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Redox Chemistry of Metal-Catechol Complexes in Aprotic Media. 2. 3,5-Di-*tert*-butylcatecholato Complexes of Manganese(IV) and Manganese(III)

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When mixtures of manganese(II) and 3,5-di-*tert*-butyl-*o*-quinone (DTBQ) with mole ratios of 1:3 and 1:2 are reduced in aprotic solvents, stable $Mn^{IV}(DTBC)_3^{2-}$ and $Mn^{III}(DTBC)_2^{-}$ complexes are formed, respectively (DTBC represents the dianion of di-*tert*-butylcatechol). These complexes and their oxidation-reduction products have been characterized by cyclic voltammetry, controlled-potential electrolysis, optical spectroscopy, ESR spectroscopy, and magnetic susceptibility measurements in dimethylformamide, dimethyl sulfoxide, and acetonitrile solvents. On the basis of these results, a self-consistent redox mechanism is presented for the interconversion of the various species of manganese(II)-DTBQ systems with mole ratios of 1:1, 1:2, and 1:3. The catechol complexes of manganese(II), -(III), and -(IV) are versatile electron-transfer agents and should be effective redox catalysts and oxygen activators.

Manganese is an essential cofactor in a number of biological systems,[1] and particularly it is necessary for the catalysis of oxygen evolution in photosystem II.[2-4] Manganese also catalyzes the oxidative delignification of wood pulp by oxygen.[5-7] In both cases, manganese appears to serve as an electron-transfer agent in reactions with molecular oxygen. Because quinones are present in significant quantities in chloroplasts[8] and are thought to be involved in the primary reactions of photosystem II,[9-11] an understanding of the interactions of quinones and their reduction products (semiquinones and catechols) with manganese is desirable. A recent investigation[12] has demonstrated that certain quinones present in wood pulp accelerate the pulping rate and selectivity of delignification by oxygen, possibly in conjunction with manganese.

Several mechanisms for the involvement of manganese as the redox center of photosystem II have been proposed;[1,13-15] all require that manganese exist in several oxidation states. This has prompted studies to discover and characterize stable complexes of manganese(II), -(III), and -(IV) that might act as effective mimics for the manganese cofactor in photosystem II and as catalysts for the delignification of wood pulp by oxygen. Polyhydroxy complexes of manganese are attractive model systems because of their ability to stabilize the Mn(III) and Mn(IV) oxidation states.[16-20] Several of these complexes react reversibly with molecular oxygen and peroxide ion,[16-18,20] which may be important to the catalytic mechanisms. Additional studies have been undertaken to determine the redox properties of both aqueous and nonaqueous catechol complexes of manganese(II), -(III), and -(IV) as well as their O_2 adducts.[19,21,22]

Although the redox chemistry of quinones has been extensively studied by electrochemical methods in both aqueous and nonaqueous media,[23,24] most of the data are not intercomparable due to the variety of solvents and electrodes used. Because most of the electrochemistry for metal-catechol complexes involves the ligand rather than the metal, an understanding of the thermodynamics for the redox processes for the catechol-semiquinone-quinone system as a function of solvent and acidity is essential. The previous paper[25] of this series provides a detailed characterization of the redox reactions for a group of *o*-quinones and their reduction products in several aprotic solvents. The electrochemistry and spectroscopy for 3,5-di-*tert*-butycatechol ($DTBCH_2$), 3,5-di-*tert*-butyl-*o*-semiquinone ($DTBSQ^{-}\cdot$), and 3,5-di-*tert*-butyl-*o*-quinone (DTBQ) in dimethyl sulfoxide, dimethylformamide, and acetonitrile represent the focus of the study. The anion of $DTBCH_2$ is an effective and relatively stable ligand for a variety of transition metal ions as well as non-transition metals.[19,21,22,26-33]

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The present study summarizes electrochemical, spectroscopic, and magnetic characterization of the stable catechol and *o*-semiquinone complexes of manganese(III) and -(IV) that result from the reduction of excess 3,5-di-*tert*-butyl-*o*-quinone in the presence of manganese(II) in acetonitrile (CH_3CN), dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO).

Experimental Section

Equipment. A three-electrode potentiostat (Princeton Applied Research Model 173 potentiostat/galvanostat with Model 175 universal programmer and Model 179 digital coulometer) was used for the cyclic voltammetric and controlled-potential electrolysis experiments. Some of the controlled-potential electrolysis syntheses made use of a Bioanalytical Systems Model SP-2 potentiostat. Cyclic voltammograms were recorded on a Houston Instrument Series 200 recorder.

The Leeds and Northrup electrochemical cell was equipped with a Beckman platinum-inlay working electrode (area, 0.23 cm^2), a platinum-flag auxiliary electrode, and an Ag/AgCl reference electrode filled with an aqueous tetramethylammonium chloride solution and adjusted to 0.000 V vs. SCE.[34] The latter was contained in a Pyrex tube with a soft-glass cracked tip; this electrode was placed inside a luggin capillary. For controlled-potential electrolysis, a platinum-mesh working electrode and auxiliary electrode were employed.

