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Redox Chemistry of Metal-Catechol Complexes in Aprotic Media. 5. 3,5-Di-*tert*-butylcatecholato and 3,5-Di-*tert*-butyl-*o*-benzosemiquinonato Complexes of Zinc(II)

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Reduction of mixtures of zinc(II) and 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) at mole ratios of 1:1 and 1:2 in dimethyl sulfoxide yields several stable zinc(II)-catecholato ($DTBC^{2-}$) and -semiquinonato ($DTBSQ^-$) complexes: $Zn^{II}(DTBSQ)^+$, $Zn^{II}(DTBC)$, $Zn^{II}(DTBSQ)_2$, and $Zn^{II}(DTBC)(DTBSQ)^-$. These complexes and their oxidation-reduction products have been characterized by cyclic voltammetry, UV-visible spectroscopy, and magnetic susceptibility measurements. The stability constants, K_f, for the $Zn^{II}(DTBSQ)^+$ and $Zn^{II}(DTBC)$ complexes have values in dimethyl sulfoxide of approximately 2×10^8 and 4×10^{27} M^{-1}, respectively. Formation of stable zinc(II)-semiquinonato complexes provides versatile one-electron redox pathways for the oxidation and reduction of the zinc(II)-catechol-quinone system, which may be pertinent to the redox chemistry of related systems in biology.

The previous papers of this series have been concerned with the redox reactions for the 3,5-di-*tert*-butylcatecholato ($DTBC^{2-}$) and *o*-semiquinonato ($DTBSQ^-$) complexes of manganese(II, III, IV),[1] iron(II, III),[2] and vanadium(II, III, IV, V).[3] Because each of these metals is redox active within the potential range for ligand electron-transfer reactions,[4] the electrochemical results are complicated by intramolecular charge-transfer processes. In particular, the formation and characterization of $DTBSQ^-$ complexes of the lower oxidation states of these metal ions have been precluded.

The zinc(II) ion, which is redox inactive for the conditions where bound $DTBC^{2-}$ and $DTBSQ^-$ are electroactive, is a hard acid and forms strong coordinate bonds with oxo ligands.[5-7] The latter characteristic should favor strong complexation of zinc(II) by DTBC and DTBSQ; the degree of interaction should be equal to or greater than what it is with these ligands toward manganese(II)[1] and iron(II).[2] Preliminary observations indicate that addition of zinc(II) ion to alkaline solutions of $DTBC^{2-}$ retards the rate of ligand oxidation by air and stabilizes $DTBSQ^-$ solutions.[8]

Hence, characterization of the redox chemistry of bound $DTBC^{2-}$ and $DTBSQ^-$ in their zinc(II) complexes provides important insights to the electron-transfer processes that occur within similar complexes of redox-active metal ions. The present paper summarizes the results of an electrochemical, spectroscopic, and magnetic characterization of the stable $DTBC^{2-}$ and $DTBSQ^-$ complexes of zinc(II) in acetonitrile (CH_3CN), dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO).

Experimental Section

Equipment. A three-electrode potentiostat (Bioanalytical Systems Model CV-1) and a Houston Instrument Model 100 Omnigraphic X-Y recorder were used for the cyclic voltammetric experiments. Controlled-potential coulometric electrolysis was accomplished with a Princeton Applied Research Model 173/179 potentiostat/digital coulometer.

A Leeds and Northrup electrochemical cell was used for the electrochemical measurements and was equipped with a Beckman platinum-inlay working electrode (area 0.23 cm^2) for the voltammetric experiments. The latter was polished with No. 3 alumina (Buehler Ltd. No. 40-6353) before each set of experiments. The auxiliary electrode was a platinum-flag electrode, which was isolated from the bulk solution by a glass tube with a medium-porosity glass frit at the end; it contained a concentrated solution of supporting electrolyte. The reference electrode was a Ag/AgCl (aqueous tetramethylammonium chloride) cracked glass-bead electrode, which was adjusted to 0.000 V vs. SCE.[9] The reference electrode was located inside a luggin capillary in the cell assembly. Platinum-mesh working and auxiliary electrodes were used for the controlled-potential electrolysis experiments.

