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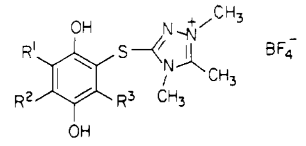
Kinetics of Oxidation of Triazoliothiohydroquinones by 1,4-Benzoquinones: Evidence for a Hydride-Transfer Pathway

Michael P. Youngblood

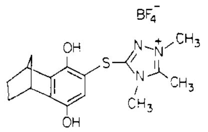
Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. *Received May 6, 1985*

Abstract: Redox potentials of eight triazoliothiohydroquinones (TT-hydroquinones) were measured by using cyclic voltammetry. The redox potentials of the TT-hydroquinones and of benzoquinone oxidants can be varied significantly by varying substituents on the hydroquinone or benzoquinone ring. The equilibrium constants (K_{eq}) for two-electron oxidation of TT-hydroquinones by benzoquinones can thus be varied by 6 orders of magnitude. The redox kinetics are first-order in reductant and in oxidant and inverse first-order in hydrogen ion under all conditions examined, showing that only the singly deprotonated hydroquinones are kinetically important from pH 2.9 to 7.0. Rate constants for quinone oxidations of the singly deprotonated TT-hydroquinones (k_2) range from 6.8×10^5 to 2.1×10^8 M^{-1} s^{-1}, depending on the free energy of reaction. The correlation between log k_2 and log K_{eq} is in reasonable agreement with the Marcus formalism. The absence of general acid–base catalysis together with significant deuterium kinetic isotope effects (ca. 3–6) is consistent with a hydride-transfer mechanism.

The reversible two-electron oxidation of *p*-hydroquinones to their *p*-benzoquinone forms is of considerable importance in biological systems[1] as well as in photographic science.[2] Thermodynamic properties of hydroquinone/quinone redox systems have been thoroughly studied, primarily by electrochemical techniques.[3-8] Although these thermodynamic studies date back many years, only relatively recently have many reports appeared that deal with the kinetics of hydroquinone redox reactions.[9-26] This paper reports the electrochemical characterization of hydroquinones containing a 3-thio-1,4,5-trimethyl-1,2,4-triazolium substituent (**1–8**) and the kinetics of oxidation of these hydroquinones by various benzoquinones.



1 $R^1 = R^2 = R^3 = H$
5 $R^1 = H$, $R^2 = R^3 = CH_3$
6 $R^1 = R^3 = CH_3$, $R^2 = H$
7 $R^1 = R^2 = CH_3$, $R^3 = H$
8 $R^1 = R^2 = R^3 = CH_3$



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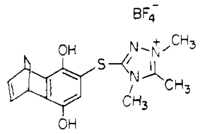

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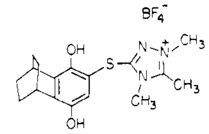

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Numerous kinetic studies have been reported of the oxidation of hydroquinones by a variety of oxidants including Fe(III),[9-12] Cu(II),[13,14] Ir(IV),[15,16] Co(III),[17] Np(VI),[18] Pu(VI),[19] Pu(IV),[19] Ce(IV),[20] V(V),[21] Mn(III),[22,23] Ni(IV),[24] Ni(III),[24] Tl(III),[25] and IO_4^-.[26] All these oxidants, except Tl(III) and IO_4^-, are one-electron agents. However, in none of these studies was a semiquinone observed directly, and only with Fe(III),[10] Pu(VI),[19] and Pu(IV)[19] was any evidence found that semiquinone species are kinetically significant. Hence, in general for noncomplementary oxidation of hydroquinones by one-electron oxidants, semiquinones are formed only as fleeting transients (eq 1–3, where HQ, SQ, and Q represent the hydroquinone, semiquinone, and quinone, respectively, and Ox and Red represent a one-electron oxidant and its reduced form). For Fe(III),[10] Pu(VI),[19] or Pu(IV)[19] as the

$$\mathrm{Ox + HQ} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Red + SQ} \tag{1}$$

$$\mathrm{Ox + SQ} \xrightarrow{k_2} \mathrm{Red + Q} \tag{2}$$

$$k_2 \gg k_{-1} \tag{3}$$

oxidant, rates of reaction are affected by the concentration of Red, suggesting that eq 3 does not hold. In the studies with the two-electron oxidants Tl(III)[25] and IO_4^-,[26] the oxidations of hydroquinones were considered as simultaneous two-electron transfers.

Benzoquinones are well-known as oxidants and dehydrogenating agents for synthetic organic chemistry.[27] Kinetic studies on quinone oxidants (except for photochemical studies) have been largely limited to dehydrogenation of hydroaromatic compounds[28,29] and triphenylmethanes,[30] in which hydride-transfer

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mechanisms prevail. These reactions show large deuterium and tritium kinetic isotope effects. Two-electron oxidations of hydroquinones by quinones of higher redox potential are common reactions and have been utilized in a number of quinone syntheses.[31-34] However, kinetic and mechanistic studies of this type of reaction are virtually nonexistent.