Cary Model 17D and Model 219 spectrophotometers were used for UV–visible spectrophotometric measurements. ESR data were obtained with a Varian Model V-4500 spectrometer. The magnetic susceptibility measurements were made with a Varian EM-390 NMR spectrometer by the method of Evans[35] as modified by Rettig[36] and made use of the paramagnetic shift of the methyl protons of *tert*-butyl alcohol as an internal standard in DMF. Diamagnetic corrections were made.[37]

Reagents. The reagents for the investigations and syntheses included $Mn^{II}(ClO_4)_2{\cdot}6H_2O$ (G. Fredrick Smith), $Mn^{II}SO_4{\cdot}H_2O$ (Allied Chemical), $Mn^{II}Cl_2{\cdot}4H_2O$ (Mallinckrodt), 3,5-di-*tert*-butylcatechol ($DTBCH_2$) (Aldrich), 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) (Aldrich), tetraethylammonium hydroxide (TEAOH) (25% in methanol, Eastman), tetramethylammonium chloride (Aldrich), sodium perchlorate (G. Frederick Smith), tetramethylammonium perchlorate (TEAP) (G. Frederick Smith), and *tert*-butyl alcohol (Mallinckrodt). Burdick and Jackson pesticide-grade solvents were used without further purification for all of the experiments; dimethylformamide (DMF), dimethyl sulfoxide (Me_2SO), acetonitrile (CH_3CN), and pyridine. High-purity argon gas was used to deaerate solutions.

Preparation of Complexes. Several Mn(II) complexes were prepared by conventional methods: $[Mn^{II}(DMU)_6](ClO_4)_2$ (DMU = 1,3-dimethylurea),[38] $[Mn^{II}(bpy)_3](ClO_4)_2$ (bpy = 2,2′-bipyridine),[39] and $Mn^{II}(acac)_2$ (acac = 2,4-pentanedione).[40] Because the solvate waters of the $Mn^{II}(ClO_4)_2{\cdot}6H_2O$ salt interferred with the stoichiometric formation of the semiquinone and catechol complexes of manganese, $[Mn^{II}(DMU)_6](ClO_4)_2$ was used in the electrosynthesis reactions with DTBQ.

The Mn^{II}(DTBC) complex was prepared by combining 1 equiv of $Mn^{II}(ClO_4)_2{\cdot}6H_2O$ and 2 equiv of $DTBCH_2$ in deaerated CH_3CN prior to the addition of 2 equiv of either TEAOH or NaOH.[41] A light-pink precipitate of Mn^{II}(DTBC) resulted, which was extremely air sensitive (it slowly became a red-brown product in a nitrogen glovebox with an oxygen content of less than 1 ppm). Elemental and gravimetric analyses confirmed that the isolated percipitate contained one DTBC per Mn(II) ion.

Several manganese complexes were formed by adding 1, 2, or 3 equiv of DTBQ to 1 equiv of $[Mn^{II}(DMU)_6](ClO_4)_2$ prior to controlled-potential electrolysis at −0.65 V vs. SCE.

Disodium Salt of Tris(3,5-di-*tert*-butylcatecholato)manganese(IV) ($Na_2[Mn^{IV}(DTBC)_3]$). Equimolar quantities of Mn^{II}(DTBC) and $DTBCH_2$ were added to CH_3CN and brought into solution by the addition of 2 equiv of NaOH (1.86 M in methanol).[42] Addition of 1 equiv of DTBQ to the colorless solution caused it to turn dark blue immediately. The dark blue $Mn^{IV}(DTBC)_3^{2-}$ solution was then heated with anhydrous Na_2SO_4 for 30 min, filtered, evaporated, and cooled to yield a dark blue precipitate. The latter was recrystallized twice from CH_3CN. The solutions and crystals were sensitive to oxygen, and the latter formed a brown jelly upon standing in air. The entire synthesis and purification were conducted in an inert-atmosphere box. Characterization of the isolated complex by elemental analysis, spectroscopy, and single-crystal X-ray diffraction has confirmed that it has the formula $Na_2Mn^{IV}(DTBC)_3{\cdot}6CH_3CN$ with the six catechol oxygen atoms arranged around the Mn(IV) ion in a symmetrical octahedral configuration. Anal. Calcd for $C_{54}H_{78}N_6O_6Na_2Mn_1$: C, 64.35; H, 7.75; Na, 4.57; Mn, 5.46; O, 9.53. Found: C, 63.85; H, 8.10; Na, 4.62; Mn, 5.38; O, 9.75 (Galbraith Laboratories, Inc.).

Barium Salt of Tris(3,5-di-*tert*-butylcatecholato)manganese(IV) ($Ba[Mn^{IV}(DTBC)_3]$). Combination of 1.8 g of $Mn^{II}(ClO_4)_2{\cdot}6H_2O$ with 2 equiv of $DTBCH_2$ and excess finely powdered $Ba(OH)_2$ in 50 mL of DMF (with activated molecular sieves and under a highly purified nitrogen atmosphere) yielded a mixture that was stirred for 4 h prior to the addition of 1 equiv of DTBQ. With careful attention to the synthetic conditions, a blue solution resulted immediately after the addition of the DTBQ oxidant.[43] The solution was stirred for an additional hour and filtered; the filtrate was added to pure deaerated water. A dark-blue precipitate was formed, which was heated in CH_3CN for 30 min prior to its collection by filtration. The solid was dissolved in DMF and filtered, and the filtrate was evaporated to yield pure $Ba[Mn^{IV}(DTBC)_3]$. Its spectroscopic and electrochemical properties are consistent with those for the $Na_2Mn^{IV}(DTBC)_3$ complex.

