

Results and Discussion

(I) Behavior in Pure Media. All quinones studied show two reduction peaks in nonaqueous aprotic media, corresponding to two single-electron reductions to give mono- and dianions (Figure 1, "a" curves). The values of $E_{1/2}$ vs SCE, for the first and second reduction steps for all of the quinones, are given in Table 2 and are in good agreement with the literature.[2b,40] The ratio of the cathodic peak current to the anodic peak current for the first redox process is close to unity for all of the quinones, throughout the sweep rate range from 20 to 500 mV/s. However, at slower sweep rates (20 mV/s), the ratio of peak currents for the second redox process was found to be 0.8−0.9, indicating slight irreversibility. Cathodic to anodic peak separations were typically 70−80 mV for the first reduction wave and about 100 mV for the second wave.

It is interesting that the height of the second peak is less than that of the first in the voltammograms of all of the observed quinones. The effect becomes more marked in passing from TCBQ to TMBQ (Figure 1). Among several mechanisms considered in attempted simulations, the assumption of a complexation reaction between a quinone and its dianion (reaction I) gave excellent agreement with this feature of the

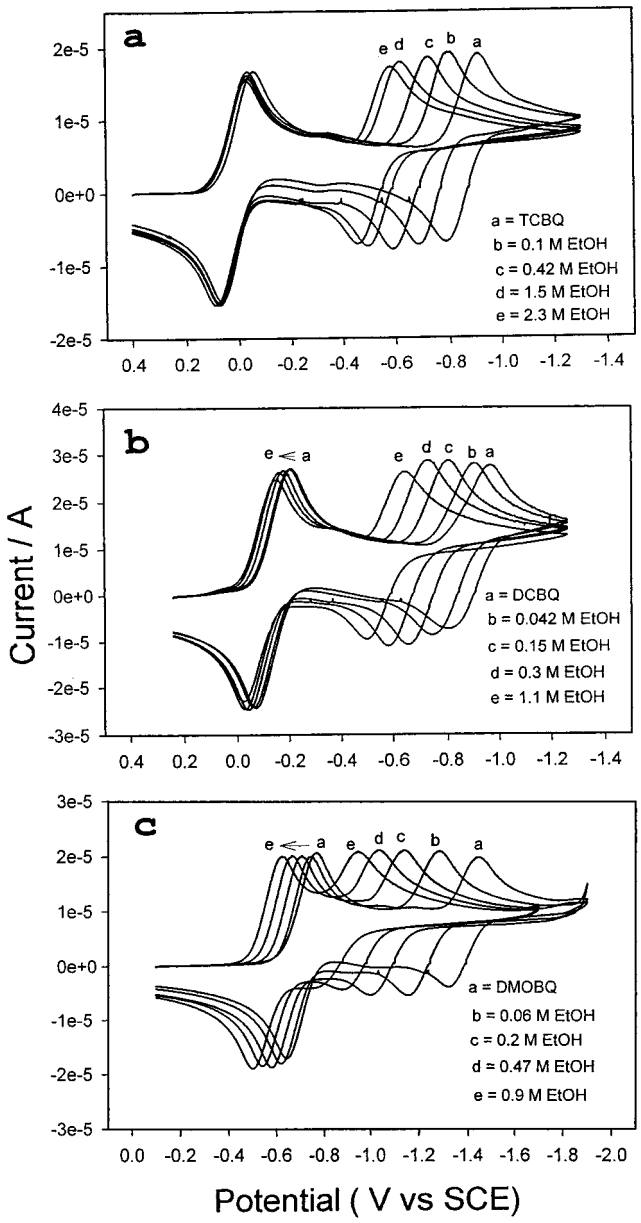

Figure 1. Cyclic voltammograms of (a) TCBQ, (b) DCBQ, and (c) DMOBQ at different concentrations of ethanol in PhCN. Sweep rate = 100 mV/s.

experimental curves.[41,42]

$$Q + Q^{2-} \rightleftharpoons [QQ]^{2-} \qquad (I)$$

It is important to note that while this suggested complexation reaction accounts very well for the difference in peak heights, it turns out to have no effect on the reduction potentials of the

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(42) Cyclic voltammograms of quinones in which the second wave is lower than the first have been observed by others, but this behavior seems to have excited little comment.[17,21] In one case, Marcus and Hawley[21] show explicitly that the first wave corresponds to one-electron reduction, so that neither the disproportionation[55] nor protonation followed by reduction (ECE)[27] of semiquinone can explain the decrease in the second wave. We are of course aware that the assumption of reaction I poses various difficulties, such as the apparent stability of the complex toward thermodynamically favored dissociation to $2Q^{-\bullet}$, etc. Nevertheless, as long as this, or any other, mechanism does not modify the shifts in peak potentials, the conclusions drawn here regarding hydrogen-bonding effects are still valid. Further studies of this interesting problem are now in progress; results will be published elsewhere.