The redox potentials of substituted hydroquinones are markedly affected by the nature of the substituents.[35,36] Hence, hydroquinones are interesting reductants for testing electron-transfer theories by examining the correlation of their redox reaction rates with the free energies of reaction. Indeed, in many of the studies cited above, the observed electron-transfer kinetics were considered in terms of Marcus theory.[12,37,38] Marcus' equations have been successful in predicting estimates of rate constants for hydroquinone oxidation by Fe(III),[12] Cu(II),[13] Ir(IV),[15] Np(VI),[18] Mn(III),[22] Ni(IV),[24] and Ni(III).[24] The effects of various combinations of 3-thio-1,4,5-trimethyl-1,2,4-triazolium substituents and alkyl substituents on hydroquinone redox potentials have been studied by cyclic voltammetry. These various combinations together with substituent effects on the quinone oxidant make possible a wide range of free energies of reaction. The resulting correlation of rates with free energies and a large kinetic deuterium isotope effect raise some interesting questions regarding the nature of two-electron redox reactions between hydroquinones and quinones.

Experimental Section

Cyclic voltammetry was done at room temperature (23 ± 1 °C) on a Princeton Applied Research Model 170 electrochemistry system equipped with a glassy-carbon working electrode, a standard calomel reference electrode (SCE), and a platinum auxiliary electrode. Solutions for cyclic voltammetry were typically 5×10^{-4} M in TT-hydroquinone, 0.010 M in buffer, and 0.5 M in KCl. Coulometric experiments (23 °C) were done on unbuffered solutions of TT-hydroquinones in 0.5 M KCl adjusted to pH ~3 with HCl. For coulometry, the Model 170 system was equipped with a platinum-basket working electrode to which a constant potential of +0.600 V vs. SCE was applied. Electrolysis usually required ~45 min to reach completion. UV–visible spectra were recorded with a Perkin-Elmer Model 576 spectrophotometer.

For kinetic measurements, a Dionex Model D-110 spectrophotometer interfaced to a homemade Motorola M6800-based microprocessor was used. Kinetics were determined at 25 °C by mixing solutions of TT-hydroquinone (typically 2×10^{-4} M) with a well-buffered solution containing the oxidant in a 10-fold or greater excess (typically $>2 \times 10^{-3}$ M) and monitoring the absorbance increase at 390 nm. All solutions for kinetic studies were 0.5 M in KCl (or KNO_3 in a few instances). Buffers used in stopped-flow experiments (0.01–0.05 M) are listed in the footnotes of Table II. For rate constants determined in D_2O (Aldrich, 99.8 atom % deuterium), all reagents were dissolved directly in the deuterated solvent, and the pHs of *p*-benzoquinone solutions buffered by morpholinoethanesulfonic acid were adjusted with a 40% solution of NaOD in D_2O (Columbia Organic Chemicals Co.). The activity of D_3O^+ in solution was assumed to follow the relationship pD = pH (reading) + 0.40.[39]

The synthesis of TT-hydroquinones has been described elsewhere.[40] Benzoquinone (Kodak Laboratory Chemicals) was recrystallized from ligroin before use in kinetic studies. Chloro-*p*-benzoquinone and potassium *p*-benzoquinonesulfonate were prepared as described in the literature by oxidation of chlorohydroquinone[41] (Kodak Laboratory Chemicals) and of potassium hydroquinonesulfonate[42] (Aldrich).

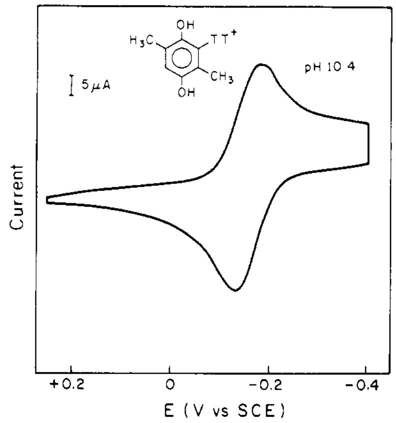

Figure 1. Cyclic voltammogram of **6**, pH 10.4, $\mu = 0.5$, $T = 23$ °C, scan rate = 100 mV/s.

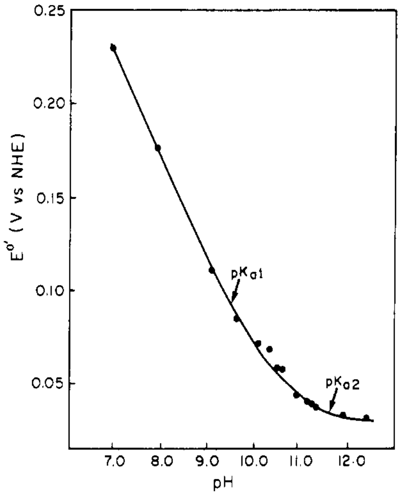

Figure 2. Dependence of observed redox potential of **7** upon pH; $\mu = 0.5$, $T = 23$ °C.

