Association for the alkali metal perchlorates has been studied previously in water,[18] anhydrous methanol, acetonitrile, and sulfolane,[19] and in all cases $K_A$ increases as the radius of the cation increases. Tables III and IV show that this order is generally preserved for the alkali metal perchlorates in acetic acid at all temperatures studied. The order suggests that solvent separated ion pairs are the predominent species in solution. The reverse order for $CsClO_4$ and $RbClO_4$ has been previously observed by Evans and Matesich[20] for the association constants of alkali metal and tetraalkylammonium chlorides in ethanol. These authors suggested that, by the time the radius reaches $Cs^+$, solvation is no longer important and $K_A$ decreases with further increase in size. A similar situation may be operative in the present study. The decrease in solvation as the size of the group 1A cations increase has been discussed quantitatively by Abraham and Liszi.[21] These authors used a one-layer continuum model to calculate the free energies of solvation for a number of univalent cations in a variety of nonaqueous solvents over the dielectric constant range of 30–7. The calculated values were in agreement with present experimental accuracy and showed that the ionic solvation free energy of $Rb^+$ is ~10–12% greater than that of $Cs^+$ in these solvents.

Although the dissociation data reported here can be rationalized by the new model derived by Fuoss,[17] it should be pointed out that it is necessary to make an important assumption. Fuoss[16] cautions that his model neglects the effects of higher association and should be applied to solvents of dielectric constant >10. Bruckenstein and Kolthoff[10] observed small spectral shifts when small amounts of water were added to acetic acid solutions of indicator bases or colorless bases such as pyridine or diethylaniline. These shifts were found to be due to the presence of hydronium acetate which had a tendency to form ion quadruplets and triplets with these bases. The potentiometric measurements in the present study did not exhibit this sensitivity to moisture when water content of the indicator electrode was deliberately increased in two trial runs to 0.25% and 0.50%, respectively. Nevertheless, all measurements reported here were made in rigorously dried glacial acetic acid.

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**Registry No.** LiOAc, 546-89-4; NaOAc, 127-09-3; KOAc, 127-08-2; RbOAc, 563-67-7; CsOAc, 3396-11-0; $LiClO_4$, 7791-03-9; $NaClO_4$, 7601-89-0; $KClO_4$, 7778-74-7; $RbClO_4$, 13510-42-4; $CsClO_4$, 13454-84-7; HOAc, 64-19-7; HCl, 7647-01-0; py, 110-86-1.

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# Redox Chemistry of Metal–Catechol Complexes in Aprotic Media. 1. Electrochemistry of Substituted Catechols and Their Oxidation Products

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Cyclic voltammetric measurements of 3,5-di-*tert*-butylcatechol, catechol, hydroquinone, tetrachlorocatechol, and tetrafluorocatechol have been utilized to determine their redox chemistry and thermodynamics in acetonitrile, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide. The effects of solution acidity upon the electrochemistry of these catechols, their corresponding quinones, and their redox products have been determined. On the basis of these results, electron-transfer mechanisms are proposed. The degree of interaction between a series of metal cations and the 3,5-di-*tert*-butyl-*o*-semiquinone anion has been determined.

During the past decade the importance of catechol complexes in biology has become evident. Enterobactin, the powerful sequestering agent for iron transport in *Salmonella typhimurium* and *Escherichia coli*,[1] is a tricatechol siderophore which binds iron(III) through the oxygens of the catechol moiety.[2] The importance of catecholato complexes to iron transport has been discussed in detail.[1-8] Likewise, the effectiveness of catechol as a "hard base" ligand for manganese,[9-13] molybdenum,[14-20] and vanadium[21-23] ions has been demonstrated for both aqueous and aprotic media. In addition, there have been numerous reports of *o*-semiquinone complexes of transition-metal ions in aprotic solvents.[24-29]

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Because catechol, *o*-semiquinones, and *o*-quinones are redox active, the effects of media and acidity upon their electron-transfer thermodynamics are important for a complete understanding of their coordination chemistry with transition-metal ions. Although there have been numerous studies of catechols and their corresponding quinones,[30-33] most of the data are not intercomparable due to the varied solvent media and electrodes which have been used. This paper summarizes the results of a detailed study of the redox reactions for 3,5-di-*tert*-butylcatechol and 3,5-di-*tert*-butyl-*o*-benzoquinone in acetonitrile, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide and relates the data to that obtained for other catechols, quinones, and hydroquinone under the same experimental conditions.

## Experimental Section

The cyclic voltammetric experiments were performed either with a three-electrode potentiostat–amperostat which has been described previously[34] or with a Princeton Applied Research Model 173/179 combination potentiostat–galvanostat in conjunction with a Houston Instruments Omnigraph 2000 X-Y recorder. The working electrode (Beckman No. 39273) was a platinum inlay electrode with a surface area of 0.23 $cm^2$. Its surface was polished to a mirror-bright finish with polishing alumina before each experiment. The platinum flag auxiliary electrode was isolated from the bulk solution by a medium-porosity glass frit. The reference electrode was a Ag/AgCl (aqueous tetramethylammonium chloride) electrode which was adjusted to 0.00 V vs. the saturated calomel electrode (SCE).[35] The reference electode was located inside a Luggin capillary in the cell compartment. All solutions were deaerated with high-purity argon for 15 min prior to analysis.