The UV-visible spectra were obtained with Cary Model 17D and Beckman Model ACTACV spectrophotometers. The magnetic susceptibility measurements were made with a Varian EM-390 NMR spectrophotometer by the method of Evans[10] as modified by Rettig[11] and made use of the paramagnetic shift of the methyl protons of Me_4Si as an internal standard. Diamagnetic corrections were made.[12]

Reagents. Because the solvate waters of the $Zn^{II}(ClO_4)_2{\cdot}6H_2O$ salt interfered with the stoichiometric formation of the semiquinone and catechol complexes of zinc, $[Zn^{II}(DMU)_6](ClO_4)_2$ (DMU = dimethylurea) was used as the source of Zn(II) ions.[13] The other reagents for the investigation included 3,5-di-*tert*-butylcatechol ($DTBCH_2$) (Aldrich), 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ), (Aldrich), tetraethylammonium hydroxide ((TEA)OH) (25% in methanol; Eastman), tetramethylammonium chloride (Aldrich), and tetramethylammonium perchlorate (TEAP) (G. Frederick Smith). Burdick and Jackson pesticide grade ("distilled in glass") solvents were used without further purification for all of the experiments: dimethylformamide (DMF), dimethyl sulfoxide (Me_2SO), and acetonitrile (CH_3CN). High-purity argon was used to deaerate the solutions.

Results

Electrochemistry. The limited solubility of the 1:1 zinc(II):3,5-di-*tert*-butylcatecholato (DTBC) complex has precluded meaningful electrochemical measurements in CH_3CN, DMF, or Me_2SO. Attempts to prepare in situ solutions of this complex in DMF or Me_2SO have been frustrated because it precipitates as a white amorphous solid, which slowly oxidizes

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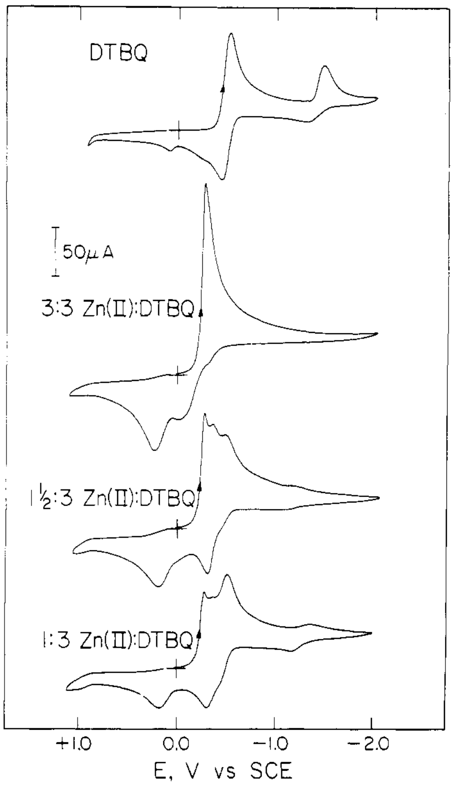

Figure 1. Cyclic voltammograms in dimethyl sulfoxide (Me_2SO) (0.1 M tetraethylammonium perchlorate (TEAP)) of (a) 3.0 mM 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ), (b) 3.0 mM DTBQ plus 3 mM $[Zn^{II}(DMU)_6](ClO_4)_2$, (c) 3.0 mM DTBQ plus 1.5 mM $[Zn^{II}(DMU)_6](ClO_4)_2$, and (d) 3.0 mM DTBQ plus 1.0 mM $[Zn^{II}(DMU)_6](ClO_4)_2$ (scan rate 0.1 V s^{-1}; Pt electrode (area 0.23 cm^2)).

in the air. Solutions of this complex in CH_3CN remain clear, but film formation on the electrode surface interferes with the electrochemical measurements.

So that these problems could be circumvented, 3,5-di-*tert*-butyl-*o*-benzoquinone solutions that contain equimolar, or less, quantities of $[Zn^{II}(DMU)_6](ClO_4)_2$ have been reduced electrochemically (cyclic voltammetry and controlled-potential coulometry). The results provide insight into the formation and stability of zinc(II)–catecholato (DTBC) and –*o*-semiquinonato (DTBSQ) complexes. Figure 1 illustrates the cyclic voltammograms for 1:1, 1:2, and 1:3 combinations of $[Zn^{II}(DMU)_6](ClO_4)$ and DTBQ in Me_2SO. The results indicate that reduction of DTBQ in the presence of an equimolar quantity of Zn(II) occurs at a peak potential that is 0.26 V more positive than for DTBQ in a metal-free solution. For the 1:1 Zn(II):DTBQ combination the cathodic peak height corresponds to a two-electron process; reduction of free semiquinone ($DTBSQ^-$) (−1.48 V vs. SCE) is not observed.