Table I. Thermodynamic Parameters of Hydroquinones

compd	$E°$,[a] V vs. NHE	$E°'$, V vs. NHE (pH 10.4)	pK_{a1}	pK_{a2}
1		0.177		
2		0.134		
3		0.101		
4	0.665	0.081	9.0	>11
5		0.060		
6	0.644	0.053	9.2	>11
7	0.618	0.042	9.3	11.6
8	0.575	−0.012	9.6	>11
1,4-hydroquinone[b]	0.699	0.102	9.91	11.56
2-chloro-1,4-hydroquinone[b]	0.712	0.144	8.90	11.0
1,4-hydroquinone-2-sulfonate[b]	0.767	0.178	9.57	11.9

[a] Redox potential extrapolated to unit hydrogen ion activity. Observed pH-dependent redox potentials measured by cyclic voltammetry at $T = 23$ (±1) °C in 0.5 M KCl and ≤0.050 M buffer concentration. [b] Data from ref 2.

Results and Discussion

Electrochemistry of Triazoliothiohydroquinones (TT-Hydroquinones). A number of TT-hydroquinones were examined by cyclic voltammetry at pH 10.4 ($\mu = 0.5$). The cyclic voltammograms exhibit two-electron quasi-reversible waves with anodic and cathodic peaks separated by 35–70 mV at a scan rate of 100 mV/s. Figure 1 shows an example of the cyclic voltammetric behavior. Constant-potential electrolysis of several TT-hydroquinones in acid solution (pH 3) confirmed that the electrode reaction is a two-electron oxidation (*n* values 2.0 ± 0.1). Comparison of UV–visible spectra of electrolysis products with those of authentic TT-quinones showed that the anodic oxidation is a

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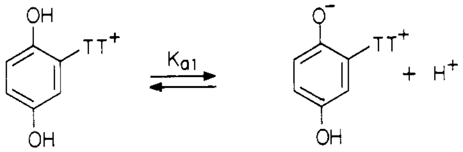
simple conversion of hydroquinone to quinone.

Table I summarizes the electrochemical results obtained for a variety of TT-hydroquinones by using cyclic voltammetry and includes literature data for several other hydroquinone/quinone couples used in this study. The pH dependence of the apparent redox potentials, $E°'$, for TT-hydroquinones is typical of that observed for other 1,4-hydroquinones.[2] The two-electron electrooxidation occurs only after both hydroxy groups have been ionized (eq 4–6). This model predicts the dependence of $E°'$ on pH given by eq 7, where $E°$ is the redox potential in 1.0 M H^+ and K_{a1} and K_{a2} are the successive dissociation constants for the hydroquinone. Figure 2 illustrates the dependence of $E°'$ upon pH for compound 7. The curve in Figure 2 is calculated from eq 7 with $E° = 0.618$ V (vs. NHE), $K_{a1} = 10^{-9.26}$, and $K_{a2} = 10^{-11.63}$.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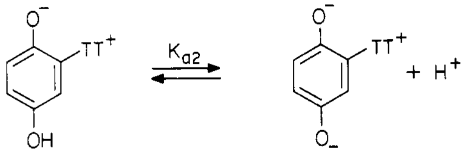
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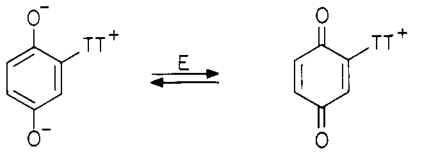

(6)

$$E°' = E° + \frac{RT}{nF}\ln([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) \qquad (7)$$

Comparison of $E°'$ (pH 10.4) values in Table I shows that changes in ring substitution cause significant changes in redox potential. The major cause for changes in $E°'$ with structure change is the inductive effects of ring substituents. For example, inspection of Table I shows that each methyl substituent on the hydroquinone ring lowers $E°'$ by ~60 mV. The TT substituent, on the other hand, increases the redox potential by ~75 mV. These observations are consistent with a decrease in quinone/hydroquinone redox potential brought about by electron-donating groups and an increase caused by electron-withdrawing groups.[35,36] A less obvious but significant trend in Table I involves three hydroquinones with fused ring substituents. Comparison of $E°'$ for **2**, **3**, and **4** shows that increased ring strain in the fused ring causes a shift to increased positive potentials. This suggests that the ring strain destabilizes the quinone to a greater extent than it does the hydroquinone, perhaps because the hydroquinone can better accommodate a deviation from planarity and 120° bond angles around the carbon atoms at the ring fusion. Riecke et al.[43] also observed a trend to more positive potentials with increased ring strain in fused-ring naphthoquinones. They attributed the ring-strain effect to a "hybridization effect model", which postulates that the ring-juncture carbons are rehybridized to accommodate the small bond angles imposed by the strain. The net result of the rehybridization is a decrease in the electronegativities of the ring-juncture carbons and an increase in electronegativities of the carbonyl carbons of the quinones. The increased electronegativities of the quinone carbonyl carbons are manifested by an increase in the redox potential.

Stoichiometry of TT-Hydroquinone Oxidation by Benzoquinone. The stoichiometry of the reaction of **7** with *p*-benzoquinone at pH 6.0 was established spectrophotometrically. UV–visible spectra were recorded as the molar ratio of *p*-benzoquinone to **7** was varied. As the ratio was increased, a peak grew at 387 nm, λ_{max} for authentic oxidized **7**. The resulting mole-ratio plot (Figure 3) clearly shows 1:1 stoichiometry and that the oxidation of **7** by *p*-benzoquinone occurs according to eq 8. The stoichiometries for all other redox reactions reported here were not determined. It is assumed that one-to-one stoichiometry holds in each case and that the reactions, like eq 8, are two-electron redox reactions.