The ultraviolet–visible absorption spectra were recorded with either a Cary Model 17D or a Cary Model 219 spectrophotometer. The concentration of the supporting electrolyte in the matched reference and sample cells was the same as in the electrochemical experiments, 0.1 M tetraethylammonium perchlorate (TEAP). ESR spectra for solution samples in quartz cells were recorded with a Varian Model V4500 spectrometer.

Tetrafluorocatechol was synthesized,[36] and its purity and identity were confirmed by $^1H$ and $^{19}F$ NMR as well as by its melting point. Tetrachlorocatechol, tetrachloro-*o*-benzoquinone, 3,5-di-*tert*-butylcatechol, and 3,5-di-*tert*-butyl-*o*-benzoquinone (Aldrich Chemical Co.) were used as received. Reagent grade benzoquinone was sublimed prior to use. Catechol and hydroquinone were reagent grade and were used as received. The transition-metal perchlorates (hexahydrates) were obtained from G. Frederick Smith Chemical Co. and were dried under vacuum for 48 h prior to use. Anhydrous salts of Zn(II), Cr(III), Mn(II), Co(II), Ni(II), and Cd(II) were obtained by replacing the waters of hydration with 1,3-dimethylurea to give the hexakis complexes.[37] Triethyl orthoformate was used as the dehydrating agent, and 1,3-dimethylurea (DMU) was obtained from the Aldrich Chemical Co.

Acetonitrile, dimethylformamide, dimethyl sulfoxide, and dimethylacetamide (Burdick and Jackson, distilled in glass, UV grade) were obtained in quart bottles to minimize contamination by water and were used as received. Tetraethylammonium perchlorate was used as the supporting electrolyte at 0.1 M concentration. Perchloric acid (2.0 M), tetraethylammonium hydroxide (Eastman Kodak Co., 25% TEAH in ethanol) and malonic acid (Matheson Coleman & Bell) were used to adjust the solution acidity.

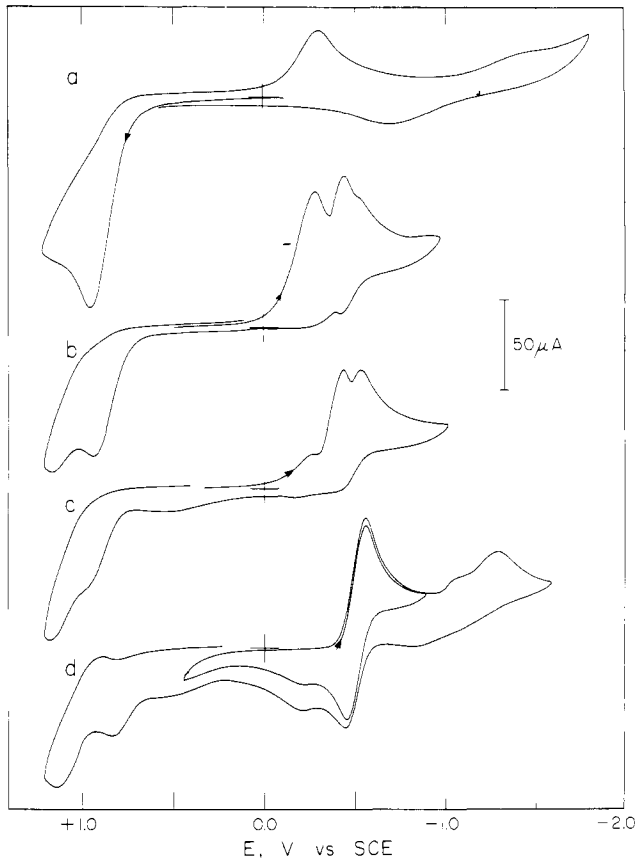


**Figure 1.** Cyclic voltammograms for (a) 1.45 mM 3,5-di-*tert*-butylcatechol, (b) solution a after exhaustive oxidation at +1.25 V, (c) solution b plus 1.45 mM tetraethylammonium hydroxide, and (d) solution b plus 2.90 mM tetraethylammonium hydroxide. All solutions were in dimethylformamide that contained 0.1 M tetraethylammonium perchlorate at a Pt electrode (surface area 0.23 $cm^2$). Scan rate was 0.1 V $s^{-1}$.

## Results

The cyclic voltammogram of 3,5-di-*tert*-butylcatechol (DTBC) in dimethylformamide exhibits two reduction peaks for an initial negative scan. The first ($E_{p,c}$ −1.47 V vs. SCE) is broad, rounded, and irreversible and has no observable anodic peak coupled to it. The second reduction peak ($E_{p,c}$ −2.25 V) is at the edge of the solvent cutoff and is only observable with exceptionally dry solvent. An irreversible oxidation peak occurs at +0.97 V for an initial positive scan of a DTBC solution to give a product which is reduced at −0.32 V (Figure 1a). Substitution of the diffusion coefficient for the corresponding quinone, 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ), into the Randles–Sevcik equation indicates that the peak current for the catechol oxidation is twice that expected for the reduction of the same concentration of DTBQ.[35] The broadness (130 mV) of the oxidation peak, $E_p - E_{p/2}$, confirms that it is electrochemically irreversible (the theoretical value for a two-electron reversible process is 28.5 mV, and for a one-electron process it is 57 mV).[38]