Controlled-potential electrolysis of a 1:1 combination of Zn(II) and DTBQ at −0.50 V vs. SCE requires two electrons/DTBQ and yields a colorless solution, which exhibits voltammetric oxidation peaks at −0.03 V vs. SCE and at +0.23 V in its cyclic voltammogram (Figure 1). Controlled-potential electrolysis of this solution at +0.05 V vs. SCE indicates that the product complex is oxidized by a one-electron process and yields a blue solution. Controlled-potential electrolysis of the latter solution at +0.40 V vs. SCE also is a one-electron process and yields a brown-red solution (similar in appearance to the original Zn(II)–DTBQ combination).

The cyclic voltammogram for a Me_2SO solution that contains a 1:2 mole ratio of $[Zn^{II}(DMU)_6(ClO_4)_2]$ relative to DTBQ (Figure 1) includes reduction peaks at −0.28 V vs. SCE, −0.37 V, and −0.50 V, plus a small, ill-defined peak at −1,2 V. Scan reversal yields a small anodic peak at −1.15 V, a shoulder at −0.45 V, and well-defined peaks at −0.30 and +0.20 V.

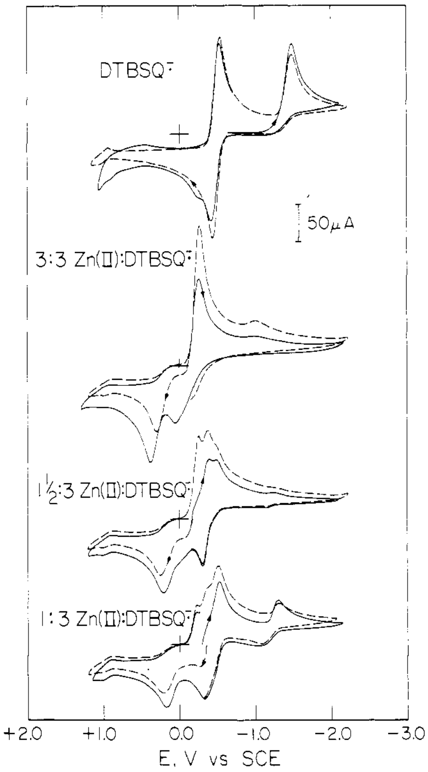

Figure 2. Cyclic voltammograms in dimethyl sulfoxide (Me_2SO) (0.1 M TEAP) of (a) 3 mM 3,5-di-*tert*-butyl-*o*-semiquinone anion radical ($DTBSQ^-\cdot$), (b) 3 mM $DTBSQ^-\cdot$ plus 3 mM $[Zn^{II}(DMU)_6](ClO_4)_2$, (c) 3 mM $DTBSQ^-\cdot$ plus 1.5 mM $[Zn^{II}(DMU)_6](ClO_4)_2$, and (d) 3 mM $DTBSQ^-\cdot$ plus 1 mM $[Zn^{II}(DMU)_6](ClO_4)_2$ (scan rate 0.1 V s^{-1}; Pt electrode (area 0.23 cm^2)).

The cyclic voltammogram for a 1:3 mole ratio of $[Zn^{II}(DMU)_6](ClO_4)_2$ relative to DTBQ (Figure 1) is similar to that for the 1:2 combination, but the relative peak heights are different. The most intense reduction peaks occur at −0.28 V vs. SCE and at −0.50 V vs. SCE, and the peak at −0.37 V is small. Also, an additional redox couple ($E_{p,c} = -1.35$ V, $E_{p,a} = -1.17$ V) is clearly evident. Another important difference is that the shoulder at −0.45 V has a much larger current.