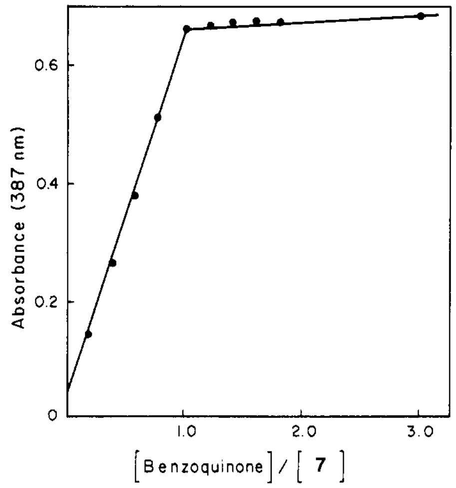
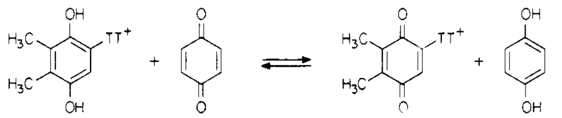


Figure 3. Mole-ratio plot for the oxidation of **7** by *p*-benzoquinone at pH 6.0.


(8)

Rate Law. The kinetics of oxidation of **4**, **6**, **7**, and **8** were studied by using *p*-benzoquinone, chloro-*p*-benzoquinone, and *p*-benzoquinonesulfonate as oxidants. In well-buffered solution with at least a 10-fold excess of oxidant over reductant, the oxidation of each of these TT-hydroquinones by any of the benzoquinones follows first-order kinetics, obeying the rate law given by eq 9, where TTH_2Q^+ and TTQ represent the TT-hydroquinone and TT-benzoquinone (product), respectively, and the subscript T denotes the TT-hydroquinone in all its degrees of protonation. Table II summarizes the kinetic data collected.

$$\frac{-d[TTH_2Q^+]_T}{dt} = \frac{d[TTQ]}{dt} = k_{obsd}[TTH_2Q^+]_T \qquad (9)$$

For several TT-hydroquinones, the dependence of k_{obsd} on the concentration of excess oxidant was examined (see Table II), and in all cases, the kinetics were first-order in oxidant. Figure 4 illustrates the first-order dependence on oxidant concentration at pH 4.0 and 6.5 for the reaction of **7** with *p*-benzoquinone. Figure 4 also shows a strong rate dependence on pH.

The dependence of k_{obsd} on pH (at constant oxidant concentration) was examined over the range pH 2.5–7.0 for the reactions of **7** and of **8** with *p*-benzoquinone. The slopes of −1.0 for plots of log k_{obsd} vs. pH (Figure 5) for these reactions show an inverse first-order rate dependence on hydrogen ion concentration. Thus, k_{obsd} takes the form given in eq 10, where k_{app} is an apparent first-order rate constant characteristic of each redox reaction and Q represents the quinone oxidant.

$$k_{obsd} = \frac{k_{app}[Q]}{[H^+]} \qquad (10)$$

The effect of buffer concentration (acetate buffer, pH 4.7) on the rates of oxidation of **7** and **8** by benzoquinone was examined, and no buffer-concentration dependence was observed. In addition, the effect of changing solvent from H_2O to D_2O was examined for the oxidations of **6**, **7**, and **8** by benzoquinone; rather large kinetic isotope effects were observed. These results suggest that

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Table II. Summary of Observed Rate Constants (T = 25 °C, μ = 0.5)