Variation of the scan rate has a pronounced effect on the peak potentials and peak currents for the oxidation and reduction of DTBC. Increasing the scan rate ($v$) causes the oxidation peak potential to shift in the positive direction. The value of $\Delta E_p/(\Delta \log v)$ determined from the slope of the $E_{p,a}$ vs. log $v$ plot is 117 mV. Because the shift in peak potential

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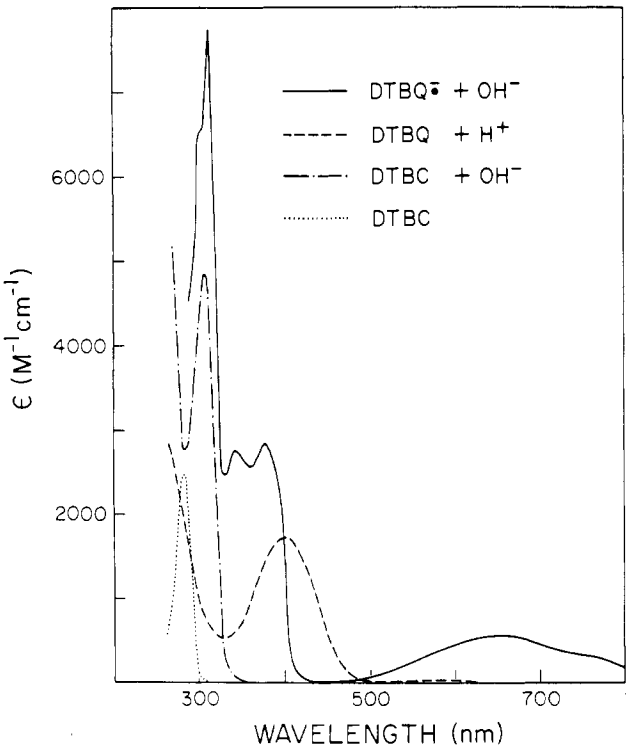


**Figure 2.** Absorption spectra of 2.0 mM solutions of 3,5-di-*tert*-butylcatechol, 3,5-di-*tert*-butylcatechol monoanion, 3,5-di-*tert*-butyl-*o*-benzoquinone plus 2.0 mM $HClO_4$, and 3,5-di-*tert*-butyl-*o*-benzosemiquinone plus 2.0 mM tetraethylammonium hydroxide in dimethylformamide.

is 59 mV/$\alpha n_a$ for every tenfold increase in the scan rate for an irreversible process, this shift implies that the number of electrons in the rate determining step, $n_a$, is 1 (assuming the transfer coefficient, $\alpha$, is 0.50). Plots of $i_{p,a}/v^{1/2}$ vs. log $v$ at low concentrations of DTBC appear to be constant; for higher concentrations, the ratio decreases as the scan rate is increased.

In neutral or acidic solution, controlled-potential electrolysis of DTBC at +1.25 V removes two electrons per molecule, and the resulting solution is amber in color. The spectrum of the oxidized solution is identical with that of DTBQ.[39] Controlled-potential reduction of this oxidized solution at −0.55 V vs. SCE requires two electrons per molecule of quinone and yields a clear solution with the spectroscopy[39] and voltammetry of DTBC. The cyclic voltammogram for the oxidized DTBC solution is shown in Figure 1b. Reduction peaks are observed at −0.29, −0.45, and −0.54 V. The peak at −0.45 V corresponds to the reduction of free protons,[40] and the peak at −0.54 V is due to the reduction of DTBQ to 3,5-di-*tert*-butyl-*o*-benzosemiquinoe (DTBSQ$^{-\bullet}$). Addition of 1 equiv of tetraethylammonium hydroxide (TEAH) causes the first peak to shift to −0.31 V and decreases its peak current to approximately one-fourth its original value (Figure 1c); concurrently, the peak currents for the reduction peaks at −0.45 and −0.55 V increase. When a second equivalent of TEAH is added to the oxidized solution, the peaks at −0.29 and −0.45 V are no longer present (Figure 1d), but the redox couples for DTBQ at $E^{\circ\prime}_1$ = −0.49 V and $E^{\circ\prime}_2$ = −1.34 V are observed. Further addition of TEAH causes the solution to turn green.

Electrochemical studies of tetrafluorocatechol (TFC), tetrachlorocatechol (TCC), catechol (C), and hydroquinone (HQ) give results similar to those for DTBC. However, free proton and quinone reduction peaks are not observed for the reverse scan of an initial positive scan. The addition of 2 equiv of TEAH to these catechols results in anodic voltammetry that yields a quinone reduction peak for the reverse scan. The cyclic voltammograms of HQ, C, and DTBC also have broadened reduction waves, and the reverse process is complicated by reoxidation of adsorbed hydrogen on the platinum electrode. The catechols with electron-withdrawing substituents do not exhibit the adsorbed-hydrogen wave and have nearly reversible redox couples. Hence, the reduction of the catechols and hydroquinone must first lead to the formation of the radical anion, $H_2Cat^{-\bullet}$, which subsequently dissociates to the catechol anion, $HCat^-$, and molecular hydrogen. This dissociation is enhanced by electron-donating substituent groups. The second reduction peak observed at more negative values represents the reduction of $HCat^-$ to the dianion and hydrogen.