So that it could be ascertained whether the semiquinone anion radical ($DTBSQ^-$) interacts with zinc ions or is involved as a redox intermediate, 1, 2, and 3 equiv of $DTBSQ^-$ have been combined with 1 equiv of Zn(II) (Figure 2). When 1 equiv of Zn(II) is added to 1 equiv of $DTBSQ^-$, the solution color changes from blue to blue-green and yields the cyclic voltammogram illustrated in Figure 2b. The latter indicates that a small fraction of the DTBSQ undergoes disproportionation to free quinone and bound catechol. (The reduction peak at −1.00 V is due to a slight excess of Zn(II).) A noteworthy feature of the cyclic voltammogram is that for an initial negative scan the reduction peak at −0.27 V corresponds to a one-electron process. An initial positive scan yields a one-electron-oxidation peak at +0.3 V, which, upon scan reversal, gives a two-electron-reduction peak at −0.27 V.

The cyclic voltammogram for a 1:2 combination of Zn(II) and $DTBSQ^-$ (Figure 2) indicates that the solution contains a significant fraction of a species with an anodic peak at −0.1 V. Hence, for these conditions disproportionation of $DTBSQ^-$ occurs to a greater extent than for a 1:1 combination. An initial negative scan for the 1:2 Zn(II):$DTBSQ^-$ combination yields voltammetric reduction peaks at −0.27 V (shoulder), −0.37 V, and −0.50 V; with scan reversal there is a new anodic peak at −0.3 V (Figure 2). The latter is not observed for the

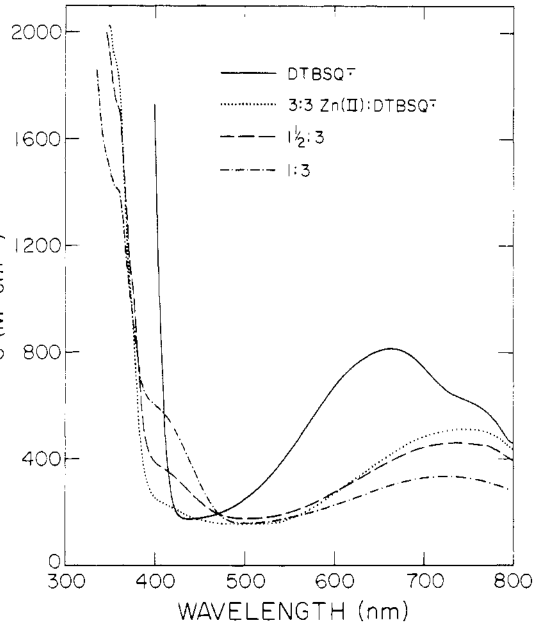

Figure 3. Absorption spectra in Me_2SO (0.1 M TEAP) of $DTBSQ^{-}\cdot$ and of $[Zn^{II}(DMU)_6](ClO_4)_2$–$DTBSQ^{-}\cdot$ mixtures with mole ratios of (a) 1:1, (b) 1:2, and (c) 1:3. Each solution had an initial concentration of 5 mM $DTBSQ^{-}\cdot$. The molar absorptivities, ε, are in relation to the total $DTBSQ^{-}\cdot$ concentration.

1:1 combination. When 3 equiv of $DTBSQ^-$ is combined with 1 equiv of Zn(II), the blue color of free $DTBSQ^-$ is changed to yellow-green. The cyclic voltammogram for this condition appears to be a composite of those for the 1:2 combination and free DTBQ.

The electrochemical results for these Zn(II) and DTBC or DTBSQ combinations in DMF and CH_3CN solutions are similar to those for Me_2SO solutions (Figures 1 and 2). In CH_3CN the cyclic voltammogram for the 1:1 Zn(II):DTBQ combination exhibits two one-electron processes at +0.27 and −0.05 V for an initial negative scan.

When solutions that contain equimolar amounts of DTBQ and $DTBCH_2$ are combined with 2 equiv of base, a blue solution results, which has electrochemical and spectroscopic properties that are characteristic of the free $DTBSQ^{-}\cdot$ anion radical. Addition of Zn(II) to these solutions to yield Zn(II):$DTBSQ^-$ mole ratios of 1:1 and 1:2 results in some disproportionation of the $DTBSQ^-$, especially for the 1:2 combination. The observations are analogous to those for electrogenerated $DTBSQ^-$.