pH	[reductant], M	[oxidant], M	k_{obsd}
Reductant = **8**, Oxidant = *p*-Benzoquinone			
2.9[a]	1.0×10^{-4}	1.0×10^{-3}	0.041 ± 0.001
4.2[b]	1.0×10^{-4}	1.0×10^{-3}	0.88 ± 0.02
5.0[c]	1.0×10^{-4}	1.0×10^{-3}	4.8 ± 0.4
5.0[c]	1.0×10^{-4}	2.0×10^{-3}	8.3 ± 0.8
5.0[c]	1.0×10^{-4}	4.0×10^{-3}	20 ± 2
5.6[d]	1.0×10^{-4}	1.0×10^{-3}	22 ± 3
6.1 (pD)[d,e]	5.0×10^{-4}	5.0×10^{-3}	24.2 ± 0.9
Reductant = **8**, Oxidant = *p*-Benzoquinonesulfonate			
4.0[b]	1.0×10^{-4}	1.0×10^{-3}	0.50 ± 0.02
4.0[b]	1.0×10^{-4}	5.8×10^{-3}	2.91 ± 0.06
Reductant = **7**, Oxidant = *p*-Benzoquinone			
4.0[b]	1.0×10^{-4}	1.0×10^{-3}	0.045 ± 0.003
4.0[b]	1.0×10^{-4}	3.0×10^{-3}	0.140 ± 0.002
4.0[b]	1.0×10^{-4}	5.0×10^{-3}	0.25 ± 0.01
4.5[c]	1.0×10^{-4}	1.0×10^{-3}	0.150 ± 0.008
5.1[c]	1.0×10^{-4}	1.0×10^{-3}	0.56 ± 0.03
5.5[d]	1.0×10^{-4}	1.0×10^{-3}	1.40 ± 0.09
6.1[d]	1.0×10^{-4}	1.0×10^{-3}	6.51 ± 0.05
6.1 (pD)[d,e]	1.0×10^{-4}	1.0×10^{-3}	0.23 ± 0.03
6.5[d]	5.0×10^{-5}	5.0×10^{-4}	7.4 ± 0.5
6.5[d]	5.0×10^{-5}	1.0×10^{-3}	16 ± 1
6.5[d]	1.0×10^{-4}	2.5×10^{-3}	34 ± 2
6.5[d]	1.0×10^{-4}	5.0×10^{-3}	63 ± 3
7.0[f]	1.0×10^{-4}	1.0×10^{-3}	78 ± 2
Reductant = **7**, Oxidant = Chloro-*p*-Benzoquinone			
4.0[b]	1.0×10^{-4}	1.0×10^{-3}	0.231 ± 0.003
4.0[b]	1.0×10^{-4}	3.0×10^{-3}	0.815 ± 0.002
4.0[b]	1.0×10^{-4}	4.0×10^{-3}	1.06 ± 0.02
Reductant = **7**, Oxidant = *p*-Benzoquinonesulfonate			
4.0[b]	1.0×10^{-4}	1.0×10^{-3}	0.38 ± 0.01
4.0[b]	1.0×10^{-4}	2.0×10^{-3}	0.91 ± 0.04
4.0[b]	1.0×10^{-4}	3.0×10^{-3}	1.15 ± 0.05
Reductant = **6**, Oxidant = *p*-Benzoquinone			
4.0[b]	1.0×10^{-4}	1.0×10^{-3}	0.0266 ± 0.0007
6.1 (pD)[d,e]	5.0×10^{-4}	5.0×10^{-3}	1.90 ± 0.03
Reductant = **6**, Oxidant = Chloro-*p*-Benzoquinone			
4.1[b]	1.0×10^{-4}	1.0×10^{-3}	0.67 ± 0.01
Reductant = **6**, Oxidant = *p*-Benzoquinonesulfonate			
4.0[b]	1.0×10^{-4}	1.0×10^{-3}	0.112 ± 0.005
Reductant = **4**, Oxidant = *p*-Benzoquinone			
3.9[b]	1.0×10^{-4}	1.0×10^{-3}	0.0054 ± 0.0004

[a] Chloroacetate buffer. [b] Potassium hydrogen phthalate buffer. [c] Acetate buffer. [d] Morpholinoethanesulfonate buffer. [e] D_2O solvent; pD = pH + 0.40. [f] Phosphate buffer.

Table III. Resolved Bimolecular Redox Rate Constants (T = 25 °C, μ = 0.5)

reaction no.	reductant	oxidant	log K_{eq}[a]	k_2,[b] $M^{-1}\,s^{-1}$	log k_2
1	**4**	*p*-benzoquinone	0.25	6.8×10^5	5.8
2	**6**	*p*-benzoquinone	1.16	4.2×10^6 1.2×10^6[c]	6.6
3	**7**	*p*-benzoquinone	2.14	9.5×10^6 1.4×10^6[c]	7.0
4	**6**	chloro-*p*-benzoquinone	2.60	8.4×10^7	7.9
5	**7**	chloro-*p*-benzoquinone	3.59	5.5×10^7	7.7
6	**8**	*p*-benzoquinone	3.90	2.1×10^8 3.8×10^7[c]	8.3
7	**7**	*p*-benzoquinonesulfonate	4.78	7.7×10^7	7.9
8	**8**	*p*-benzoquinonesulfonate	6.50	2.0×10^8	8.3

[a] See eq 17. [b] See eq 15. [c] D_2O as solvent.

the rate-determining step in the redox process involves proton transfer but that the proton transfer is not assisted by general acid or general base.

Discussion of Mechanism. The observed rate law (eq 10) suggests a mechanism in which the singly protonated TT-hydroquinone is the only kinetically significant reductant species under the conditions studied. The three possible reductant species and their reactions with quinone oxidant are given in eq 11–13.

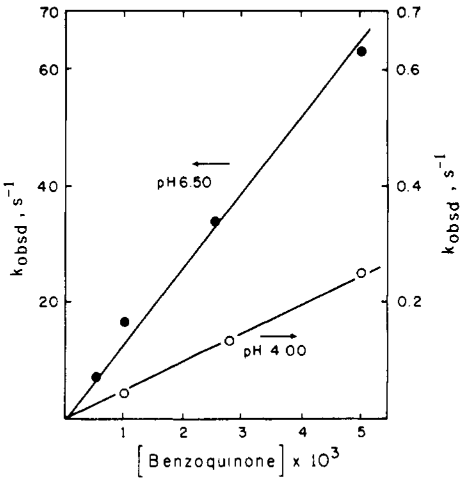


Figure 4. Dependence of k_{obsd} upon oxidant concentration for the oxidation of 7 by *p*-benzoquinone at pH 4.0 (r = 0.9991) and 6:5 (r = 0.9990).

