3692 *Inorg. Chem.* **1982**, *21*, 3692-3698

Contribution from the Department of Chemistry,
University of California, Riverside, California 92521

Redox Chemistry of Metal–Catechol Complexes in Aprotic Media. 3. 3,5-Di-*tert*-butylcatecholato and *o*-Semiquinonato Complexes of Iron(III)

STEPHEN E. JONES, LUIS E. LEON, and DONALD T. SAWYER*

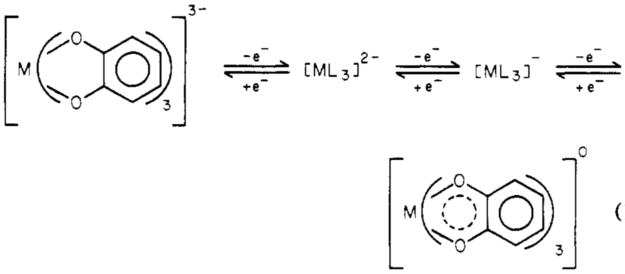
Received October 20, 1981

When mixtures of iron(II) or iron(III) and 3,5-di-*tert*-butyl-*o*-quinone (DTBQ) with mole ratios of 1:2 and 1:3 are reduced in aprotic solvents, iron(III)–semiquinone complexes are formed initially, but in acetonitrile, dimethylformamide, or dimethyl sulfoxide media, these disproportionate to give free quinone and iron(III)–catechol–semiquinone and iron(III)–catechol complexes. In dimethylformamide and dimethyl sulfoxide binuclear μ-oxo-bridged complexes result because of the strongly acidic iron species and the water present in these solvents. The complexes and their oxidation–reduction products have been characterized by cyclic voltammetry, controlled-potential electrolysis, optical spectroscopy, and magnetic susceptibility measurements. On the basis of these results, self-consistent redox mechanisms are presented for the interconversion of the various species of the iron(II)–DTBQ and iron(III)–DTBQ systems with mole ratios of 1:1, 1:2, and 1:3.

The interaction of iron with catechol derivatives has been a major interest of several groups.[1-13] Such systems represent models for biological transport of iron, particularly for the enterobactin series of siderophores.[14-17] The role of catecholato complexes in iron transport has been discussed in detail.[18-21] The enterobactins are cyclic triesters of (2,3-dihydroxy)benzoylserine, which are produced and secreted by microorganisms to achieve an adequate uptake of iron. In an aerobic environment, the amount of iron present in aqueous systems is severely limited by the low solubility of ferric hydroxide (10^{-18} M at pH 7).[22] The extremely high stability of the ferric siderophores (ferric enterobactin has a stability constant near 10^{52})[16] allows microorganisms to overcome severe iron stress.

The redox chemistry of metal–catecholato complexes involves electron transfer within the quinone–semiquinone–catechol system.[23-28] The effectiveness of each of these ligands for metals such as manganese,[28-33] molybdenum,[34-40] and vanadium[41-43] is dominated by a "hard base–hard acid" interaction of the oxoanions on the ligand and the highest available oxidation state of the metal.

Raymond and co-workers have proposed that the tris(catecholato) complex of a trivalent metal ion such as Fe(III) undergoes a series of reversible redox reactions (eq 1).[24] To



(1)

---

(1) Buchanan, R. M.; Kessel, S. L.; Downs, H. H.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 7894.

(2) Brown, D. G.; Johnson, W. L., III. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 712.

(3) Tyson, C. A.; Martell, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 3379.

(4) Mentasti, E.; Pelizzetti, E.; Saini, G. *J. Inorg. Nucl. Chem.* **1976**, *38*, 785.

(5) Avdeef, A.; Sofen, S. R.; Bregante, T. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 5362.

(6) Raymond, K. N.; Isied, S. S.; Brown, L. D.; Fronczek, F. R.; Nibert, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 1767.

(7) Carrano, C. J.; Raymond, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 5401.