Optical Spectroscopy. The UV–vis spectra of DTBQ, $DTBSQ^-$, and $DTBCH_2$ have been presented in a previous paper.[4] Figure 3 illustrates spectra for free $DTBSQ^-$ and for 1:1, 1:2, and 1:3 mole ratios of Zn(II) and $DTBSQ^-$ in Me_2SO. The shoulder at 400 nm, which corresponds to the absorption maximum for free DTBQ,[4] increases as the ratio of $DTBSQ^-$ relative to Zn(II) is increased. This is consistent with a metal ion induced disproportionation of $DTBSQ^-$ to DTBQ and $DTBC^{2-}$. The $DTBSQ^-$ complexes of Zn(II) have an absorption maximum at 740 nm. Reference to Figure 3 indicates the presence of an isobestic point at 470 nm, which is consistent with an equilibrium between a Zn(II)–DTBSQ complex and the disproportionation products, DTBQ and $Zn^{II}(DTBC)$. The fact that a solution with a 1:1 Zn(II):$DTBSQ^-$ mole ratio does not exhibit significant disproportionation (absence of absorption at 400 nm for DTBQ, Figure 3) confirms that a stable $Zn^{II}(DTBSQ)^+$ complex is formed. Analogous results are obtained in CH_3CN and DMF.

Magnetic Measurements. The magnetic moment for a solution that contains 50 mM $[Zn^{II}(DMU)_6](ClO_4)_2$ and 50 mM $DTBSQ^-$ (generated electrochemically) in Me_2SO is 1.85 μ_B (on the basis of the measured susceptibility and the assumption of a mononuclear $Zn^{II}(DTBSQ)^+$ complex). If the $DTBSQ^-$ anion is produced by reaction of DTBQ, $DTBCH_2$, and 2 equiv of base, the magnetic moment for a solution with a 1:1 Zn(II):$DTBSQ^-$ mole ratio is 1.82 μ_B. Both results are consistent with the formation of a stable $Zn^{II}(DTBSQ)^+$ complex.

Discussion and Conclusions

The electrochemical (Figure 1 and 2) and spectroscopic (Figure 3) data indicate that Zn(II) forms stable 1:1 complexes with the $DTBC^{2-}$ and $DTBSQ^-$ anions in aprotic media. However, the reduction of free DTBQ in the presence of Zn(II) (to form $Zn^{II}(DTBSQ)^+$) and the reduction of the $Zn^{II}(DTBSQ)^+$ complex (to form $Zn^{II}(DTBC)$) occur at approximately the same potential (−0.28 V vs. SCE) in Me_2SO and DMF (at slow scan rates (1 mV s^{-1}) a slight peak separation of about 20 mV is observed, and in CH_3CN two distinct one-electron peaks are observed). Hence, the reduction mechanism is believed to consist of two sequential one-electron processes:

$$\mathrm{Zn(II) + DTBQ + e^-} \xrightarrow{-0.28\ \mathrm{V}} \mathrm{Zn^{II}(DTBSQ)^+} \qquad (1)$$

$$\mathrm{Zn^{II}(DTBSQ)^+ + e^-} \xrightarrow{-0.28\ \mathrm{V}} \mathrm{Zn^{II}(DTBC)} \qquad (2)$$

The spectroscopic and electrochemical data establish that a 1:1 combination of Zn(II) and $DTBSQ^-$ yields stable $Zn^{II}(DTBSQ)^+$. Furthermore, electrolysis at −0.5 V to the extent of 1 equiv of reduction for a 1:1 combination of Zn(II) and DTBQ yields 1 equiv of a stable $Zn^{II}(DTBSQ)^+$ solution.

The electrochemical reoxidation of the $Zn^{II}(DTBC)$ complex occurs in two well-defined steps:

$$\mathrm{[Zn^{II}(DTBC)]} \xrightarrow{-0.03\ \mathrm{V}} \mathrm{[Zn(DTBSQ)]^+ + e^-} \quad E_3{}^{\circ\prime} \qquad (3)$$

$$\mathrm{[Zn(DTBSQ)]^+} \xrightarrow{+0.23\ \mathrm{V}} \mathrm{Zn(II) + DTBQ + e^-} \quad E_4{}^{\circ\prime} \qquad (4)$$

If the solutions contain an excess of DTBQ or $DTBSQ^-$ relative to Zn(II), the initial reduction is followed by an equilibration and disproportionation reaction:

$$\mathrm{Zn(II) + DTBQ + 2e^-} \xrightarrow{-0.3\ \mathrm{V}} \mathrm{Zn^{II}(DTBC)} \qquad (5)$$

$$\mathrm{Zn^{II}(DTBC) + DTBQ} \rightleftharpoons \mathrm{Zn^{II}(DTBSQ)_2} \qquad (6)$$