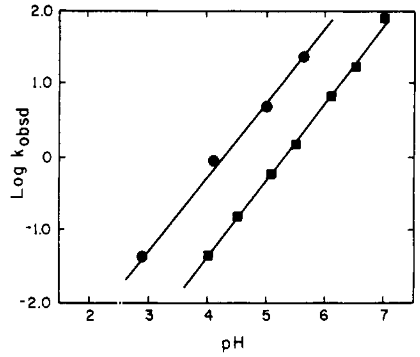
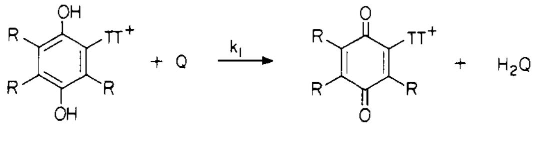
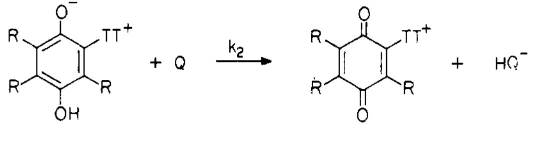


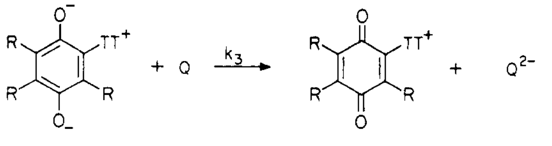
Figure 5. Dependence of k_{obsd} upon pH for the oxidation of 7 (■, slope = 1.06 ± 0.06, r = 0.9921) and 8 (●, slope = 1.02 ± 0.02, r = 0.9997) by *p*-benzoquinone (1.0×10^{-3} M).



(11)



(12)



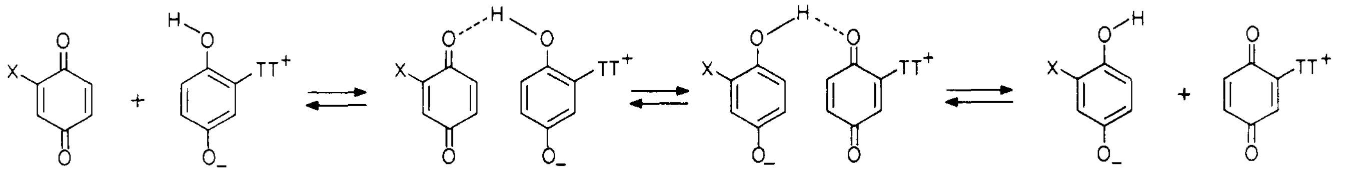
(13)

The full rate law derived from eq 11–13 is given in eq 14, where K_{a1} and K_{a2} are the acid dissociation constants of the TT-hydroquinones and k_1, k_2, and k_3 are the bimolecular rate constants for oxidation of each reductant species. In the pH range examined

$$\frac{-d[TTH_2Q^+]_T}{dt} = \frac{(k_1[H^+]^2 + k_2K_{a1}[H^+] + k_3K_{a1}K_{a2})[Q][TTH_2Q^+]_T}{([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})} \quad (14)$$

(2.5–7.0), only the $[H^+]^2$ term in the denominator is significant. The observed $[H^+]^{-1}$ kinetic dependence (eq 10) then suggests

Scheme I



that only the $k_2K_{a1}[H^+]$ term is significant in the numerator in the pH range 2.5–7.0. Hence, eq 10 may be rewritten as eq 15,

$$k_{obsd} = \frac{k_2K_{a1}[Q]}{[H^+]} \qquad (15)$$

where k_2K_{a1} and k_{app} are equivalent. Values of $k_2K_{a1}/[H^+]$ were determined from slopes of k_{obsd} vs. oxidant concentration or from $k_{obsd}/[Q]$ for reactions where only one oxidant concentration was examined. Values of k_2K_{a1} were then calculated for each pH, and the values from each pH were averaged to give the "best" value of k_2K_{a1}. From the values of K_{a1} determined by using cyclic voltammetry (Table I), the values of k_2 were determined; these are summarized in Table III. For the reactions in D_2O, K_{a1} values were estimated from the empirical relationship[44] given in eq 16.

$$pK_a^{D_2O} - pK_a^{H_2O} = 0.020pK_a^{H_2O} + 0.41 \qquad (16)$$

From the available kinetic data, it is impossible to evaluate rate constants for oxidation of doubly protonated TT-hydroquinones (k_1) or the fully ionized forms (k_3). The inverse first-order $[H^+]$ dependence for the rate of oxidation of **8** by benzoquinone at pH as low as 2.9 shows the extremely low reactivity of TTH_2Q^+ compared to TTHQ. At pH >7.0, the rates of TT-hydroquinone oxidation exceed the stopped-flow capabilities, making it impossible to detect any kinetic contribution from TTQ^- (k_3 pathway). At pH 7.0, no kinetic contribution from TTQ^- would be expected even if k_3 were 10^{10} M^{-1} s^{-1} (diffusion limit). Inverse first-order hydrogen ion dependence over a wide range of pH has been observed in several other kinetic studies of hydroquinone oxidation.[10,12,13] In general, these observations were interpreted as an indication that monoprotonated hydroquinones are the kinetically significant reductant in neutral and weakly acid solution.