The 3,5-di-*tert*-butyl-*o*-semiquinone anion radical ($DTBSQ^{-}\cdot$) was formed in DMF or Me_2SO by controlled-potential electrolysis of DTBQ at −0.65 V vs. SCE.

Results

Electrochemistry. The limited solubility and extreme oxygen sensitivity of the Mn^{II}DTBC complex has precluded meaningful electrochemical measurements in CH_3CN, DMF, or Me_2SO. However, reduction of 3,5-di-*tert*-butyl-*o*-quinone in the presence of equimolar, or less, quantities of $[Mn^{II}(DMU)_6](ClO_4)_2$ provides insight to the formation of manganese–catechol and –semiquinone complexes and a means to their electrosynthesis and characterization. Figure 1, parts a and b, illustrates the cyclic voltammograms for DTBQ and for a 1:1 $[Mn^{II}(DMU)_6](ClO_4)_2$–DTBQ solution. Reduction of DTBQ in the presence of Mn(II) occurs at a potential that is 0.06 V positive of that for the quinone in a metal-free solution. This is the result of a significant interaction between Mn(II) and the semiquinone anion radical reduction product ($DTBSQ^{-}\cdot$).[25] An initial negative scan only yields a single reduction peak at −0.46 V vs. SCE. Controlled-potential electrolysis at −0.65 V requires 1.5 electrons per DTBQ and yields a pale green solution. Reoxidation of the product solution, which exhibits an anodic peak at +0.44 V, requires 1.5 electrons per DTBQ and yields the starting materials.

The cyclic voltammogram for a DMF solution that contains a 1:2 mole ratio of $[Mn^{II}(DMU)_6](ClO_4)_2$ relative to DTBQ is illustrated in Figure 1c. An initial negative scan yields a reduction peak at −0.46 V; the reverse scan yields an anodic peak at +0.10 V. Controlled-potential reduction of this system also requires 1.5 electrons per DTBQ and yields a pale green

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(41) A light pink precipitate that did not dissolve in excess base resulted if (a) $Mn^{II}(ClO_4)_2{\cdot}6H_2O$ was mixed with only 1 equiv of $DTBCH_2$, (b) the base was added too rapidly, or (c) the solution was not vigorously stirred. Gravimetric experiments established that only 0.5 equiv of $DTBCH_2$ per manganese(II) was present in this insoluble pink precipitate.

(42) The CH_3CN used in the synthesis was pretreated with anhydrous Na_2SO_4.

(43) If the solution did not turn to dark blue instantaneously at this stage, the $DTBCH_2$ was not fully deprotonated.

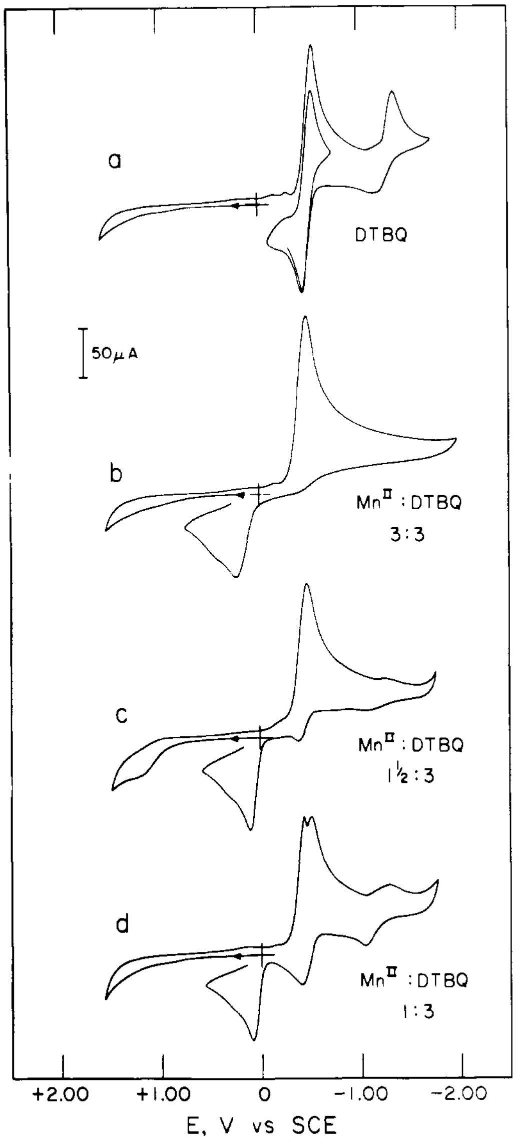

Figure 1. Cyclic voltammograms in dimethylformamide (DMF) (0.1 M tetraethylammonium perchlorate, TEAP) of (a) 3.0 mM of 3,5-di-*tert*-butyl-*o*-quinone (DTBQ), (b) 3 mM DTBQ plus 3 mM $[Mn^{II}(DMU)_6](ClO_4)_2$, (c) 3 mM DTBQ plus 1.5 mM $[Mn^{II}(DMU)_6](ClO_4)_2$, and (d) 3 mM DTBQ plus 1 mM $[Mn^{II}(DMU)_6](ClO_4)_2$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