Table 2. Electrochemical Parameters: Reduction of Quinones in Presence of Hydrogen-Bonding Agents

quinones	solvent	$-E_{1/2}^{(1)}$ [a]	$-E_{1/2}^{(2)}$ [a]	reagent	n	$K_{eq}^{(1)}$ [b]	$m-n$	m	$K_{eq}^{(2)}$ [b]
TCBQ	PhCN	0.05	0.83	-	-	-	-	-	-
	PhCN			EtOH	*c*	*c*	2.9	2.9	2.6×10^4
	PhCN			TFE	*c*	*c*	3.5	3.5	3×10^{10}
	CH_3CN	0.04	0.81	-	-	-	-	-	-
	CH_3CN			EtOH	*c*	*c*	3.1	3.1	6.3×10^3
	CH_3CN			TFE	*c*	*c*	3.4	3.4	5×10^7
DCBQ	PhCN	0.20	0.95	-	-	-	-	-	-
	PhCN			EtOH	0.75	15	3.0	3.75	2.5×10^6
	PhCN			TFE	1.0	30	4.6	5.6	1.8×10^{14}
	CH_3CN	0.20	0.93	-	-	-	-	-	-
	CH_3CN			EtOH	*c*	*c*	3.0	3.0	1.2×10^4
	CH_3CN			TFE	~0.5	*c*	3.7	~4.2	2×10^{11}
	DMSO	0.18	0.98	-	-	-	-	-	-
	DMSO			EtOH	*c*	*c*	3.1	3.1	1.9×10^3
	DMSO			TFE	*c*	*c*	3.0	3.0	8×10^6
BQ	PhCN	0.53	1.21	-	-	-	-	-	-
	PhCN			EtOH	1.2	50	3.9	5.2	1.0×10^9
DMBQ	PhCN	0.7	1.38	-	-	-	-	-	-
	PhCN			EtOH	1.4	30	3.3	4.7	$\sim 10^8$
DPBQ	PhCN	0.52	1.23	-	-	-	-	-	-
	PhCN			EtOH	1.1	50	3.7	4.8	2.0×10^8
DMOBQ	PhCN	0.74	1.42	-	-	-	-	-	-
	PhCN			EtOH	2.03	370	4.5	6.5	2.2×10^{11}
	PhCN			2-PrOH	0.87	10	2.6	3.5	2.0×10^6
	PhCN			*t*-BuOH	0.76	10	1.8	2.6	3.0×10^4
TMBQ	PhCN	0.9	1.56	-	-	-	-	-	-
	PhCN			EtOH	1.3	85	4.2	5.5	8.5×10^9

[a] Potentials vs aqueous SCE [b] Values of equilibrium constants are estimated by taking n and $m-n$ values ± 0.5 to obtain best fit to data. Units of $K_{eq}^{(1)} = M^{-n}$ and $K_{eq}^{(2)} = M^{-m}$. Accuracy $\pm 30\%$.[60] [c] Potential shifts are very small. We take n and $K_{eq}^{(1)}$ to be negligible in these cases.

two waves and therefore does not modify the hydrogen-bonding equilibrium constants derived therefrom (see below). Thus, in simulations, a plot of $E_{1/2}^{(2)}$ calculated without reaction I vs $E'_{1/2}{}^{(2)}$ with reaction I was linear with slope 1.0 for all values of $E_{1/2}^{(2)}$.[42] A small reduction peak was observed between the two main reductions for many quinones (DMBQ, BQ, and DMOBQ) and has been seen also in reduction of analogs of ubiquinone.[22] This small peak disappeared at high sweep rate and may be attributed to the reduction of a dimer formed by the reaction between two semiquinone molecules.[25,43,44]

(II) Effect of Weak Hydrogen-Bonding Agents: Ethanol, 2-Propanol, and *tert*-Butyl Alcohol. Addition of ethanol to benzonitrile solutions of all quinones studied results in positive shifts of both reduction steps, which increase smoothly with ethanol concentration and with no further loss of reversibility (up to 2.5 M ethanol).[45] Representative cyclic voltammograms are shown in Figure 1. For given ethanol concentration, the shift is much larger for the second wave and, for both waves, increases with quinone basicity, as in passing from TCBQ to DMOBQ or TMBQ (Figure 1). These marked effects are apparent even at ethanol concentrations less than 0.05 M, in an already somewhat polar medium (benzonitrile $\epsilon = 25.2$). Thus, they cannot be due to changes in bulk polarity, but must evidently be ascribed to quite specific ethanol−quinone interactions (i.e., hydrogen-bonding) which increase with both the degree of reduction (i.e., anionic charge) and the basicity of the quinone. Earlier observations of similar shifts in the potential of different quinones caused by the addition of water to aprotic solvents have been ascribed to fast protonation of the dianion.[28,29] We may rule out the possibility of protonation of quinone monoanions simply on the basis of the unfavorable pK_a values of these semiquinones. The pK_a of the semiquinones of BQ and TMBQ are 4.0 and 5.1, respectively, in aqueous medium,[9,46] which are so much lower than the pK_a of ethanol (see Table 1) that we may safely assume a correspondingly large difference in benzonitrile. Water-based pK_a values are used here, since related data in aprotic solvents are not available for the reduced quinones. However, we note that the charge on unprotonated quinone reduction products is more delocalized than that on the alcohol anion. Thus, in passing from water to benzonitrile or DMSO, the alcohols will become even weaker acids (Table 1) relative to the protonated quinone monoanions, since the loss of hydration energy will be greater for alcohol anions.[47] This applies also to the dianions of BQ and the other more basic quinones (Figure 1). Changes in energies of quinones on reduction, caused by dispersion forces, should be small compared with energies of hydrogen-bonding and protonation.[48] No complications due to ion-pairing appear in this work using $TBAPF_6$ as supporting electrolyte.[15]