Although the lack of contribution from TTQ^- is easily explicable by inaccessible rate measurements above pH 7.0, the extremely low reactivity of TTH_2Q^+ is not readily apparent. Clemmer et al. attributed the lower reactivity of H_2QX compared with HQX^- to a much less favorable free-energy change for the former.[13]

Upon considering eq 12, it is apparent that in the k_2 pathway, the redox reaction involves a net transfer of one proton. Thus, it is conceivable that proton transfer could occur during the rate-determining step. The lack of any measurable rate dependence on buffer concentration suggests that neither general acid nor general base is required to assist in proton transfer during the rate-determining step of the redox process. The large deuterium isotope effects (Table III), however, do strongly suggest that a proton is partially transferred in the transition state. Hence, the results suggest that the hydrogen nucleus is transferred directly from the hydroquinone to the benzoquinone (or through a water bridge) without assistance by general acid or base. Scheme I illustrates a simple mechanism that is consistent with the kinetic results.

Scheme I formally represents a hydride-transfer process. Hydride transfer indeed does provide the simplest mechanism for oxidation of monoprotonated hydroquinones by benzoquinones (e.g., eq 12). It is noteworthy that large deuterium isotope effects have been observed in reactions between quinones and triphenylmethanes, where there is convincing evidence supporting a hydride-transfer mechanism.[30] Hydride-transfer reactions commonly occur with hydride donors for which the transferred hydrogen nucleus is nonlabile with respect to proton transfer. This is obviously not the case for hydroquinones. Hence, the two-electron redox might be envisioned as occurring with simultaneous proton transfer and two-electron transfer. However, a distinction between the hydride-transfer and the simultaneous proton/electron-transfer mechanisms probably cannot be made experimentally. Indeed, even a theoretical distinction between the two alternatives is questionable, since it would imply that the location of the two transferred electrons in the transition state, which is probably highly delocalized, can be specified.

The only experimental evidence that could definitely preclude both hydride transfer and two-electron transfer is a demonstration of two successive one-electron transfers. Given the paucity of kinetic evidence for semiquinone intermediates even in oxidation of hydroquinones by one-electron oxidants,[13-18,20-24] it is unlikely that semiquinones can be kinetically detected when hydroquinones are oxidized by benzoquinones of higher redox potential. In a sequential electron-transfer scheme, the first step would form a pair of semiquinones with significantly different redox potentials. Pulse radiolysis studies reported by Meisel[45] suggest that the rates of disproportionation of semiquinones in water approach the diffusion limit if the free energy of reaction is more negative than about −3 kcal/mol. Hence, it is likely that the second electron transfer in a hydroquinone/quinone redox reaction of even moderate driving force would occur before the semiquinone intermediates could diffuse apart, and sequential electron transfer would become simultaneous in essence.[46] The observable kinetic evidence for oxidation of TT-hydroquinones by benzoquinones suggests an apparently simultaneous two-electron transfer in which a hydrogen nucleus is also transferred. The most straightforward interpretation of these results is that these reactions occur by a hydride-transfer mechanism.

Correlation of Rates with Free Energies of Reaction. The wide range of redox potentials resulting from changes in structures of the hydroquinones and quinones used in this study provides a basis for correlating the rates of the redox reactions with the free energies of reaction. The logarithms of equilibrium constants, log K_{eq}, for oxidation of monoprotonated TT-hydroquinones by benzoquinones were calculated from E°_{ox} and E°_R, the redox potentials (1.0 M H^+) for the oxidant and reductant half-cells, respectively, and from the first acid dissociation constants, pK_{a1}^{ox} and pK_{a1}^R, for the hydroquinones of each half-cell (eq 17). The

$$\log K_{eq} = \frac{E^\circ_{ox} - E^\circ_R}{0.0295} + pK_{a1}^R - pK_{a1}^{ox} \qquad (17)$$

calculated values of log K_{eq} are included along with log k_2 values in Table III. Clearly, the rate constants increase with increased driving force.

Although the Marcus theory was originally derived for outer-sphere electron-transfer reactions, Marcus' equations have been formally useful in describing correlations between rate constants and free energies of reaction for atom-transfer and group-transfer reactions,[47] including hydride transfers.[48] The Marcus relationship is given by eq 18 and 19, where k is the bimolecular rate constant,

$$k = Ze^{-\Delta G^*/RT} \qquad (18)$$

$$\Delta G^* = W_r + \lambda/4(1 + \Delta G^\circ/\lambda)^2 \qquad (19)$$

Z is the collision frequency in solution (10^{11} M^{-1} s^{-1}), ΔG^* is the excess free energy of activation,[12] W_r is the work required to bring the reactants together into an encounter complex, and λ is the

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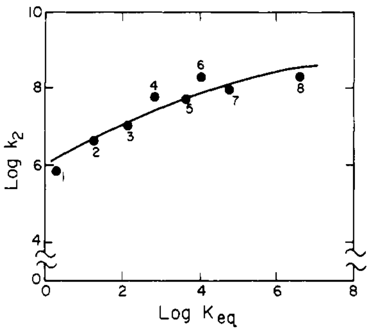