The resultant bis(semiquinonato) complex, $Zn^{II}(DTBSQ)_2$, is reduced by a one-electron process:

$$\mathrm{Zn^{II}(DTBSQ)_2 + e^-} \xrightarrow{-0.37\ \mathrm{V}} \mathrm{[Zn^{II}(DTBC)(DTBSQ)]^-} \qquad (7)$$

The mixed-ligand complex from this reduction is hydrolyzed and disproportionated by residual water in the solvent, and any free $DTBSQ^-$ anion is hydrolyzed and disproportionated by residual water:

$$\mathrm{2Zn^{II}(DTBC)(DTBSQ)^- + H_2O} \rightleftharpoons \mathrm{2Zn^{II}(DTBC) + DTBCH^- + DTBQ + OH^-} \qquad (8)$$

The disproportionation of $DTBSQ^-$ appears to be catalyzed by the zinc(II) complexes. For systems with three or more DTBQ molecules per Zn(II) ion, the voltammograms include reduction peaks for free DTBQ and $DTBSQ^-$[4]

$$\mathrm{DTBQ + e^-} \xrightarrow{-0.50\ \mathrm{V}} \mathrm{DTBSQ^-} \qquad (9)$$

$$\mathrm{DTBSQ^- + e^-} \xrightarrow{-1.35\ \mathrm{V}} \mathrm{DTBC^{2-}} \qquad (10)$$

and reoxidation peaks for $DTBC^{2-}$ and $DTBSQ^-$[4]

$$\mathrm{DTBC^{2-}} \xrightarrow{-1.17\ \mathrm{V}} \mathrm{DTBSQ^- + e^-} \quad E_{11}{}^{\circ\prime} \qquad (11)$$

$$\mathrm{DTBSQ^-} \xrightarrow{-0.43\ \mathrm{V}} \mathrm{DTBQ + e^-} \quad E_{12}{}^{\circ\prime} \qquad (12)$$

The intermolecular reaction of eq 6 yields $Zn^{II}(DTBSQ)_2$, which is oxidized by two one-electron steps to give free Zn(II) and DTBQ:

$$\mathrm{Zn^{II}(DTBSQ)_2} \xrightarrow{-0.31\ \mathrm{V}} \mathrm{Zn^{II}(DTBSQ)^+ + DTBQ + e^-} \tag{13}$$

$$\mathrm{Zn^{II}(DTBSQ)^+} \xrightarrow{+0.18\ \mathrm{V}} \mathrm{Zn(II) + DTBQ + e^-} \tag{14}$$

Reference to Figure 3 indicates that the $\mathrm{Zn^{II}(DTBSQ)^+}$ complex is stable with an absorption maximum (λ_{max} at 740 nm (ϵ 500 M^{-1} cm^{-1})). However, for those systems with 2:1 and 3:1 mole ratios of $\mathrm{DTBSQ^-}$ relative to Zn(II), the spectra indicate that significant free DTBQ (λ_{max} 400 nm (ϵ 1750 M^{-1} cm^{-1}))[4] is formed via intra- and intermolecular disproportionation of the $\mathrm{Zn^{II}(DTBSQ)_2}$ complex and its interaction with $\mathrm{DTBSQ^-}$ (λ_{max} 650 nm (ϵ 820 M^{-1} cm^{-1})):

$$\mathrm{Zn^{II}(DTBSQ)_2 \rightleftharpoons Zn^{II}(DTBC) + DTBQ} \quad K_{15} \tag{15}$$

$$\mathrm{Zn^{II}(DTBSQ)_2 + DTBSQ^- \rightleftharpoons Zn^{II}(DTBC)(DTBSQ)^- + DTBQ} \quad K_{16} \tag{16}$$

Analysis of the spectral data for the 2:1 and 3:1 systems, respectively, yields approximate values for these two equilibrium constants for $\mathrm{Me_2SO}$ solutions: $K_{15} = 4 \times 10^{-5}$ M and $K_{16} = 1.9$. Hence, the degree of disproportionation of the $\mathrm{Zn^{II}(DTBSQ)_2}$ complex is increased by dilution of its solutions and by the addition of excess $\mathrm{DTBSQ^-}$. For the experimental conditions of Figure 3, the 2:1 DTBSQ:Zn(II) system is primarily (about 85 mol %) in the form of the bis complex, $\mathrm{Zn^{II}(DTBSQ)_2}$ (λ_{max} 730 nm (ϵ 1075 M^{-1} cm^{-1})).