(8) Que, L., Jr.; Lipscomb, J. D.; Munck, E.; Wood, J. M. *Biochim. Biophys. Acta* **1977**, *485*, 60.

(9) Que, L., Jr.; Lipscomb, J. D.; Zimmerman, R.; Munck, E.; Orme-Johnson, W. H.; Orme-Johnson, N. R. *Biochim. Biophys. Acta* **1976**, *452*, 320.

(10) Wrobleski, J. T.; Brown, D. B. *Inorg. Chem.* **1979**, *18*, 2738.

(11) Wrobleski, J. T.; Brown, D. B. *Inorg. Chem.* **1979**, *18*, 498.

(12) Buchanan, R. M.; Downs, H. H.; Shorthill, W. B.; Pierpont, C. G.; Kessel, S. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 4318.

(13) McBryde, W. A. E. *Can. J. Chem.* **1964**, *42*, 1917.

(14) Cooper, S. R.; McArdle, J. V.; Raymond, K. N. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3551.

(15) Harris, W. R.; Carrano, C. J.; Raymond, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 2722.

(16) Harris, W. R.; Carrano, C. J.; Cooper, S. R.; Sofen, S. R.; Avdeef, A. E.; McArdle, J. V.; Raymond, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 6097.

(17) Raymond, K. N.; Carrano, C. J. *Acc. Chem. Res.*, **1979**, *12*, 183.

(18) Weitl, F. L.; Harris, W. R.; Raymond, K. N. *J. Med. Chem.* **1979**, *22*, 1281.

(19) Neilands, J. B., Ed. "Microbian Iron Metabolism"; Academic Press: New York, 1974.

(20) Llinas, M.; Wilson, D. M.; Neilands, J. B. *Biochemistry* **1973**, *12*, 3836.

(21) Carrano, C. J.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 5371.

(22) Biedermann, G.; Schindler, P. *Acta Chem. Scand.* **1957**, *11*, 731.

(23) Stallings, M. D.; Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1981**, *20*, 2655.

(24) Sofen, S. R.; Ware, D. C.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 234.

(25) Carrano, C. J.; Cooper, S. R.; Raymond, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 599.

(26) Goel, R. G.; Henry, P. M.; Polyzou, P. C. *Inorg. Chem.* **1979**, *18*, 2148.

(27) Downs, H. H.; Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1736.

(28) Jones, S. E.; Chin, D. H.; Sawyer, D. T. *Inorg. Chem.* **1981**, *20*, 4257.

(29) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 989.

(30) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *Inorg. Chem.* **1978**, *17*, 515.

(31) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *Inorg. Chem.* **1980**, *19*, 492.

(32) Grinstead, R. R. *Biochemistry* **1964**, *3*, 1308.

(33) Tyson, C. A.; Martell, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 939.

(34) Mentasti, E.; Pellizzetti, E.; Pramaurd, E.; Girandi, G. *Inorg. Chim. Acta* **1975**, *12*, 61.

(35) Scharff, J. P.; Genin, R. *Anal. Chim. Acta* **1975**, *78*, 201.

(36) Wilshire, J. P.; Leon, L.; Bosserman, P.; Sawyer, D. T. *J. Am. Chem. Soc.* **1979**, *101*, 3381.

(37) Liu, S. T.; Kustin, K. *J. Am. Chem. Soc.* **1973**, *95*, 2487.

(38) Soni, R. N.; Bartusek, M. J. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2557.

(39) Henry, R. P.; Mitchell, P. C. H.; Prue, J. E. *J. Chem. Soc., Dalton Trans.* **1973**, 1156.

(40) Pierpont, C. G.; Buchanan, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 6450.

(41) Kustin, K.; Liu, S.; Nicolini, C.; Toppen, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 7410.

(42) Henry, R. P.; Mitchell, P. C. H.; Prue, J. E. *J. Chem. Soc. A* **1971**, 3392.

(43) Wilshire, J. P.; Sawyer, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 3972.