Similarly, the pK_a of BQ dianion is 11−12[1,14] and, hence, should not favor protonation by ethanol in PhCN. While, pK_a values for the dianions of more basic TMBQ and DMOBQ are not available in the literature, they are presumed to be higher than that for BQ.[49] To check the possibility of protonation of these dianions by ethanol, we compare the effects observed with the weaker acids 2-propanol and *tert*-butyl alcohol for which such protonation is less likely. Qualitatively similar but smaller, continuous positive shifts of the second peak were observed for these alcohols even in reduction of DMOBQ. We thus rule out the possibility of protonation of DMOBQ and TMBQ dianions by these alcohols in PhCN, at the experimental concentrations of Figure 1.[45] Quite different, unambiguous protonation effects, such as much larger potential shifts and irreversible and merging waves, are caused by hydroxylic additives more strongly acidic than ethanol and will be described

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(49) The pK_a of the 2,3-dimethoxy-5-methyl-6-isoprenyl-1,4-benzoquinone dianion in acetonitrile is 11.3.[22]

later. We therefore assign the potential shifts typically illustrated in Figure 1 to changes in fast hydrogen-bonding equilibria which are closely coupled to reduction.

In order to treat the situation more quantitatively, we take the hydrogen-bonding constant of the quinone to be negligible compared to that with mono- and dianion (no change is observed in absorption spectra of duroquinone on addition of ethanol in PhCN). Accordingly, we write the following:

$$Q + e \rightleftharpoons Q^{-\bullet}$$

$$Q^{-\bullet} + n\text{EtOH} \rightleftharpoons Q^{-\bullet}(\text{EtOH})_n$$

$$Q^{-\bullet}(\text{EtOH})_n + e \rightleftharpoons Q^{2-}(\text{EtOH})_n$$

$$Q^{2-}(\text{EtOH})_n + (m-n)\text{EtOH} \rightleftharpoons Q^{2-}(\text{EtOH})_m$$

Peover and Davis[15] have noted the dependence of quinone reduction potentials on the concentration and properties of cations and have interpreted these reactions in terms of cation−anion association equilibria.[50−52] By analogy with their treatment, we write for the first reduction step

$$E_{1/2} = E^\circ_{1/2} + \left(\frac{RT}{F}\right)\ln(1 + K_{eq}^{(1)}[\text{EtOH}]^n) \qquad (1)$$

where $E^\circ_{1/2}$ is the half-wave potential in the absence of ethanol. If $K_{eq}^{(1)}[\text{EtOH}]^n \gg 1$, a plot of $E_{1/2}$ vs log[EtOH] should give a straight line with slope $2.3nRT/F$, from which the value of n can be estimated. This procedure can be reasonably applied only to the more strongly bonded basic quinones where we find larger shifts in $E_{1/2}^{(1)}$. Values of n thus obtained are listed in Table 2 and are less than 1 for quinones of low basicity and close to 2 for the more basic quinones.

The equilibrium constant for the first reduction step can be estimated by rearranging eq 1 to obtain

$$\exp(f\Delta E_{1/2}) = 1 + K_{eq}^{(1)}[\text{EtOH}]^n \qquad (2)$$

where $f = F/RT$ and $\Delta E_{1/2} = E_{1/2} - E^\circ_{1/2}$. Values of $K_{eq}^{(1)}$, estimated for different quinones, are listed in Table 2. For binding of ethanol, $K_{eq}^{(1)}$ is highest for DMOBQ, lowest for DCBQ, and negligible for TCBQ, consistent with their respective basicities.

Using the same analogy between cation association and hydrogen-bonding equilibrium for the second reduction step,[52] we have

$$\exp(f\Delta E_{1/2}) = \frac{1 + K_{eq}^{(2)}[\text{EtOH}]^m}{1 + K_{eq}^{(1)}[\text{EtOH}]^n} \qquad (3)$$

where m and $K_{eq}^{(2)}$ are the number of molecules of ethanol hydrogen-bonded to Q^{2-} and $K_{eq}^{(2)}$ is the corresponding equilibrium constant, respectively. For strong hydrogen-bonding, we may neglect 1 in the denominator and numerator and obtain the value of $m - n$ by plotting $E_{1/2}$ for the second step vs the log[EtOH], as shown in Figure 2. Taking n from the first reduction step, values of m are estimated for all of the quinones and are listed in Table 2. Having established m, n, and $K_{eq}^{(1)}$, eq 3 then permits evaluation of $K_{eq}^{(2)}$ (Table 2). As indicated

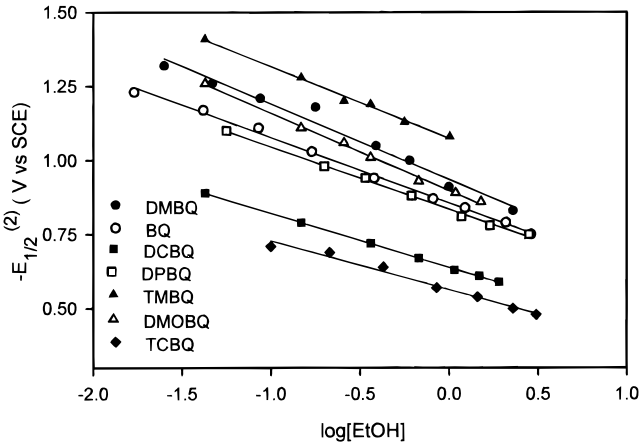

Figure 2. Change in $-E_{1/2}^{(2)}$ for different quinones vs log[EtOH] in PhCN.