Because there is no apparent interaction between Zn(II) and DTBQ, the shift in oxidation potential for $\mathrm{Zn^{II}(DTBSQ)^+}$ (eq 4, Figure 2) relative to that for free $\mathrm{DTBSQ^-}$ (eq 12, Figure 2) provides an approximate measure of the stability constant for the $\mathrm{Zn^{II}(DTBSQ)^+}$ complex in $\mathrm{Me_2SO}$. Consideration of the voltammetric data for free $\mathrm{DTBSQ^-}$ and DTBQ (Figures 1 and 2) and eq 9 and 12 indicates that the thermodynamic redox potential ($E_{12}°'$) for the $\mathrm{DTBSQ^-/DTBQ}$ couple has a value between $E_{p,a}$ (–0.43 V) and $E_{p,c}$ (–0.50 V); a reasonable estimate is that

$$E_{12}°' \approx E_{p,a} - (\Delta E_{p/2}) \approx E_{p,a} - 0.03_5 = -0.46 \text{ V vs. SCE} \tag{17}$$

In the case of the $\mathrm{Zn(DTBSQ)^+/[Zn(II) + DTBQ]}$ couple (Figures 1 and 2, eq 2 and 4), the thermodynamic redox potential ($E_4°'$) must have a value between $E_{p,a}$ (+0.23 V) and $E_{p,c}$ (–0.28 V). This substantial peak separation is believed to be the result of two *ec* processes rather than slow electron-transfer kinetics:[9]

$$\begin{tikzcd}
\mathrm{Zn(DTBSQ)^+} \arrow[r, shift left, "E_{p,a}"] & \mathrm{[Zn(DTBQ)^{2+}] + e^-} \arrow[l, shift left] \arrow[d, "\text{fast}"] \\
\mathrm{Zn(II) + DTBSQ^-} \arrow[u, "\text{slow}"] & \mathrm{Zn(II) + DTBQ} \arrow[l, "e^-"', "E_{p,c}"]
\end{tikzcd} \tag{18}$$

If such a reaction sequence is assumed, then a reasonable postulate is that the initial voltammetric oxidation of $\mathrm{Zn(DTBSQ)^+}$ is as facile as the oxidation of free $\mathrm{DTBSQ^-}$. Thus, the value of $E_4°'$ can be approximated by use of the relation for the $\mathrm{DTBSQ^-/DTBQ}$ couple (eq 17)

$$E_4°' = E_{p,a} - 0.03_5 = +0.20 \text{ V vs. SCE} \tag{19}$$

Subtraction of eq 4 from eq 12 (with these estimated values for $E_4°'$ and $E_{12}°$) gives

$$\mathrm{Zn(II) + DTBSQ^- \rightleftharpoons Zn(DTBSQ)^+} \quad K_{f(\mathrm{Zn(DTBSQ)})} \tag{20}$$

The difference in formal potentials, $\Delta E_{12,4}°' = E_{12}°' - E_4°'$, provides a direct measure of $K_{f(\mathrm{Zn(DTBSQ)})}/[\mathrm{Zn(II)}]$:

$$\Delta E_{12,4}°' = -0.66 = -0.059 \log (K_{f(\mathrm{Zn(DTBSQ)})}/[\mathrm{Zn(II)}]) \tag{21}$$

$$K_{f(\mathrm{Zn(DTBSQ)})}/[\mathrm{Zn(II)}] = 10^{0.66/0.059} = 1.44 \times 10^{11} \tag{22}$$

A reasonable estimate for the concentration of free zinc ion at the electrode surface during the voltammetric measurement of $E_{p,a}$ (and estimation of $E_4°'$) is 1.5 mM Zn(II). Substitution in eq 22 yields an approximate value for $K_{f(\mathrm{Zn(DTBSQ)})}$ in $\mathrm{Me_2SO}$ of 2×10^8 M^{-1}.