Addition of 1 equiv of TEAH to DTBC causes the solution to turn light yellow and the currents for the two reduction processes to diminish. The cyclic voltammogram for this solution exhibits a new oxidation peak at −0.14 V which, on the basis of its peak height, is a one-electron process. Analogous results are obtained after DTBC is reduced by a one-electron controlled-potential electrolysis at −1.60 V. During the electrolysis, hydrogen gas is evolved and the spectroscopy[39] of the product solution is similar to that for the addition of 1 equiv of TEAH to DTBC. The addition of a second equivalent of TEAH does not result in the formation of the DTBC dianion but, instead, causes the oxidation peak at −0.14 V to double in height. After the addition of a second equivalent of base to HQ, TCC, and TFC, the voltammograms confirm that the dianions are formed and that TFC is the most acidic of the group.

In aprotic media the corresponding quinones of TFC, HQ, and TCC exhibit two reversible one-electron redox couples. For DTBQ the electrochemistry is slightly different (Figure 3a). The first couple represents a reversible reduction to the semiquinone anion radical; this has been confirmed by controlled-potential coulometry (slightly more than one electron per molecule), ESR, and UV–visible absorption spectroscopy. The second reduction for DTBQ is a one-electron process to give the dianion, but it is not a reversible reaction (in contrast to the other quinones). The reduction peak of the second couple is broadened and diminshed in height, and the anodic peak is nearly eliminated and shifted positively. The voltammogram also indicates that some catechol monoanion is formed ($E_{p,a}$ −0.14 V) and that the semiquinone oxidation peak has nearly the same height as the initial quinone reduction peak.

To deduce why the reduction peak of the second couple is diminished in height, we have performed a scan rate study for the first redox couple of DTBQ. The ratio of the anodic-to-cathodic peak currents increases to unity as the scan rate is increased, which indicates there is some enhancement of the cathodic peak current at low scan rates. Addition of water to DTBQ causes an additional decrease in this ratio. A plot of the current function $i_{p,c}/v^{1/2}C$ vs. the scan rate provides a means to separate the kinetic from the diffusional processes at the electrode surface. This current function increases as the concentration is increased and as the scan rate is decreased. Increased scan rates cause the peak potential for reduction to shift negatively; the slope for $\Delta E_p/(\Delta \log v)$ is approximately 33 mV. This shift is close to that expected for an ECE process or for a disproportionation reaction of the semiquinone.[44] A double-step chronoamperometric experiment has been conducted to confirm which mechanism is dominant. The results indicate that a proton-induced dismutation of the semiquinone occurs.

The semiquinone of DTBQ exhibits a reduction peak, but the reverse peak is missing (Figure 3b). The reverse positive scan indicates that DTBSQ$^{-\bullet}$ is the predominant species

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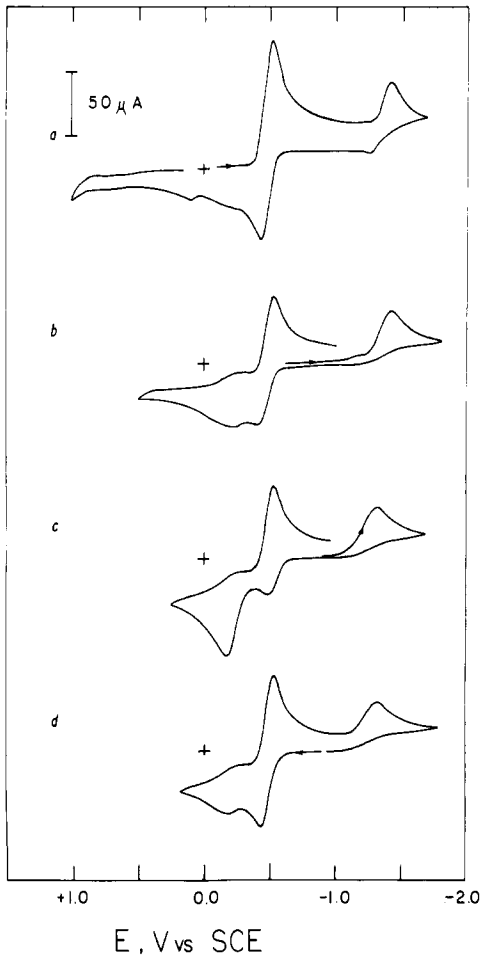


**Figure 3.** Cyclic voltammograms of (a) 2.0 mM 3,5-di-*tert*-butyl-*o*-benzoquinone, (b) 2.0 mM 3,5-di-*tert*-butyl-*o*-semiquinone anion (formed by controlled-potential electrolysis at −0.80 V), (c) solution b plus 2.0 mM tetraethylammonium hydroxide, initial cathodic scan and (d) solution c, initial anodic scan. All solutions were in dimethylformamide that contained 0.1 M TEAP at a Pt electrode (surface area 0.23 $cm^2$). Scan rate was 0.1 V $s^{-1}$.