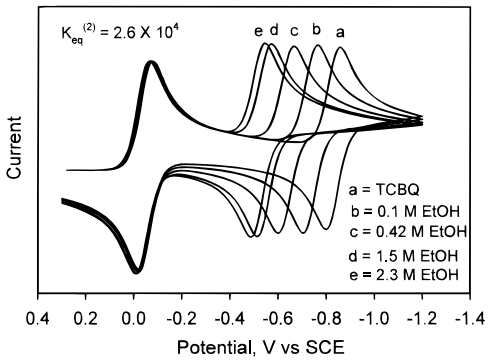

Figure 3. Simulated curves of Figure 1a using the parameters given in Table 2. Other parameters used for simulations are k_e (heterogeneous rate constant) = 1 cm s^{-1} for both redox processes, $K_{[QQ]}$ (equilibrium constant for reaction 1 = 10^5 M^{-1}, and k_f (rate constant for the formation of $[QQ]^{2-}$) = 10^5 s^{-1} M^{-1}. A wide range of values of $K_{[QQ]}$ and k_f produce good fits to the data provided reaction 1 remains to the right and reversible.

for the monoanion, the value of $K_{eq}^{(2)}$ increases from TCBQ to TMBQ in accord with the basicity of these quinones.

Figure 3 shows the results of the simulations performed for TCBQ using the parameters given in Table 2 and assuming a complexation between Q and Q^{2-}.[53] Similar shifts in potential were also obtained when complexation was ignored. As noted earlier, since the complexation reaction affects only the peak height of the second wave and not the peak potential, the values of K_{eq}, n, and m determined on the basis of shifts in potential apply with or without the complexation reaction. The good agreement between the experimental (Figure 1a) and the simulated curves (Figure 3) convincingly supports the hydrogen-bonding model and above treatment of data.

We note however, that n, m, and K_{eq} values for DMOBQ are higher than those for the presumably more basic TMBQ. This could be due to greater steric hindrance toward bonding for TMBQ. This aspect is further examined in Figure 4, which shows the variation of $E_{1/2}$ for the second reduction step of DMOBQ with log[alcohol] in PhCN for the three weakly acidic alcohols. It is apparent from the figure that the slope and therefore the value of m decrease with increasing size of the alcohol molecules, from 6.5 for ethanol to 3.5 and 2.6 for

(50) Galus, G. *Fundamentals of Electrochemical Analysis*; Ellis Harwood: Chichester, 1976; Chapter 14.

(51) Chauhan, B. G.; Fawcett, W. R.; Lasia, A. A. *J. Phys. Chem.* **1977**, *81*, 1476−1481.

(52) Fawcett, W. R.; Opallo, M.; Fedurco, M.; Lee, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 196−200.

(53) Simulations of Figure 3 are based on the *square scheme* of redox and chemical reactions (i.e., $Q + e \rightleftharpoons Q^{-\bullet}$, $Q^{-\bullet} + e \rightleftharpoons Q^{2-}$, $Q^{-\bullet} + nX \rightleftharpoons QX_n^{-\bullet}$, $Q^{2-} + mX \rightleftharpoons QX_m^{2-}$, and $QX_n^{-\bullet} + e + (m-n)X \rightleftharpoons QX_m^{2-}$). For chloranil, only the second reduction need be considered. For more basic quinones, in which both $E_{1/2}^{(1)}$ and $E_{1/2}^{(2)}$ shift, two square schemes are required. The values of $E_{1/2}$ and the equilibrium constants for the homogenous reactions were taken from Table 2.

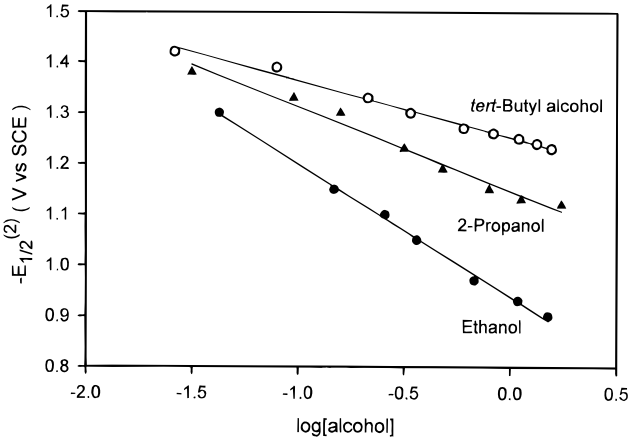

Figure 4. Plot of $-E_{1/2}^{(2)}$ for DMOBQ vs log[alcohol] for different alcohols in PhCN.