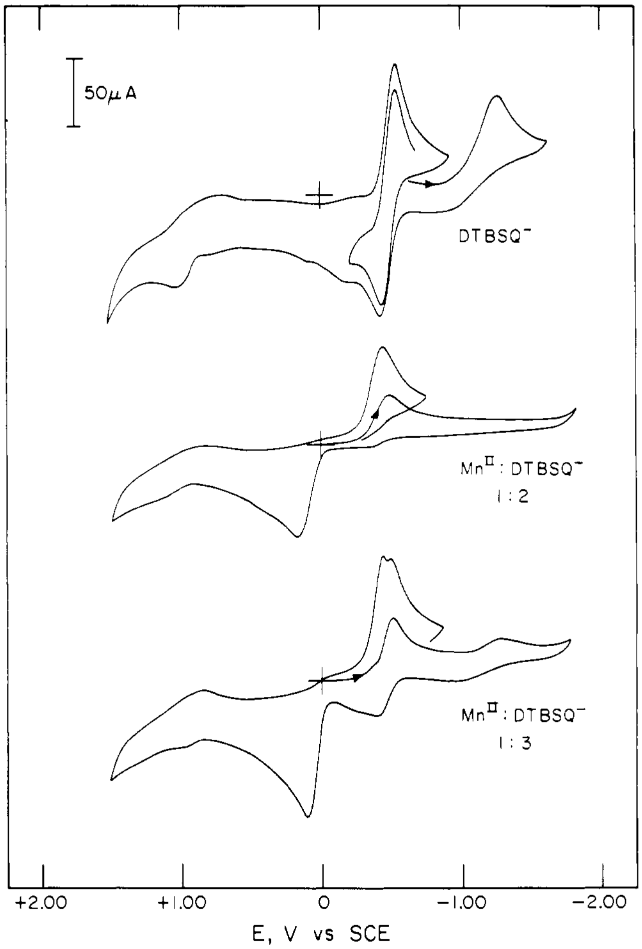

Figure 2. Cyclic voltammograms in DMF (0.1 M TEAP) of (a) 2 mM 3,5-di-*tert*-butyl-*o*-semiquinone (DTBSQ$^-\cdot$), (b) 2 mM DTBSQ$^-\cdot$ plus 1 mM $[Mn^{II}(DMU)_6](ClO_4)_2$, and (c) 3 mM DTBSQ$^-\cdot$ plus 1 mM $[Mn^{II}(DMU)_6](ClO_4)_2$ (scan rate 0.1 V s^{-1}; Pt electrode (area, 0.23 cm^2)).

solution. The latter has an oxidation peak at +0.17 V; scan reversal yields a single reduction peak at −0.46 V. The reduced solution also has an anodic peak at approximately +0.45 V. For positive scan rates of 1 V s^{-1} or greater this peak has the same height as the peak at +0.17 V. Controlled-potential electrolysis at below +0.33 V but above +0.17 V results in a complete conversion to the starting materials.

The cyclic voltammogram for a 1:3 mole ratio of $[Mn^{II}(DMU)_6](ClO_4)_2$ relative to DTBQ in DMF appears in Figure 1d. An initial negative scan yields two reduction peaks at −0.46 and −0.50 V (approximately the same location as those for the 1:2 system). An additional reduction peak is observed at −1.34 V, which is coupled with an anodic peak at −1.03 V for the reverse scan. This redox couple also is observed for the free quinone (Figure 1a). The reverse scan of an initial negative scan yields an anodic peak at −0.38 V which is coupled with the reduction peak at −0.50 V (the −0.38 V oxidation peak also is observed for the 1:2 system). Controlled-potential electrolysis at −0.65 V requires 1.5 electrons per DTBQ (4.5 electrons total) and yields a dark blue solution. The latter has an irreversible reduction peak at −1.25 V; a reverse scan has an anodic peak at +0.17 V to yield the initial species. Controlled-potential electrolysis of the dark blue solution at −1.40 V requires 1 electron per manganese and yields a pale green solution. A DMF solution of $Na_2[Mn^{IV}(DTBC)_3]$ exhibits cyclic voltammetry equivalent to that of Figure 1d (the reduction peaks at −0.46 and −0.50 V are not present for the initial negative scan).[22]

So that it could be ascertained whether the semiquinone anion radical (DTBSQ$^-\cdot$) interacts with manganese ions or is involved as a redox intermediate, 1–3 equiv of DTBSQ$^-\cdot$ have been combined with 1 equiv of Mn(II). When Mn(II) is added to a DTBSQ$^-\cdot$ solution, an immediate color change from blue to pale green occurs. Figure 2b illustrates the cyclic voltammogram for the solution that results from the combination of two DTBSQ$^-\cdot$ ions per Mn(II). The cyclic voltammogram indicates that approximately half of the DTBSQ$^-\cdot$ is converted to DTBQ (on the basis of the DTBQ reduction peak at −0.49 V). The same is true for the 3:1 DTBSQ$^-\cdot$ to Mn^{II} adduct (see Figure 2c). In this case, two reduction peaks are observed at −0.46 and −0.51 V, with the second the same as the reversible DTBQ/DTBSQ$^-\cdot$ couple (Figure 1a). The 3:1 DTBSQ$^-\cdot$–Mn^{II} solution has a dark green color. Controlled-potential reduction at −0.65 V requires 1 electron per Mn ion and yields a dark blue solution with a cyclic voltammogram that is identical with that of $Na_2[Mn^{IV}(DTBC)_3]$.