present, but some catechol monoanion ($DTBCH^-$) is formed. Controlled-potential electrolysis of DTBQ at −1.80 V consumes two electrons per molecule, and the voltammetry of the resulting solution confirms that the catechol monoanion and hydroxide ion are the electrolysis products. Parts c an d of Figure 3 illustrate the voltammograms for a $DTBSQ^-\cdot$ solution after the addition of 1 equiv of TEAH. The absorption spectrum of this solution is the same as that for $DTBSQ^-\cdot$; the voltammogram for a positive scan confirms that $DTBSQ^-\cdot$ is the species in solution. When the initial scan is in the negative direction, the semiquinone dianion reduction peak remains unchanged, but on the reverse scan, the oxidation peak for $DTBQ^-\cdot$ is diminished to approximately one-third the height it exhibits in Figure 3b and the oxidation peak for $DTBCH^-$ is proportionally larger. These results confirm that two different processes are involved. When $DTBQ^-\cdot$ is reduced to $DTBC^{2-}$ in the absence of base, a redox reaction occurs such that $DTBQ^-\cdot$ is the major product. When $DTBQ^-\cdot$ is reduced in the presence of base, the major product is $DTBCH^-$. The ratio of anodic peak currents for $DTBQ^-\cdot$ and $DTBCH^-$ indicates that $DTBCH^-$ is the predominant species present at slow scan rates. As the scan rate is increased, appreciable quantities of $DTBQ^-\cdot$ are formed.

When 2 equiv of strong acid ($HClO_4$) are added to solutions of the quinones, the voltammetric results are similar to those for solutions of the corresponding oxidized catechols (by controlled-potential electrolysis). The second redox couple no longer is present, and the reduction peak for the first couple is shifted positively and increased in height to a value which corresponds to a two-electron process. On the reverse scan, the peak for the oxidation of the semiquinone anion no longer is present, but an oxidation peak due to the catechol monoanion is observed.

Table I summarizes the redox reactions (and their redox potentials) for a series of catechols, their corresponding quinones, and hydroquinone in four aprotic solvents.

The electrochemistry of DTBQ is affected by the presence of transition-metal ions. With the addition of 1 equiv of a metal cation to a solution of DTBQ, a new peak appears at a potential which is positive relative to the first reduction peak of the quinone and the first couple begins to lose its reversibility. When the metal cation is present in tenfold excess, the reduction peak of the first couple is shifted positively and the reverse process is completely eliminated (Table II summarizes the shift in reduction potentials for several nonelectroactive metal ions). The voltammetry of the solutions confirms that the quinone reduction remains a one-electron process.

## Discussion

The electrochemistry of catechols and hydroquinone in aprotic media is summarized in Table I. All of the molecules exhibit a single irreversible two-electron oxidation at positive potentials. The cyclic voltammetry for this oxidation process for scan rates ($v$) from 0.01 to 5.0 V $s^{-1}$ yields a constant value of $i_p/v^{1/2}$ for low substrate concentrations. Similar studies by means of chronoamperometry[41] and rotating-disk voltammetry[42] yield the same result. Thus, the overall oxidation occurs at such a rapid rate that the individual steps of the electron-transfer process cannot be distinguished within the limits of these techniques. The scanrate study has established that the rate-determining step is a one-electron transfer. The spectroscopy of the oxidized solution indicates that 3,5-di-*tert*-butyl-*o*-benzoquinone is one of the products. Addition of 2 equiv of tetraethylammonium hydroxide to the oxidized solution yields a solution with the voltammetry of DTBQ. The overall result is that the catechol is oxidized by two electrons to yield the quinone and two protons (reaction 6, Table I). A reaction scheme (eq 1–6) for the multistepped oxidation of

$$H_2Cat \rightleftarrows H_2SQ^+\cdot + e^- \quad (1)$$

$$H_2SQ^+\cdot \rightleftarrows HSQ\cdot + H^+ \quad (2)$$

$$HSQ\cdot + HSQ\cdot \rightleftarrows Q + H_2Cat \quad (3)$$

$$HSQ\cdot \rightleftarrows HQ^+ + e^- \quad (4)$$

$$HSQ\cdot + H_2SQ^+\cdot \rightleftarrows HQ^+ + H_2Cat \quad (5)$$

$$HQ^+ \rightleftarrows Q + H^+ \quad (6)$$

catechols can be proposed which is consistent with the electrochemical and spectroscopic results. In this scheme the radical cation formed by the one-electron oxidation of the catechol (eq 1) rapidly loses a proton to form the semiquinone radical, HSQ· (eq 2). Either this species disproportionates to form catechol and quinone and the cycle is repeated until all the catechol is oxidized or HSQ· is oxidized. Oxidation at the electrode surface (eq 4) or by $H_2SQ^+$ in solution (eq 5) followed by deprotonation (eq 6) completes the overall two-electron process. The reduction process that is observed at −0.32 V for the reverse scan of the initial catechol oxidation is due to quinone in the presence of a strong acid (reaction 7, Table I); catechol is the overall product.