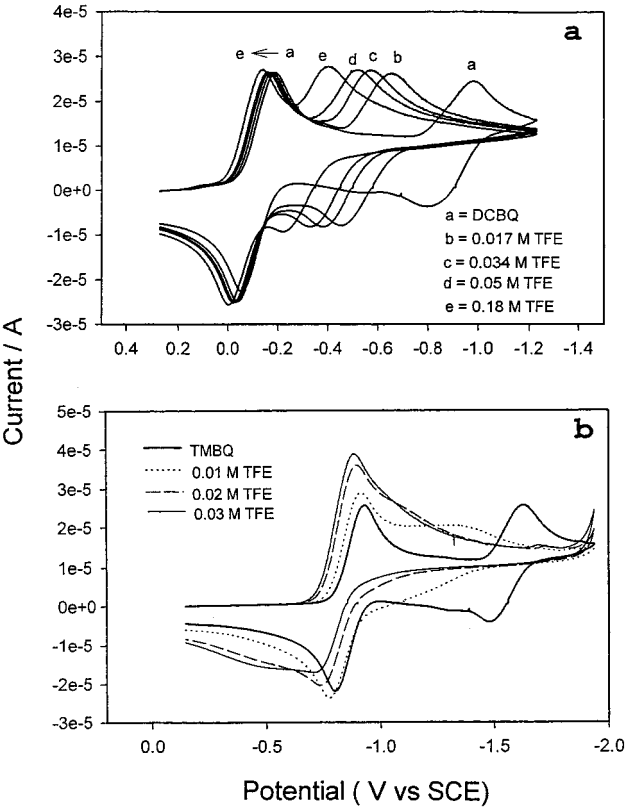

Figure 5. Cyclic voltammograms of (a) DCBQ and (b) TMBQ at different concentrations of TFE in PhCN. Sweep rate = 100 mV/s.

2-propanol and *tert*-butyl alcohol respectively (Table 2). The reduction in m from ~6 for ethanol to about ~3 for the hindered alcohols suggests a steric effect, but also agrees with a possibly sterically related influence on hydrogen-bonding power of these alcohols, as measured with respect to a common acceptor (Table 1). In either case, the assignment of the shift in potential to a hydrogen-bonded interaction is supported.

(III) Effect of Stronger Hydrogen-Bonding Agents. A. Trifluoroethanol. Addition of TFE to quinone solutions in benzonitrile leads to two very different types of redox behavior for different quinones. For quinones with low basicity, TCBQ and DCBQ, the effect as shown in Figure 5a is similar to that of ethanol. We again observe continuous positive shifts for both reduction waves, but this now occurs at much lower concentrations for TFE. Again the pK_a values for TCBQ and DCBQ semiquinones, which should be lower than that of BQ,[9] do not favor protonation of their monoanions by TFE (see Table 1), and judging from the voltammograms of Figure 5a, the same

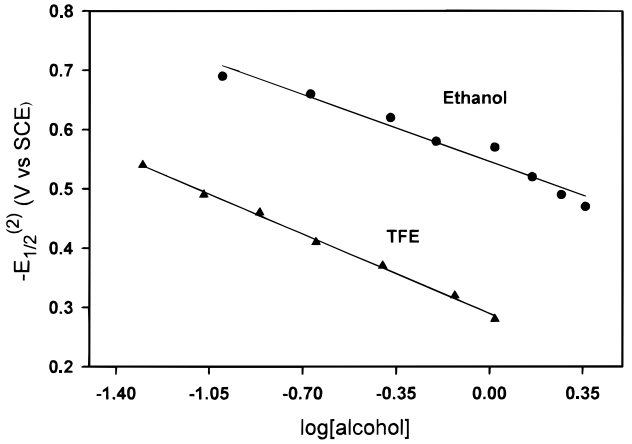

Figure 6. Dependence of $-E_{1/2}^{(2)}$ on log[alcohol] for TCBQ with two alcohols in acetonitrile.

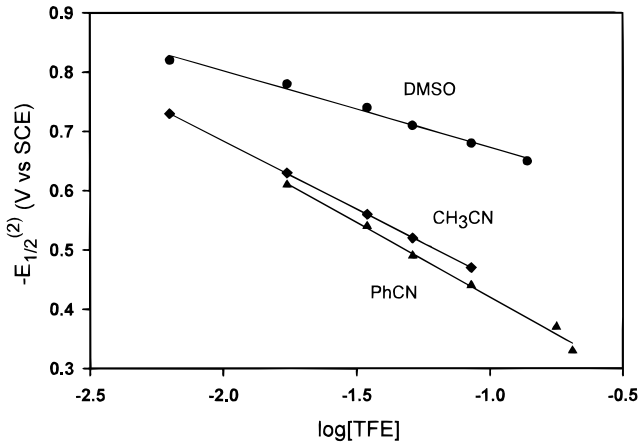

Figure 7. Plot of $-E_{1/2}^{(2)}$ for DCBQ vs log[TFE] in three solvents.

situation probably also applies to the dianions. Thus, the shifts in $E_{1/2}$ for both reduction steps are attributed primarily to hydrogen-bonding. Figure 6 shows the changes in $E_{1/2}$ of the second peak of TCBQ, caused by the addition of TFE and ethanol in acetonitrile. The slopes of the lines for the two reagents are very similar, but the displacement in $E_{1/2}$ at a given additive concentration is much larger for TFE, indicating a large difference in $K_{eq}^{(2)}$ for similar values of $m - n$ (Table 2). Estimated values of m and $K_{eq}^{(2)}$ for all of the quinones, as given in Table 2, show that, in PhCN, 5−6 molecules of TFE hydrogen-bond with DCBQ dianion compared to 4 for ethanol, while the even less basic TCBQ dianion associates with 3 or 4 TFE molecules. In addition to these differences in the number of associated molecules, $K_{eq}^{(2)}$ with TFE is 10^6 to 10^8 times higher than that with ethanol for TCBQ and DCBQ in PhCN.