The electrochemistry of Mn^{II}–DTBQ combinations in CH_3CN is somewhat different from that in either DMF or Me_2SO. The cyclic voltammogram of the 1:3 $[Mn^{II}(DMU)_6](2ClO_4)_2$-to-DTBQ system is shown in Figure 3a.

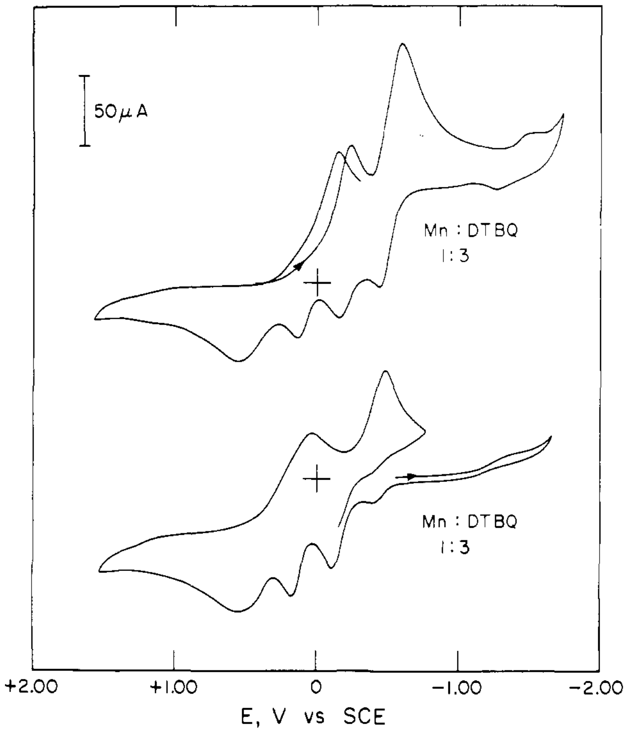

Figure 3. Cyclic voltammogram in CH_3CN (0.1 M TEAP) of (a) 3 mM DTBQ plus 1 mM $[Mn^{II}(DMU)_6](ClO_4)_2$ and (b) cyclic voltammogram after electrolysis of a at −0.72 V vs. SCE (scan rate 0.1 V s^{-1}; Pt electrode (area, 0.23 cm^2)).

An initial negative scan exhibits reduction peaks at −0.24 and −0.60 V; the reverse scan has one-electron oxidation peaks at −0.44, −0.15, and +0.14 V and a two-electron oxidation peak at +0.56 V. Controlled-potential electrolysis establishes that each of the two reduction peaks represents a two-electron process. The redox couple with the reduction peak at −1.50 V and the oxidation peak at −1.25 V is characteristic of the $DTBSQ^{-}\cdot/DTBC^{2-}$ couple in CH_3CN. Controlled-potential electrolysis at −0.71 V requires $^3/_2$ electrons per DTBQ (4.5 total) and results in a dark blue solution. Figure 3b illustrates the cyclic voltammogram of the electrolysis product. The peaks are shifted positively relative to those in DMF, and a new peak appears at −1.38 V with a peak height equivalent to a one-electron reduction.

Optical Spectroscopy. The UV–visible spectra of DTBQ,[44] $DTBSQ^{-}\cdot$,[44] $DTBCH_2$,[44] $Mn^{III}(DTBC)_3^{3-}$,[22] and $Mn^{IV}(DTBC)_3^{2-}$[22] have been presented previously. Figure 4 illustrates spectra for the product solutions that result after controlled-potential electrolysis at −0.65 V of adducts with 1:3 and 1:2 mole ratios of $[Mn^{II}(DMU)_6](ClO_4)_2$–DTBQ. The product solution from reduction of the 1:3 adduct is identical with that of the $Mn^{IV}(DTBC)_3^{2-}$ complex.[22] The absorption bands at 305 (ε 19200) and 580 nm (ε 1410) correspond to a ligand π → π* transition (similar to those observed with other metal catechol complexes[49–51]) and a ligand-to-metal charge-transfer band, respectively. The light green product solution from reduction of the 1:2 adduct has an absorption band at 285 nm (ε 20 100), which appears to be due to a π → π* transition. Reduction at −0.65 V of a 1:1 Mn^{II}–DTBQ solution yields a product whose spectrum is identical with that for the 1:2 reduction product, but half as intense. This corresponds to the formation of 0.5 equiv of $Mn^{III}(DTBC)_2^{-}$ (with half of the Mn^{II} as the free ion).