The shift in the peak potential for the oxidation of $\mathrm{Zn^{II}(DTBC)}$ (eq 3, Figures 1 and 2) relative to that for free $\mathrm{DTBC^{2-}}$ (eq 11, Figure 1) provides an approximate measure of the ratio of the stability constants $K_{f(\mathrm{Zn(DTBC)})}/K_{f(\mathrm{Zn(DTBSQ)})}$, where

$$K_{f(\mathrm{Zn(DTBC)})} = [\mathrm{Zn^{II}(DTBC)}]/([\mathrm{Zn^{II}}][\mathrm{DTBC^{2-}}]) \tag{23}$$

On the basis of arguments analogous to those for the evaluation of the formal potentials ($E_4°'$ and $E_{12}°'$) for the $\mathrm{Zn(DTBSQ)^+}$ system, the formal potentials for the reactions of eq 3 and 11 can be estimated from the voltammetric data [$(E_{p,a})_3$ and $(E_{p,a})_{11}$] and the relation of eq 17. This approach yields approximate values of $E_3°' = -0.06$ V ($E_{p,a} = -0.03$ V, $E_{p,c} = -0.28$ V) and $E_{11}°' = -1.20$ V ($E_{p,a} = -1.17$ V, $E_{p,c} = -1.35$ V).[14] Subtraction of eq 3 from eq 11 (with these estimated values for $E_3°'$ and $E_{11}°'$) gives

$$\mathrm{Zn(DTBSQ)^+ + DTBC^{2-} \rightleftharpoons Zn(DTBC) + DTBSQ^-} \qquad K_{24} = K_{f(\mathrm{Zn(DTBC)})}/K_{f(\mathrm{Zn(DTBSQ)})} \tag{24}$$

The difference in formal potentials, $\Delta E_{11,3}°' = E_{11}°' - E_3°'$, provides a direct measure of the ratio (K_{24}) for the two stability constants:[9]

$$\Delta E_{11,3}°' = -1.20 - (-0.06) = -0.059 \log (K_{f(\mathrm{Zn(DTBC)})}/K_{f(\mathrm{Zn(DTBSQ)})}) \tag{25}$$

$$K_{f(\mathrm{Zn(DTBC)})}/K_{f(\mathrm{Zn(DTBSQ)})} = 10^{1.14/0.059} = 1.88 \times 10^{19} \tag{26}$$

Substitution of the estimated value for $K_{f(\mathrm{Zn(DTBSQ)})}$ (2×10^8) into eq 26 yields a value for $K_{f(\mathrm{Zn(DTBC)})}$ of 4×10^{27} M^{-1}.

The preceding analyses provide quantitative evidence that the complexation of zinc ion by the $\mathrm{DTBC^{2-}}$ and $\mathrm{DTBSQ^-}$ anions in aprotic media is exceptionally strong. The inertness of Zn(II) to electron transfer precludes the intramolecular redox processes in the $\mathrm{Zn^{II}(DTBSQ)^+}$ complex that destabilize the $\mathrm{DTBSQ^-}$ complexes of Mn(II),[1] Fe(II),[2] and V(IV).[3] The stability of the $\mathrm{Zn^{II}(DTBSQ)^+}$ species makes it possible to observe a clean one-electron oxidation of the $\mathrm{Zn^{II}(DTBC)}$ complex. Such a pathway probably is used for the electron-transfer oxidation of all metal catechol complexes but is obscured by intramolecular electron transfers for reduced redox-active metal ions (e.g., Mn(II), Fe(II), and V(IV)). The formation of the stable semiquinonato complexes of zinc(II) ($\mathrm{Zn^{II}(DTBSQ)^+}$, $\mathrm{Zn^{II}(DTBSQ)_2}$, and $\mathrm{Zn^{II}(DTBC)(DTBSQ)^-}$) provides versatile one-electron pathways for the oxidation and reduction of the catechol–quinone system which may be pertinent to the redox chemistry of related systems in biology.

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Registry No. DTBQ, 3383-21-9; Zn, 7440-66-6; $\mathrm{Zn^{II}(DTBSQ)^+}$, 83365-27-9; $\mathrm{Zn^{II}(DTBC)}$, 83365-28-0.

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[14] The average of the anodic and cathodic peak potentials provides an alternative estimate of the formal potentials; $E_3°' = -0.15$ V and $E_{11}°' = -1.26$ V with $\Delta E_{11,3}°' \approx -1.11$ V.