(i) Solvent Effects. These interpretations are further supported by the effects of solvent variation, which are clearly displayed in the second reduction step of DCBQ. Figure 7 shows that the effect of TFE on $E_{1/2}^{(2)}$ is largest in PhCN, intermediate in CH_3CN, and smallest in DMSO, as indicated by both the slopes of the lines and their relative displacements. The values of m for TFE-binding (Table 2) decrease from 5.6 in PhCN and 4.2 in CH_3CN to 3.0 in DMSO. Correspondingly, $K_{eq}^{(2)}$ (M^{-m}), decreases from 1.8×10^{14} and 2×10^{11} to 8×10^6. This order agrees with the sequence of polarity in moving from PhCN ($\epsilon = 25.2$, $E_T(30) = 41.5$) and CH_3CN ($\epsilon = 35.9$, $E_T(30) = 45.6$) to DMSO ($\epsilon = 46.5$, $E_T(30) = 45.1$).[54a] Increasing solvent polarity favors proton transfer over hydrogen-bonding,[54b] which, in addition, is further suppressed in DMSO

(54) (a) Reichardt, C. *Solvents and Solvent effects in Organic Chemistry*; VCH Publishers: New York, 1988; p 370. (b) *Ibid.*; p 105.

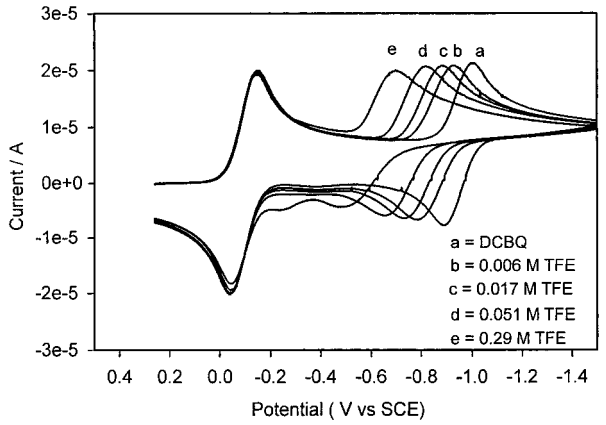

Figure 8. Cyclic voltammograms of DCBQ in DMSO at different concentrations of TFE. Sweep rate = 100 mV/s.

since this basic solvent itself forms competitive hydrogen-bonds. Thus, this sequence of solvent effects provides further compelling evidence that *the positive shift in potential is caused by hydrogen-bonding of the dianion, not protonation*. This applies *a fortiori* to the more weakly basic monoanion as well. In DMSO, addition of TFE, even up to 0.29 M, has no effect at all on the first reduction wave of DCBQ (Figure 8), although a marked positive shift of this wave occurs in benzonitrile (Figure 5a). Moreover, protonation of the dianion in polar DMSO is indicated by the onset of irreversibility at high TFE concentrations and appearance of a new anodic peak at TFE = 0.29 M. Thus, the effect of TFE on DCBQ in DMSO falls between that of ethanol in DMSO (no irreversibility) and that of TFE with basic quinones in benzonitrile, as shown below.

With more basic quinones, the character of the voltammogram changes sharply, as seen by comparing Figures 5a and 5b. Addition of TFE to benzonitrile solutions of DMBQ, DPBQ, DMOBQ, and TMBQ results in complex electrochemical behavior. The second wave shifts positively, becomes very broad and irreversible, and finally disappears at higher [TFE] (Figure 5b), quite unlike the case of DCBQ or TCBQ. At TFE = 0.03 M (Figure 5b), the first reduction peak becomes nearly 1.5 times higher than the original peak, with a decrease in the corresponding anodic peak. A new broad anodic peak at ~ -0.4 V is also seen at this concentration. In view of the pK_a values for TMBQ semiquinone[9] and TFE (Table 1), protonation of the monoanion seems very unlikely. Therefore, the increase in peak current is attributed to disproportionation of the semiquinone, facilitated by the shift in reduction potential of $Q^{-\bullet}$ due to strong hydrogen-bonding of Q^{2-}, to give quinone and the dianion.[55] The hydrogen-bonded dianion, thus formed, has a higher pK_a (compare pK_a (BQ^{2-}) = 11−12) than TFE and is likely to be protonated. The irreversibility of the first peak in Figure 5b in presence of TFE is attributed to slow deprotonation of the dianion. Our attempts to simulate these experimental observations did not give an acceptable fit to the curves because of the complex scheme of possible chemical and redox processes and the large number of unknown parameters, although gross features of the voltammogram could be reproduced.

B. Effect of Hexafluoro-2-propanol. HFIP is a stronger acid and hydrogen-bonding reagent than TFE and ethanol (Table 1). Figure 9 shows the cyclic voltammograms of DCBQ and TMBQ in benzonitrile at different concentrations of HFIP. We note that the electrochemical characteristics of DCBQ in the presence of HFIP are very similar to TMBQ with TFE (compare Figures 5b and 9a). That is, as seen above, the electrochemistry of a less-basic quinone (DCBQ) in the presence of a stronger

(55) Mastragostino, M.; Nadjo, L.; Saveant, J. M. *Electrochim. Acta* **1968**, *13*, 721−749.