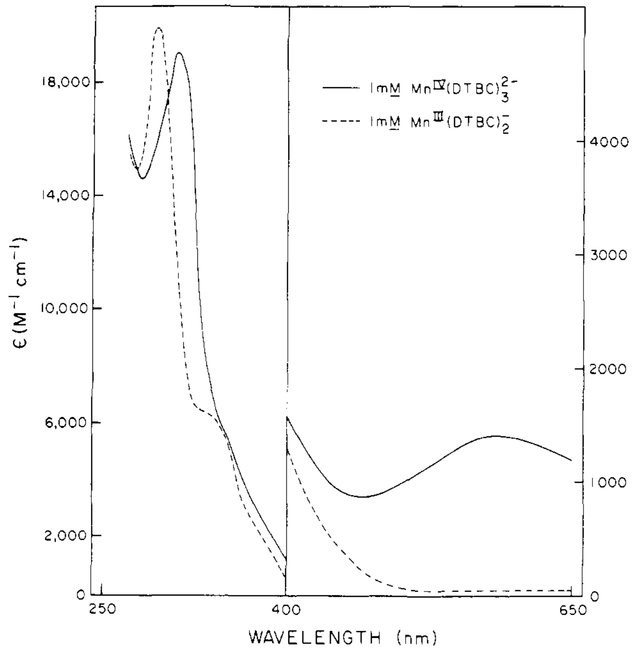

Figure 4. Absorption spectra in DMF (0.1 M TEAP) for the product solutions from controlled-potential electrolysis at −0.65 V vs. SCE $[Mn^{II}(DMU)_6](ClO_4)_2$–DTBQ mixtures with mole ratios of (a) 1:3 (equivalent to $[Mn^{IV}(DTBC)_3]^{2-}$) and (b) 1:2 (equivalent to $[Mn^{III}(DTBC)_2^{-}]$). Each solution had an initial concentration of 1 mM $[Mn^{II}(DMU)_6](ClO_4)_2$. The molar absorptivities, ε, are in relation to the total manganese concentration.

When 1–3 equiv of $DTBSQ^{-}\cdot$ are added to 1 equiv of Mn^{II}, the resulting solution has a new absorption peak at 400 nm that is due to free DTBQ.[44] In each instance, the height of this peak corresponds to a conversion to DTBQ of about half of the original $DTBSQ^{-}\cdot$. Similar results are obtained in DMF, Me_2SO, and CH_3CN.

Magnetic Measurements. The magnetic moment for a solution that contains 10 mM $[Mn^{II}(DMU)_6](ClO_4)_2$ and 20 mM DTBQ in DMF is 6.1 μ_B, as expected for a high-spin (d^5) manganese(II) ion. After electrolytic reduction of this 1:2 system at −0.65 V vs. SCE, the magnetic moment is 5.0 μ_B, which is characteristic of a high-spin (d^4) Mn^{III} complex. Reduction of −0.65 V of the 1:3 Mn^{II}–DTBQ system yields a dark blue solution that has a magnetic moment of 3.9 μ_B, which is consistent with high-spin (d^3) Mn(IV). Reduction of a $Mn^{IV}(DTBC)_3^{2-}$ solution at −1.40 V vs. SCE yields a product with a magnetic moment of 5.1 μ_B.

ESR Spectroscopy. The ESR spectra (prior to electrolysis of the 1:2 and 1:3 Mn^{II}-to-DTBQ solutions exhibit the typical manganese(II) d^5 signal. Controlled-potential electrolysis of these solutions at −1.40 and at −0.40 V results in products that are ESR silent at 77 K. The ESR spectrum and data for the $Mn^{IV}(DTBC)_3^{2-}$ and $Mn^{III}(DTBC)_3^{3-}$ complexes have been discussed previously.[22]

Discussion and Conclusions

On the basis of the experimental results, a self-consistent set of redox and formation reactions for the manganese–catechol and manganese–semiquinone systems can be formulated; these are summarized in Table I. The 1.5 electrons

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Table I. Redox Reactions for the Manganese 3,5-Di-*tert*-butylcatecholato Complexes and Their Formation from Reduction of 3,5-Di-*tert*-butyl-*o*-quinone[a]

eq	reaction	$E°$	$E_{p,c}$	$E_{p,a}$
1	$DTBQ + e^- \rightleftarrows DTBSQ^-$	−0.44	−0.55	
2	$DTBSQ^- + e^- \rightleftarrows DTBC^{2-}$	−1.17	−1.33	
3	$Mn^{II} + DTBCH_2 + 2OH^- \rightarrow Mn^{II}DTBC{\cdot}2H_2O$			
4	$2Mn^{II} + 2DTBQ + 3e^- \rightarrow Mn^{III}(DTBC)_2^- + Mn^{II}$		−0.46	
5	$Mn^{II} + 2DTBQ + 3e^- \rightarrow Mn^{III}(DTBC)_2^-$		−0.46	
6	$Mn^{II} + 3DTBQ + 4e^- \rightarrow Mn^{IV}(DTBC)_3^{2-}$		−0.46, −0.49	
7	$Mn^{IV}(DTBC)_3^{2-} + e^- \rightarrow Mn^{III}(DTBC)_3^{3-}$		−1.26	
8	$Mn^{III}(DTBC)_2^- \rightarrow Mn^{II} + 2DTBQ + 3e^-$			+0.17
9	$Mn^{IV}(DTBC)_3^{2-} \rightarrow Mn^{II} + 3DTBQ + 4e^-$			−0.38, +0.17

[a] All in DMF (0.1 M TEAP), with a scan rate of 0.1 V s^{-1} at a platinum electrode (area, 0.23 cm^2).