The reduction of DTBQ in the presence of potons occurs sufficiently positive of proton reduction that the separate

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**Table I.** Summary of Redox Data for Catechols, Quinones, and Hydroquinone in Aprotic Media[a]

| reaction | solvent[b] | redox potential, V vs. SCE[c] DTBC | C | HQ | TCC | TFC |
|---|---|---|---|---|---|---|
| 1.[e] $H_2Cat + e^- \rightarrow {}^1/_2H_2 + HCat^-$ | AN | −1.22 | −1.17 | −1.17 | −0.84 | −0.51 |
| | DMF | −1.47 | −1.33 | −1.92 | −1.15 | |
| | DMA | −1.25 | −1.38 | −1.00 | −1.22 | |
| | $Me_2SO$ | −1.84 | −1.80 | *d* | −1.80 | |
| 2.[e] $HCat^- + e^- \rightarrow HCat^{2-}\cdot \rightarrow {}^1/_2H_2 + Cat^{2-}$ | AN | *d* | −1.75 | *d* | *d* | −0.80 |
| | DMF | −2.25 | −1.69 | *d* | −1.85 | |
| | DMA | −2.15 | −1.79 | −1.54 | *d* | |
| | $Me_2SO$ | *d* | *d* | *d* | *d* | |
| 3. $Q + e^- \rightleftarrows SQ^-\cdot$ | AN | −0.51 | −0.31 | −0.44 | +0.18 | +0.17 |
| | DMF | −0.49 | −0.29 | −0.42 | +0.16 | |
| | DMA | −0.44 | −0.24 | −0.37 | +0.15 | |
| | $Me_2SO$ | −0.47 | −0.26 | −0.39 | +0.14 | |
| 4. $SQ^-\cdot + e^- \rightleftarrows Cat^{2-} \xrightarrow{H_2O} SQ^-\cdot + {}^1/_2H_2 + OH^-$ | AN | −1.30 | −0.92 | −1.12 | −0.60 | *d* |
| $Cat^{2-} \xrightarrow{H_2O} HCat^- + OH^-$ | DMF | −1.34 | −0.98 | −1.31 | −0.69 | |
| | DMA | −1.18 | −0.93 | −1.37 | −0.58 | |
| | $Me_2SO$ | −1.18 | −1.03 | −1.28 | −0.61 | |
| 5.[f] $HCat^- \rightarrow e^- + HSQ\cdot \rightarrow {}^1/_2H_2Cat + {}^1/_2Q$ | AN | −0.12 | +0.06 | −0.37 | *d* | *d* |
| | DMF | −0.14 | −0.02 | −0.39 | +0.32 | |
| | DMA | −0.14 | +0.04 | −0.42 | +0.13 | |
| | $Me_2SO$ | −0.13 | −0.07 | −0.39 | +0.14 | |
| 6.[f] $H_2Cat \rightarrow Q + 2H^+ + 2e^-$ | AN | +1.19 | +1.32 | +1.18 | +1.36 | +1.63 |
| | DMF | +0.97 | +1.12 | +0.94 | +1.27 | |
| | DMA | +1.07 | +1.02 | +0.93 | +1.22 | |
| | $Me_2SO$ | +0.96 | +1.04 | +0.92 | +1.21 | |
| 7.[e] $Q + 2H^+ + 2e^- \rightarrow H_2Cat$ | AN | +0.40 | +0.69 | +0.42 | +0.60 | +0.47 |
| | DMF | −0.32 | −0.02 | −0.19 | +0.11 | +0.10 |
| | DMA | −0.26 | −0.03 | −0.24 | +0.09 | |
| | $Me_2SO$ | −0.19 | −0.11 | −0.27 | +0.08 | |

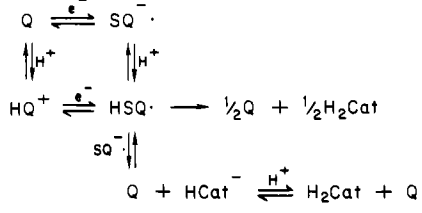
[a] $H_2Cat$ represents catechol or hydroquinone, Q quinone, $SQ^-\cdot$ semiquinone anion, $HCat^-$ catechol monoanion, and $Cat^{2-}$ catechol dianion; DTBC represents 3,5-di-*tert*-butylcatechol, C catechol, HQ hydroquinone, TCC tetrachlorocatechol, and TFC tetrafluorocatechol. [b] AN represents acetonitrile, DMF dimethylformamide, DMA dimethylacetamide, and $Me_2SO$ dimethyl sulfoxide. [c] For reversible processes, the redox potential is the mean of the cathodic and anodic peak potentials; for irreversible processes, it is the peak potential at a scan rate of 0.1 V $s^{-1}$. [d] Not observed in this solvent. [e] Irreversible; cathodic peak potential. [f] Irreversible; anodic peak potential.