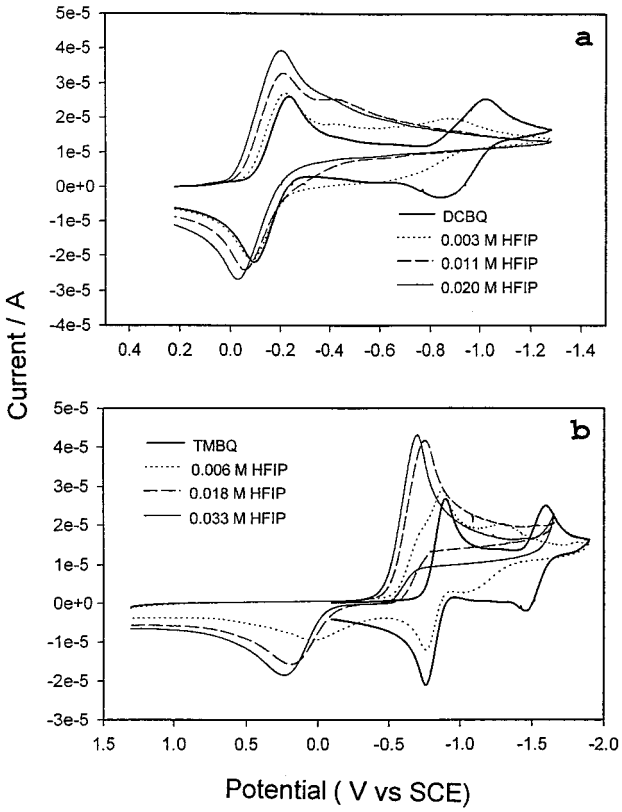

Figure 9. Cyclic voltammograms of (a) DCBQ and (b) TMBQ at different concentrations of HFIP in PhCN. Sweep rate = 100 mV/s.

hydrogen-bonding agent or acid (HFIP) is similar to a relatively more basic quinone (TMBQ) in the presence of a weaker hydrogen-bonding agent or acid (TFE). However, with HFIP, the electrochemistry of TMBQ is sharply different from that of DCBQ, as shown clearly in Figure 9b. An additional reduction peak *prior* to the first reduction of TMBQ now appears, grows in height, and shifts positively with increasing concentration of HFIP. Also, the first peak becomes irreversible and a new anodic peak at 0.27 V increases at higher concentrations of HFIP. Similar behavior is also shown by other basic quinones such as DMOBQ and DMBQ (figure not shown).

This new reduction peak prior to the original first reduction observed for TMBQ (Figure 9b) suggests the formation of another easily reducible species in the medium before the first reduction step. This species can either be protonated or hydrogen-bonded quinone. Since TMBQ is a very weak base as indicated by its pK_a ($=-1$[1]) in aqueous medium, its protonation by HFIP is ruled out. However, the UV−vis spectrum of TMBQ in PhCN shifts slightly to the red upon addition of HFIP. This effect is further enhanced in nonpolar methylene chloride and is ascribed to hydrogen-bonding between TMBQ and HFIP. (The hydrogen-bonding equilibrium constant for this system in CH_2Cl_2 is estimated from the shift in spectrum to be $\sim 2-3$ M^{-1}.) Therefore, the prior peak in Figure 9b, which increases in height with addition of HFIP, is attributed to the reduction of hydrogen-bonded TMBQ.

Since protonation of TMBQ monoanion (pK_a = 5.1) by HFIP (pK_a = 9.3) is thermodynamically unfavorable, the increase in peak current of the first wave (Figure 9b) is again assigned to the fast disproportionation mechanism. However, on the basis of the pK_a of the BQ dianion, HFIP is sufficiently acidic to protonate the more basic dianions of TMBQ and DMOBQ. Slow deprotonation of these dianions would explain the irreversibility of the first peak and the appearance of the new anodic peak at 0.27 V, which is assigned to the oxidation of hydrogen-bonded $TMBQH^-$.[23]

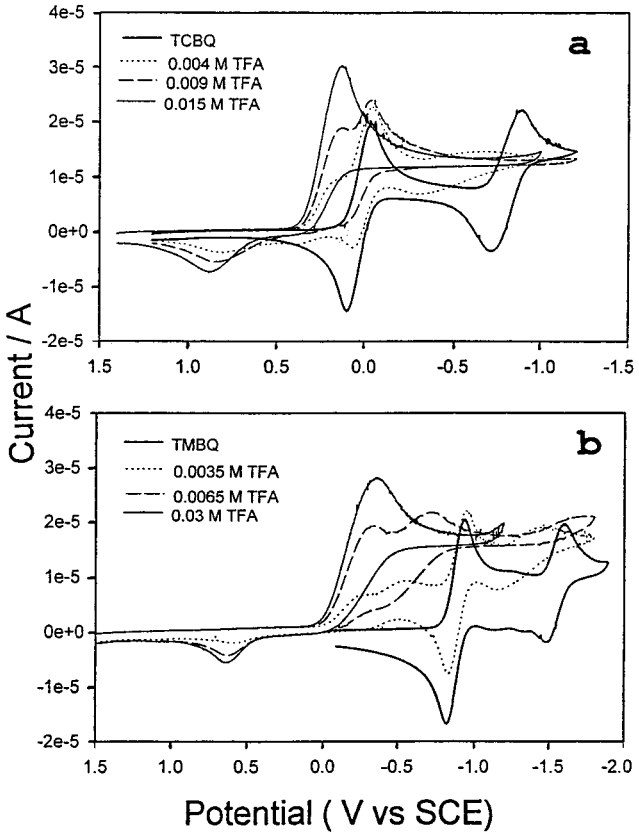

Figure 10. Cyclic voltammograms of (a) TCBQ and (b) TMBQ at different concentrations of TFA in PhCN. Sweep rate = 100 mV/s.