per DTBQ reduction stoichiometry for the 1:1 Mn^{II}–DTBQ system requires several intermediate steps. Reduction of the quinone occurs first, followed by coordination of two semiquinones to one Mn(II) ion, and subsequent disproportionation of the bound $DTBSQ^-\cdot$ groups (eq 10). The $Mn^{II}(DTBSQ)_2$

$$Mn^{II} + 2DTBQ + 2e^- \xrightarrow{-0.46\ V} Mn^{II}(DTBSQ)_2 \rightarrow Mn^{III}(DTBC)(DTBSQ) \xrightarrow[1e^-]{-0.46\ V} Mn^{III}(DTBC)_2^- \quad (10)$$

species probably is short-lived on the basis of the rapid reaction of Mn^{II} with $DTBSQ^-\cdot$. Reoxidation of the $Mn^{III}(DTBC)_2^-$ complex occurs at a much more anodic potential (+0.44 V), which probably is due to the excess Mn(II) that remains in solution in equilibrium with the $Mn^{III}(DTBC)_2^-$ complex (eq 11). Only with extremely fast scan rates or with excess Mn(II) is an appreciable amount of $Mn^{II}(DTBSQ)^+$ observed in this system.

$$Mn^{III}(DTBC)_2^- + Mn^{II} \rightleftarrows 2Mn^{II}(DTBSQ)^+ \quad (11)$$

Reduction of the 1:2 Mn^{II}–DTBQ system is represented by eq 5 (Table I). Again, the initial formation of $DTBSQ^-\cdot$ results in complexation of Mn(II), which, in turn, is oxidized by a second DTBQ with subsequent electrochemical reduction to the $Mn^{III}(DTBC)_2^-$ complex. During the course of the electrolysis, reversible couples for $DTBQ/DTBSQ^-\cdot$ and $DTBSQ^-\cdot/DTBC^{2-}$ are observed. The redox chemistry of eq 10 and 11 also is a part of this system. Electrolytic reduction of the 1:1 and 1:2 Mn^{II}–DTBQ adducts results in the formation of the $Mn^{III}(DTBC)_2^-$ complex, which has an absorption maximum at 285 nm (ϵ 20 100) and a magnetic susceptibility of 5.0 μ_B.

The 1:3 Mn^{II}–DTBQ system requires 4 electrons per manganese for reduction to the blue $Mn^{IV}(DTBC)_3^{2-}$ complex (eq 6, Table I). An initial negative scan yields two reduction peaks (Figure 1d); the first probably involves converstion of the quinone to a Mn^{II}–DTBSQ complex with subsequent disproportionation of two semiquinones to form a bound catechol and free DTBQ. The second reduction peak is due to reduction of this free quinone.

$$Mn^{II} + 3DTBQ + 3e^- \xrightarrow{-0.46\ V} Mn^{II}(DTBSQ)_3^- \rightarrow (Mn^{III}(DTBC)_2^- + DTBQ) \xrightarrow[-0.49\ V]{1e^-} Mn^{III}(DTBC)_2(DTBSQ)^{2-} \rightarrow Mn^{IV}(DTBC)_3^{2-} \quad (12)$$

Reduction of the $Mn^{IV}(DTBC)_3^{2-}$ complex occurs at −1.25 V vs. SCE to form $Mn^{III}(DTBC)_3^{3-}$. The sodium salt of $Mn^{IV}(DTBC)_3^{2-}$ is reduced at −1.10 V. In both cases the reduction is irreversible; the product species undoubtedly reacts with residual water in the solvent

$$Mn^{IV}(DTBC)_3^{2-} + e^- \xrightarrow{-1.25\ V} Mn^{III}(DTBC)_3^{3-} \xrightarrow{H_2O} Mn^{III}(OH^-)(DTBC)_2^{2-} + DTBCH^- \quad (13)$$

This is confirmed by the anodic peak at −0.17 V, which is observed for a reverse scan and is due to $DTBCH^-$ oxidation.[25]

Electrochemical oxidation of the $Mn^{IV}(DTBC)_3^{2-}$ complex begins with removal of an electron from a bound catechol (−0.38 V); this is followed by a three-electron process at +0.17 V to yield Mn^{II} and DTBQ (eq 8 and 9, Table I). Such a sequence of oxidations is confirmed by spectral and ESR data taken during the course of the electrolysis.

Combination of 3 mol of $DTBSQ^-\cdot$ with 1 mol of Mn^{II} results in 1 mol of the light green $Mn^{III}(DTBC)_2^-$ complex plus 1 mol of free DTBQ. Addition of 1 equiv of electrons (−0.65 V) to this system yields the dark blue $Mn^{IV}(DTBC)_3^{2-}$ complex, which is consistent with the mechanisms of eq 10 and 12. Thus, the $DTBSQ^-\cdot$ groups initially complex Mn(II) and then rapidly disproportionate to form the stable $Mn^{III}(DTBC)_2^-$ complex plus DTBQ. Subsequent reduction forms the final Mn(IV) complex.