Figure 6. Correlation of log k_2 with log K_{eq}. The curve is calculated from eq 18 and 19. The numbers refer to reactions described in Table III.

energy required to reorganize the solvent shells and internal bonds of each reactant within the encounter complex prior to electron transfer.[12,37,38] For outer-sphere electron-transfer reactions, the W_r term is considered mainly coulombic and is typically only a minor contribution to the overall kinetic barrier.[12] However, in applying Marcus theory to proton-transfer reactions, Hassid et al.[49] and Bannister et al.[50] postulated that the formation of the encounter complex is followed by formation of a hydrogen-bonded "reaction complex", requiring rotational realignment and interpenetration of the solvent shells of the two reactants. Hence, for proton-transfer reactions, W_r may contain noncoulombic contributions that can make it a significant or even dominant term in eq 19. The hydrogen-bonded intermediate in Scheme I is analogous to the "reaction complexes" invoked in applying the Marcus theory to proton-transfer reactions. For specific application of eq 18 and 19 to the mechanism proposed in Scheme I, it is assumed that W_r represents the work required to form the hydrogen-bonded intermediate and λ represents the reorganizational barrier to the actual hydride transfer, which consists of internal bond reorganization and solvent reorganization to make the reactant pair more closely resemble the product pair.

The correlation of log k_2 with log K_{eq} is shown in Figure 6. The solid curve represents rate constants calculated from eq 18 and 19 with $W_r = 2.2$ kcal/mol and $\lambda = 18$ kcal/mol, the values giving the best agreement with the experimental data. For each reaction in this study, at least one reactant is uncharged; coulombic contribution to W_r should therefore be negligible. However, the best fit to the experimental data in Figure 6 requires a finite value of W_r to cause the slope to approach zero at large values of log K_{eq}. This is consistent with the hydride-transfer mechanism (Scheme I), in which formation of the reaction complex poses a larger barrier than formation of a simple encounter complex.

In most of the kinetic studies reported in which quinone oxidants have been used, hydride-transfer mechanisms have been proposed and convincingly argued. Most common are quinone oxidations of triphenylmethanes[30] and dihydroaromatic hydrocarbons.[28,29] In these studies, as in the present study, the strongest evidence supporting a hydride-transfer mechanism was large deuterium and tritium kinetic isotope effects. Since the hydrogen attached to carbon in these compounds is nonlabile with respect to proton transfer and since the products of the quinone oxidations are most reasonably formed by simple abstraction of a hydride ion, the evidence supporting a hydride transfer in their quinone oxidations is virtually indisputable. A long-standing controversy over hydride-transfer vs. electron-transfer mechanisms in the oxidation of dihydropyridines by quinones appears to be approaching a resolution in favor of hydride transfer.[51] Thus, there is considerable recognition that quinones commonly react as hydride acceptors. On the other hand, proposing hydroquinones as hydride donors may be unprecedented. Note, however, that microscopic reversibility requires that the reverse of a hydride-transfer reaction of a quinone acceptor must involve a monoprotonated hydroquinone as a hydride donor. Nevertheless, the lability of a hydroquinone proton-transfer and the large number of examples in which hydroquinones obviously react by electron-transfer mechanisms[9-24] make the hydride-transfer mechanism proposed in Scheme I a highly unusual reaction pathway for hydroquinone oxidation.

The kinetic results suggest a hydride-transfer mechanism only for quinone oxidation of monoprotonated TT-hydroquinone species. Oxidation of fully protonated TT-hydroquinones (eq 11) may involve hydride transfer, but if so, the rates are so low as to be negligible compared to the monoprotonated pathway (eq 12) in the pH range examined. Whatever mechanism is involved, redox pathways in which fully protonated hydroquinones are oxidized seem to be consistently slower than oxidations of monoprotonated hydroquinones.[10,12,13] The pathway in which fully ionized TT-hydroquinones are oxidized by quinones (eq 13) obviously cannot involve hydride transfer but must occur by electron transfer, possibly with semiquinone intermediates. Although a hydride-transfer mechanism is consistent with the kinetic results presented here, it is unlikely that reactions between hydroquinones and quinones actually require such a mechanism. If hydride transfer provided the only facile pathway for quinone oxidation of hydroquinones, the redox rates in highly alkaline solution, where only fully ionized hydroquinone is present in appreciable concentration, would decrease with increasing pH. This has not been observed, as the rates of quinone oxidation of fully ionized hydroquinones in water are inaccessible by stopped-flow methods. It would seem reasonable that two-electron redox reactions between quinones and fully ionized hydroquinones are facile electron-transfer processes as are the one-electron reproportionation reactions.[45]

Registry No. 1, 88305-36-6; **2**, 92593-53-8; **3**, 92593-56-1; **4**, 92593-46-9; **5**, 98652-70-1; **6**, 92593-57-2; **7**, 92593-47-0; **8**, 94324-56-8; benzoquinone, 106-51-4; chloro-*p*-benzoquinone, 695-99-8; potassium *p*-benzoquinonesulfonate, 51368-42-4.

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