**Table II.** Potential Shifts Observed for the Reduction Peak of the 3,5-Di-*tert*-butyl-*o*-benzoquinone/3,5-Di-*tert*-butyl-*o*-benzosemiquinone Couple[a] When a Hydrated Transition-Metal Ion Perchlorate is Present and When an Anhydrous Hexakis(1,3-dimethylurea) Metal Ion Perchlorate Is Present

| ion | [DTBQ], mM | $[M^{n+}]$, mM | $M(H_2O)_6^{n+}$ $\Delta E_{p,c}$,[b] mV | $K_f$[c] | $M(DMU)_6^{n+}$ $\Delta E_{p,c}$,[b] mV | $K_f$[c] |
|---|---|---|---|---|---|---|
| $Zn^{2+}$ | 1.0 | 10.0 | 221 ± 4 | 610 | 201 ± 9 | 279 |
| $Cr^{3+}$ | 1.0 | 10.0 | 163 ± 2 | 64 | 170 ± 5 | 84 |
| $Y^{3+}$ | 1.0 | 10.0 | 134 ± 2 | 20 | | |
| $Mn^{2+}$ | 1.0 | 10.0 | 130 ± 2 | 18 | 64 ± 4 | 1.4 |
| $Co^{2+}$ | 1.0 | 10.0 | 120 ± 2 | 12 | 54 ± 2 | 0.9 |
| $Ni^{2+}$ | 1.0 | 10.0 | 96 ± 4 | 4.7 | 94 ± 2 | 4.3 |
| $Cd^{2+}$ | 1.0 | 10.0 | 17 ± 2 | 0.2 | 41 ± 3 | 0.6 |

[a] Scan rate, 0.1 V $s^{-1}$ at a Pt electrode (surface area 0.23 $cm^2$). All solutions contained 0.1 M tetraethylammonium perchlorate in dimethylformamide. [b] $\Delta E_{p,c}$, peak potential of the reduction peak for the quinone–semiquinone couple in the presence of the transition-metal ion minus the peak potential for the couple in a metal-free solution. [c] $K_f = [M(SQ\cdot)^{(n-1)+}]/([M^{n+}][SQ^-\cdot])$.

processes are discernible (Figure 1b). With the addition of protons to a quinone solution, the peak for the reduction of the anion radical to the dianion disappears, as does the anodic peak for the oxidation of the radical anion back to the quinone, but an oxidation peak for $HCat^-$ is observed. In dimethylformamide, dimethylacetamide, and dimethyl sulfoxide, the voltammetry and spectroscopy indicate that protonation occurs after the reduction of DTBQ. In acetonitrile the reduction of the quinone in the presence of strong acid is shifted far too positively to be the result of quinone reduction with subsequent addition of a proton to the anion radical. (Such a shift would require a second-order rate constant in excess of the diffusion-controlled limit.) Hence, direct reduction of the protonated quinone occurs when strong acid is added to a solution of DTBQ in acetonitrile. The reduction of protonated *p*-benzoquinone in the presence of a strong proton donor has been reported previously.[42,43] A scheme (eq 7) which is consistent




(7)

with these results leads to the formation of catechol after complete electrolysis.

Reactions 1 and 2 of Table I are equivalent to the addition of base to $H_2Cat$, and the reduction potentials for catechol and catechol monoanion correlate directly with their acidity (the more acidic the protons of the catechol, the more positive the reduction potential). Electron-withdrawing groups should cause the catechol protons to be more acidic while electron-donating substituent groups should cause the opposite effect.[24] Table I indicates that, as expected, the order of acidity is TFC > TCC > C > DTBC > HQ. With use of a procedure described previously[39] the $pK_a$'s for TFC, TCC, C, DTBC, and HQ are estimated (±0.5 $pK_a$ unit) to have values of 8.6, 11.0, 15.6, 19.9, and 24.9, respectively, in DMF. Likewise, the reduction potentials of the catechol monoanions (reaction 2 in Table I) are indicative of their acidity. The values for the

(43) Marcus, M. F.; Hawley, M. D. *Biochim. Biophys. Acta* **1970**, *222*, 163.
(44) Mastragostino, M.; Nadjo, L.; Savaent, J. M. *Electrochim. Acta* **1968**, *13*, 721.

monoanion p$K_a$'s of TFC, TCC, C, DTBC, and HQ are estimated to be 22.6, 27.1, 28.2, 29.1, and 32.0, respectively, in DMF.

In aprotic solvents, all of the quinones except DTBQ exhibit two reversible one-electron redox processes. The first (reaction 3 in Table I) corresponds to the quinone–semiquinone anion couple and the second to the semiquinone anion–catechol dianion couple. Figure 3a illustrates that the reduction peak of the second couple of DTBQ is broadened considerably and diminished in peak height. The scan rate study and double-potential-step chronoamperometry experiment for the first redox couple of DTBQ confirm that a water-catalyzed disproportionation reaction occurs after the reduction step (eq 8). This accounts for the observations that the ratio of the

$$\begin{array}{l} Q + e^- \rightleftharpoons SQ^-\cdot \xrightarrow{H_2O} HSQ\cdot + OH^- \\ \qquad\qquad\quad \downarrow SQ^-\cdot \\ \qquad\qquad\quad Q + HCat^- \end{array} \qquad (8)$$

anodic-to-cathodic peak current increases to unity as the scan rate is increased and that water causes this ratio to decrease. At slow scan rates, the reduction peak is enhanced because quinone is regenerated during the disproportionation. The decrease in the current function as the scan rate is increased is consistent with a chemical reaction occurring after the initial electron transfer. The value of 33 mV for the plot of $\Delta E_p/(\Delta \log v)$ is characteristic of an ECE or disproportion reaction. Double-potential-step chronoamperometry confirms that disproportionation is the dominate process.