The electrochemistry of the manganese–catechol complexes in CH_3CN is different from that in DMF and Me_2SO. The individual redox steps are clearly separated and the intermediate species are sufficiently stabilized to see a cascade of one-electron steps from the $Mn^{IV}(DTBC)_3^{2-}$ complex back to starting materials (Figure 3). Recognition that the redox peaks at +0.55 and +0.03 V are coupled and that the two anodic peaks at −0.11 and +0.17 V are coupled to the cathodic peak at −0.49 V permits a reasonable electron-transfer mechanism to be proposed

$$Mn^{IV}(DTBC)_3^{2-} \xrightarrow{-0.11\ V} Mn^{IV}(DTBC)_2(DTBSQ)^- + e^- \rightarrow Mn^{III}(DTBC)_2^- + DTBQ \xrightarrow{+0.17\ V} Mn^{III}(DTBC)(DTBSQ) + e^- \rightarrow DTBQ + Mn^{II}(DTBC) \xrightarrow{+0.55\ V} Mn^{II} + DTBQ + 2e^- \quad (14)$$

The broad anodic peak at +0.55 V probably represents a two-electron process; it is coupled to the known two-electron cathodic peak at +0.03 V. Although other mechanisms are possible, the reactions of eq 14 take into account the stability of known intermediates and the results of the electrochemistry shown in Figure 3.

This group of Mn(III) and -(IV) complexes are stabilized by strong "hard acid–hard base" interactions between the higher oxidation-state metal ions and the oxo anions of the catechol ligand. The degree of "hardness" is related to the charge density; with large charges and small ionic radii, the electrostatic forces are large.[52] The Mn(II) ion is considered to be fairly soft, intermittent between Zn(II) and Cu(I) ions

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on the basis of their polarizabilities.[53] Therefore, the Mn(III) and Mn(IV) ions are expected to be much harder acids because of their smaller size, their larger charges, and their lower polarizability. The hard nature of the vicinal oxo ions of catechol dianion should make the "hard-hard" interaction with the Mn(IV) ion exceptionally strong. The increased stability of the Mn(III) and Mn(IV) oxidation state in complexes with catechol anions reflect this hard acid-hard base interaction.

Interconversion of the Mn(II), -(III), and -(IV) complexes without the use of OH^- (base) (which competes for metal coordination sites) and in an aprotic medium that resembles the lipid layers of plant cells provides an interesting model system for photosystem II. The fact that this system requires the addition of four electrons to go from the Mn(II)-$(DTBQ)_3$ state to the $Mn^{IV}(DTBC)_3{}^{2-}$ complex is a unique feature. Because the $Mn^{IV}(DTBC)_3{}^{2-}$ complex also reversibly binds O_2 in aprotic media,[21] it may represent an effective activator for oxygenation reactions.

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Registry No. $Na_2[Mn^{IV}(DTBC)_3]$, 72275-17-3; $Ba[Mn^{IV}(DTBC)_3]$, 79299-87-9; Mn, 7439965; DTBQ, 3383-21-9; $DTBSQ^{-\cdot}$, 18802-82-9.

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Photoinduced Dimerization of Macrocyclic Complexes Mediated by a Metal-Assisted Oxidation of the Macrocycle

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The triplet state of benzophenone oxidizes $Ni([14]aneN_4)^{2+}$ to a Ni(III) intermediate which subsequently produces the dimer of the complex as a product. The nature of the product was confirmed by structural studies. $[Ni(13\text{-}At)]^+$ reacts with the triplet of fluorenone and ^2E state of $Cr(bpy)_3{}^{3+}$ forming also a dimer in a reaction that involves different intermediates. Intermediates in the photoinduced oxidations of the macrocycles have been investigated by flash photolysis. The mechanism of the photoinduced oxidation is discussed in terms of the reported properties of the macrocycles.

Introduction

A number of studies on the ligand oxidation of nickel(II) macrocyclic tetraaza complexes have postulated the involvement of nickel(III) intermediates in the reaction.[1-9] Such a participation of the tripositive oxidation state of nickel is in agreement with results obtained by electrochemical and reaction kinetic techniques.[1-5,10-13] Indeed, the study of the transformations of nickel(III) macrocycles by stop-flow, pulse radiolysis and flash photolysis has revealed several points of interest in their chemical reactivity. That the coordination of acido ligands, e.g., Cl^-, Br^-, and SCN^-, in the axial positions of the complex enhances the thermodynamic and kinetic stability of the nickel(III) species has been demonstrated in several studies.[10,12,14] Moreover, the hydrolysis of the coordinated acido ligands is a slow process. Rate constants $k \leq 20\ s^{-1}$ have been reported for such hydrolysis.[12,14,15] The dehydrogenation of the macrocycle, induced by nickel(III) intermediates, is a base-assisted process. Hence, the generation of nickel(II)-ligand radicals from nickel(III) intermediates seems to be controlled by the deprotonation of the macrocycle.[10,12,16] A mechanism for the oxidative dehydrogenation can be summarized by means of eq 1-4. The species [O], eq 1, represents the electrochemical or chemical oxidant, namely, Ce^{IV}, Cl_2^-, Br_2^-, $(SCN)_2^-$, and Br_2. The dehydrogenation process can be explained in terms of the oxidation of the Ni(II)-ligand radical by excess oxidant (eq 5), the disproportionation of the Ni(II)-ligand radical (eq 6), and reaction between Ni(II)-ligand radicals and excess Ni(III) species (eq 7). Ligand degradation products and Ni(II) can also be produced in reactions 5-7.

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