(IV) Effect of Strong Acid. Trifluoroacetic Acid. Figures 10a and 10b show the effect of the strong acid TFA on the electrochemistry of the representative weakly and strongly basic quinones TCBQ and TMBQ in PhCN. The sequence of voltammograms of TCBQ with added TFA is generally similar to that observed for TMBQ in presence of HFIP (compare Figures 9b and 10a). A cathodic peak prior to the first original reduction peak grows in height at the expense of the original peak, suggesting the presence of two reducible species in equilibrium. At higher TFA concentrations (0.015 M), the prior peak increases to 1.6 times the height of the original peak and become fully irreversible, while an anodic peak develops around 0.7 V shifting slightly positive with increasing TFA. The relative pK_a values of BQ (−7)[1,56] and TFA (0.52) show that protonation of TCBQ by TFA is highly unfavorable. This is supported by the lack of significant change in absorption of chloranil in benzonitrile upon addition of TFA, up to 0.5 M. Moreover, the positive shift of the first peak from −0.06 to 0.2 V is too small to be caused by protonation.[1,2a] Furthermore, in polar DMSO no prior peak and only a small (smaller than observed for PhCN) continuous positive shift in potential of the first reduction step is observed on addition of TFA to chloranil, unlike the result in PhCN. We therefore attribute the prior peak, as for the TMBQ−HFIP system, to the reduction of hydrogen-bonded chloranil. This is consistent with the strong hydrogen-bonding power of TFA. Since TFA is significantly more acidic than the semiquinone of TCBQ,[57] the increase in peak current at 0.2 V is now assigned to immediate reduction of the protonated semiquinone (ECE process)[27] rather than to disproportionation. The anodic peak at 0.75 V is attributed to the oxidation of $TCBQH_2$ formed by the two-electron reduction and protonation of chloranil at 0.2 V.[23]

Addition of TFA to the more basic TMBQ brings out yet another process in that the voltammogram now shows *two* new prior reduction peaks at −0.24 and −0.62 V, shifted positively by 0.66 and 0.28 V from the original peak (Figure 10b). At 0.0065 M TFA, these two peaks grow in height and the original quinone peaks disappear. At TFA = 0.03 M, the peak at −0.62 V also disappears and only one peak is finally observed. These two peaks are attributed respectively to the reduction of hydrogen-bonded (−0.62 V peak) and protonated (−0.24 V peak) TMBQ, which are consistent with both the pK_a of TMBQ and the size of their respective positive displacements.[1,2a] At a higher concentration of acid, most of the quinone is finally protonated, and hence, only the peak at −0.24 V is observed. This is supported by the change in UV−vis spectrum of TMBQ caused by addition of TFA (up to 0.3 M). Similar spectral changes were obtained with methylsulfonic acid (pK_a = −0.6)[58] and are attributed to the protonation of TMBQ. The anodic peak at 0.62 V (Figure 10b) shifts to more positive potential with an increase in acid concentration, stabilizes at 0.72 V at 0.1 M TFA, and is assigned to the oxidation of $TMBQH_2$.[23]

Conclusions

1. In the electrochemistry of quinones in neutral aprotic solvents, hydroxylic additives cause such large effects at such low concentrations that specific interactions between additives and quinone species must occur.

2. The effect of these agents depends essentially on the degree of hydrogen-bonding interactions. Weakly basic quinones paired with strongly bonding additives behave similarly to strongly basic quinones with weakly bonding agents.

3. The effect of hydrogen-bonding can be clearly distinguished from that of protonation by consideration of appropriate pK_a values and the characteristics of the cyclic voltammogram itself. Continuous shifts in potential with no change in wave height, reversibility, or appearance of new waves indicate hydrogen-bonding of reduction products. Even if the first wave increases in height at the expense of the second, hydrogen-bonding is not excluded, since a disproportionation mechanism assisted by hydrogen-bonding may be responsible.

4. Analysis of shifts in potential as a function of additive concentration gives trends in the values of the hydrogen-bonding parameters n, m, and K_{eq} in agreement with the expected strength of hydrogen-bonding interaction in a given quinone-additive pair.

5. Simulation studies of the relative heights of the first and second reduction waves suggest the formation of a quinone−quinone dianion complex.

Acknowledgment. It is a pleasure to thank Dr. Stephen W. Feldberg for helpful discussions regarding digital simulations. Work done at Brookhaven National Laboratory was supported under U.S. Department of Energy contract no. DE-AC02-76CH00016. We much appreciate support of this work by the Division of Chemical Sciences, Office of Basic Sciences, U.S. Department of Energy (grant no. FG02-89EB 14072 to Brandeis University).

JA970028J

(56) Laviron, E. *J. Electroanal. Chem.* **1984**, *164*, 213−224.

(57) The change in pK_a of the BQ semiquinone on addition of methyl groups is only 0.25 units per group;[9] thus, the change from $BQH^•$ (pK_a = 4.0) to $TCBQH^•$ should certainly not reduce the latter pK_a to that of TFA (pK_a = 0.52).

(58) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463.

(59) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295−3298.

(60) Errors in measurement of the small changes in $E_{1/2}$ of the first peak lead to large uncertainties in the values of $K_{eq}^{(1)}$ and contribute thereby to errors also in $K_{eq}^{(2)}$.