0020-1669/82/1321-3692$01.25/0 © 1982 American Chemical Society

date only the Cr(III)–catechol system appears to obey this rigidly,[24,27] but an analogous redox sequence has been proposed for the Fe(III)–catechol system to yield semiquinone complexes.[2,44,46] Such complexes of cobalt have been observed.[47,48]

The previous paper in this series[28] has shown that a general pattern exists for first-row transition metals such as manganese and iron. During the process of reductive electrolysis of quinones (3,5-di-*tert*-butyl-*o*-quinone (DTBQ)) in the presence of divalent transition metals (or by addition of semiquinone (DTBSQ)), intramolecular homogeneous electron transfer occurs if the metal has available electrons to donate. The 1:2 metal–quinone reaction system is reduced via a series of steps (eq 2). Likewise, for the 1:3 metal–quinone system the sequence is shown in eq 3. The metal–semiquinone complex rapidly disproportionates to a metal–catechol–semiquinone complex and, in the case of the 1:3 system, free quinone. In all cases quinone or semiquinone is the electroactive substrate and *reduction* promotes the *oxidation* of the transition-metal ion.

$$M^{II} + 2DTBQ \xrightarrow{2e^-} M^{II}(DTBSQ)_2 \xrightarrow{fast} M^{III}(DTBC)(DTBSQ) \xrightarrow{1e^-} M^{III}(DTBC)_2^- \qquad (2)$$

$$M^{II} + 3DTBQ \xrightarrow{3e^-} M^{II}(DTBSQ)_3^- \xrightarrow{fast} M^{III}(DTBC)_2^- + DTBQ \xrightarrow{1e^-} M^{III}(DTBC)_2(DTBSQ)^{2-} \qquad (3)$$

Hydrolysis,[49-53] polymerization,[54,55] and dimer formation[56-59] via μ-oxo bridges are important characteristics of iron(III) in solution. Although solutions of ferric perchlorate in methanol, dimethyl sulfoxide, and acetonitrile are mainly monomeric,[52] addition of water causes their molar magnetic susceptibility to decrease. This appears to be the result of hydrolysis and dimerization via hydroxo and oxo bridging. On the basis of pH,[60] infrared,[52] and NMR[61] measurements there is evidence for the formation of polymeric species as well.[50,52,62]

The present investigation summarizes the results of electrochemical, spectroscopic, and magnetic studies of the iron(II) and iron(III) complexes with 3,5-di-*tert*-butylcatechol (DTBC) and 3,5-di-*tert*-butyl-*o*-semiquinone (DTBSQ) in three aprotic solvents. Detailed electron-transfer reactions are proposed for the formation and interconversion of these complexes.

Experimental Section

Equipment. A three-electrode potentiostat (Princeton Applied Research Model 173 potentiostat/galvanostat with a Model 175 universal programmer and Model 179 digital coulometer) was used for the cyclic voltammetric and controlled-potential electrolysis experiments. Synthesis by controlled-potential electrolysis made use of a Bioanalytical Systems Model SP-2 potentiostat. Cyclic voltammograms were recorded on a Houston Instruments Series 200 recorder. The scans were initiated at the rest potential of each solution.

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 aqueous tetramethylammonium chloride solution and adjusted to 0.000 V vs. SCE.[63] 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. All of the electrochemical electrodes and degassing apparatus were contained inside a Brinkman electrochemical cell equipped with an O-ring seal.

Cary Model 17D and Model 219 spectrophotometers were used for UV–visible spectrophotometric measurements. The magnetic susceptibility measurements were made with a Varian EM-390 NMR spectrophotometer by the method of Evans[64] as modified by Rettig[65] and made use of the paramagnetic shift of the methyl protons of the Me_2SO, DMF, and CH_3CN solvents as the measured NMR parameter. For solid samples the susceptibilities were determined by the Faraday method on a Cahn Model 2000 balance. Three relations were used to calculate the magnetic moments (μ_B) from the measured susceptibilities given in eq 4–6, where χ_M is the molar susceptibility,