The absence of a significant oxidation peak for the second redox couple of DTBQ (Figure 3a) is attributed to the strong basicity of the dianion, which removes protons from the solvent (residual water present as an impurity) to form the catechol monoanion.

$$Cat^{2-} + H_2O \rightleftarrows HCat^- + OH^- \qquad (9)$$

On the reverse positive scan, a significant peak due to semiquinone anion oxidation is observed in addition to that for the catechol monoanion. Several authors attribute this to the oxidation of the catechol monoanion by quinone that diffuses to the electrode surface.[43]

$$HCat^- + Q \rightarrow 2SQ^-\cdot + H^+ \qquad (10)$$

This explanation, however, does not explain the results illustrated by Figure 3. If the catechol dianion were to act solely as a base (eq 9), then addition of hydroxide ion to $DTBSQ^-\cdot$ should result in peaks for the monoanion and dianion of catechol during the reverse positive scan (Figure 3c). However, the actual effect is a substantial decrease in the amount of semiquinone anion that results from the electrochemical formation of catechol dianion. Thus, in addition to the hydrolysis reaction (eq 9), the catechol dianion ($DTBC^{2-}$) acts as a one-electron reductant of residual water in DMF solvent.

$$DTBC^{2-} + H_2O \rightarrow {}^1/_2H_2 + OH^- + DTBSQ^-\cdot \qquad (11)$$

When $DTBSQ^-\cdot$ is reduced in the presence of base, the effective acidity of the residual water is reduced (reaction 11 is suppressed) and the dianion acts primarily as a strong base to form the catechol monoanion (eq 9). In the absence of added base, the dianion reduces the acidic water protons that are present in the solvent as an impurity. During controlled-potential electrolysis of DTBQ, reaction 11 is suppressed by the hydroxide ion that is generated via reaction 9. Hence, only peaks due to the catechol monoanion and the hydroxide ion oxidations are observed for the final product solution.

Studies of the effect of transition-metal cations on the electrochemistry of DTBQ have been undertaken because recent papers have concluded that neutral semiquinone transition-metal complexes are formed.[27] The data of Table II provide a convenient measure of the relative stabilities of several metal–semiquinone one-to-one complexes. The quantitative extent of such complexation can be estimated from the Nernst equation (eq 12) where $[SQ^-\cdot]$ represents the

$$E = E^\circ_{Q/SQ^-\cdot} + \frac{0.059}{n} \log \frac{[Q]}{[SQ^-\cdot]} \qquad (12)$$

concentration of free semiquinone anion. The rapid removal of the latter by complexation should increase the ratio of $Q/SQ^-\cdot$ and cause a concomitant positive shift in the reduction potential. If it is assumed that there is no interaction by the quinone species, then the shift in reduction potential (Table II) provides a direct measure of $[SQ^-\cdot]$ in the formation reaction

$$M^{n+} + SQ^-\cdot \rightleftarrows M(SQ\cdot)^{(n-1)+} \quad K_f \qquad (13)$$

Because the metal ion is present in tenfold excess, only the one-to-one complex needs to be considered and the concentration of ($M^{n+}$) can be assumed to be $4.5 \times 10^{-3}$ M. With these assumptions, the values of $K_f$ in Table II have been estimated. These represent lower limits because the potential shifts result from the instantaneous formation of the semiquinone complex. If there are kinetic limitations, then the estimated value of $K_f$ will be low. Subsequent papers will discuss the interactions of several metal ions with catechol and *o*-semiquinone anions in aprotic media.

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**Registry No.** DTBC, 1020-31-1; $DTBCH^-$, 65767-25-1; DTBQ, 3383-21-9; $DTBSQ^-$, 18802-82-9; C, 120-80-9; $CH^-$, 5593-75-9; *o*-Q, 583-63-1; *o*-$SQ^-$, 20526-43-6; HQ, 123-31-9; $HQH^-$, 3225-30-7; *p*-Q, 106-51-4; *p*-$SQ^-$, 3225-29-4; TCC, 1198-55-6; $TCCH^-$, 56018-48-5; TC-*o*-Q, 2435-53-2; TC-*o*-$SQ^-$, 22104-97-8; TFC, 1996-23-2; $TFCH^-$, 77661-75-7; TF-*o*-Q, 1423-12-7; TF-*o*-$SQ^-$, 77661-76-8; $[Zn(H_2O)_6](ClO_4)_2$, 36995-25-2; $[Cr(H_2O)_6](ClO_4)_3$, 27535-70-2; $[Y(H_2O)_6](ClO_4)_3$, 77662-09-0; $[Mn(H_2O)_6](ClO_4)_2$, 15305-65-4; $[Co(H_2O)_6](ClO_4)_2$, 15305-50-7; $[Ni(H_2O)_6](ClO_4)_2$, 10171-10-5; $[Cd(H_2O)_6](ClO_4)_2$, 59053-24-6; $[Zn(DMU)_6](ClO_4)_2$, 14284-45-8; $[Cr(DMU)_6](ClO_4)_3$, 15603-37-9; $[Mn(DMU)_6](ClO_4)_2$, 16038-13-4; $[Co(DMU)_6](ClO_4)_2$, 14284-41-4; $[Ni(DMU)_6](ClO_4)_2$, 14284-42-5; $[Cd(DMU)_6](ClO_4)_2$, 14284-46-9.