$$\chi_M = \frac{3}{2\pi}\left(\frac{\Delta f}{f}\right)\frac{(\text{mol wt of complex})}{(\text{g of complex/mL})} = \frac{3}{2\pi}\left(\frac{\Delta f}{f}\right)\frac{1000}{M} \qquad (4)$$

$$\chi_M' = \chi_M + \chi_D \qquad (5)$$

$$\mu_B = 2.84(\chi_M'T)^{1/2} \qquad (6)$$

f the NMR spectrometer frequency, Δf the difference in the reference-peak frequencies, M the molarity of the complex (the systems were assumed to be mononuclear in iron), χ_D the diamagnetic correction, and T the temperature of the NMR probe (304 K).

Reagents. Dimethyl sulfoxide (Me_2SO), *N,N*-dimethylformamide (DMF), acetonitrile (CH_3CN), and methylene chloride (CH_2Cl_2) (all Burdick and Jackson Laboratories "distilled in glass")[66] were used as received for the studies in the solution phase. Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP) (G. Frederick Smith) were used as supporting electrolytes in the electrochemical studies. The solutions of iron(II) and iron(III) ions for the electrochemical studies were prepared from $Fe^{II}(ClO_4)_2 \cdot 6H_2O$ and $Fe^{III}(ClO_4)_3 \cdot 6H_2O$ (G. Frederick Smith). Both solids were vacuum-dried at room temperature before use. 3,5-Di-*tert*-butylcatechol ($DTBCH_2$), 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ), and tetramethylammonium chloride were obtained from the Aldrich Chemical Co. and tetraethylammonium hydroxide (TEA(OH)) from Eastman Kodak Co. as a 25% solution in methanol (1.42 M OH^- on the basis of a titration). $Fe^{II}Cl_2 \cdot 4H_2O$ was purchased from Mallinckrodt; prior to use it was dissolved in ethanol and the solution was filtered. High-purity argon gas (presaturated by passage through the solvent–electrolyte solution) was used to deaerate the sample solutions.

The solutions for electrochemical studies were prepared with 0.1 M tetraethylammonium perchlorate (TEAP) as the supporting electrolyte and Me_2SO, DMF, and CH_3CN as the solvents. In the case of CH_2Cl_2, 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) was used as supporting electrolyte. All of the solutions for electrochemical and NMR measurements contained 1 mM iron and 5 mM iron, respectively. The solutions were prepared in situ by the com-

---

(44) Buchanan, R. M.; Kessel, S. L.; Downs, H. H.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 7894.

(45) Razuvaev, G. A.; Shal'nova, K. G.; Abakumiva, L. G.; Abakumov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977** (7), 1642.

(46) Lauffer, R. B.; Heistand, R. H., II; Que, L., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 3947.

(47) Buchanan, R. M.; Pierpont, C. G.; Fitzgerald, B. J. *Inorg. Chem.* **1979**, *18*, 3439.

(48) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951.

(49) Leffler, A. J. *Inorg. Chem.* **1979**, *18*, 2529.

(50) Spiro, T. G.; Allerton, S. E.; Renner, J.; Terzis, A.; Bils, R.; Saltman, P. *J. Am. Chem. Soc.* **1966**, *88*, 2721.

(51) Milburn, R. M.; Vosburgh, W. C. *J. Am. Chem. Soc.* **1955**, *77*, 1352.

(52) Gustafson, R. L.; Martell, A. E. *J. Phys. Chem.* **1963**, *67*, 576.

(53) Ehman, D. L.; Sawyer, D. T. *Inorg. Chem.* **1969**, *8*, 900.

(54) Wrobleski, J. T.; Brown, D. B. *Inorg. Chem.* **1979**, *18*, 2738.

(55) Wrobleski, J. T.; Brown, D. B. *Inorg. Chem.* **1979**, *18*, 498.

(56) Wilkins, R. G.; Yelin, R. E. *Inorg. Chem.* **1969**, *8*, 1470.

(57) Schugar, H.; Walling, C.; Jones, R. B.; Gray, H. B. *J. Am. Chem. Soc.* **1967**, *89*, 3712.

(58) Schugar, H. J.; Hubbard, A. T.; Anson, F. C.; Gray, H. B. *J. Am. Chem. Soc.* **1969**, *90*, 71.

(59) Schugar, H. J.; Rossman, G. R.; Barraclough, C. G.; Gray, H. B. *J. Am. Chem. Soc.* **1972**, *94*, 2683.

(60) Mulay, L. N.; Selwood, P. W. *J. Am. Chem. Soc.* **1955**, *77*, 2693.

(61) Broersma, S. *J. Chem. Phys.* **1957**, *26*, 1405.

(62) Zuyagintsev, O. E.; Lopatto, Y. S. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1961**, *6*, 439.

(63) Sawyer, D. T.; Roberts, J. L., Jr. "Experimental Electrochemistry for Chemists"; Wiley-Interscience: New York, 1974; pp 144–145.

(64) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(65) Rettig, M. F., University of California, Riverside, CA, private communication.

(66) Manufacturer's specified water content: Me_2SO, 0.020%; DMF, 0.018%; CH_3CN, 0.004%; CH_2Cl_2, 0.007%.

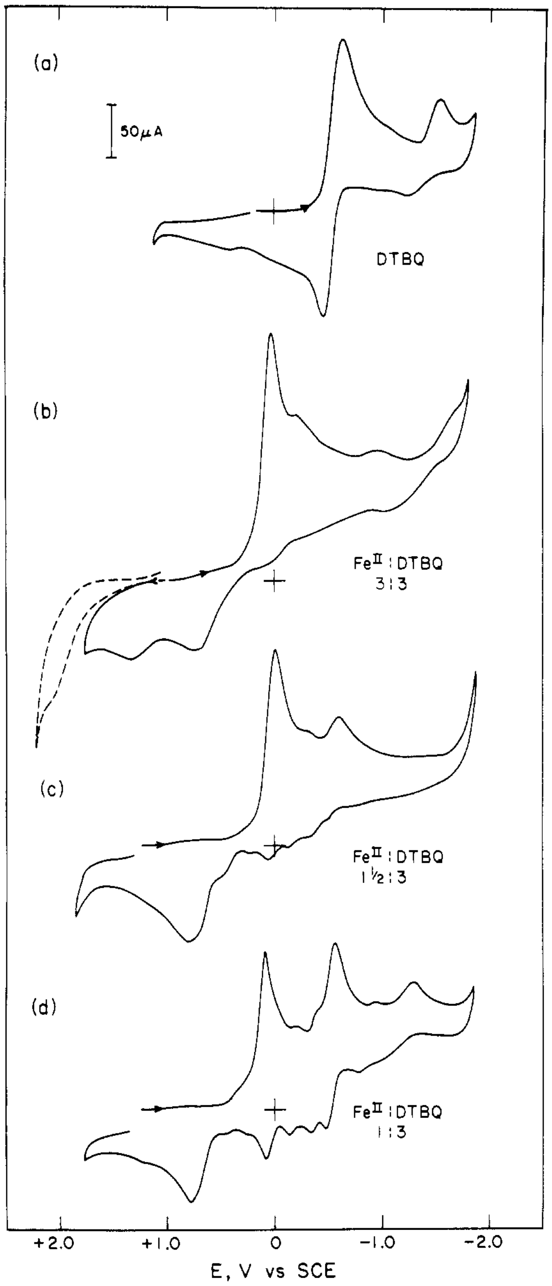


Figure 1. Cyclic voltammograms in acetonitrile (CH_3CN) (0.1 M tetraethylammonium perchlorate, TEAP) of (a) 3.0 mM 3,5-di-*tert*-butyl-*o*-quinone (DTBQ), (b) 3.0 mM DTBQ plus 3.0 mM $[Fe^{II}(H_2O)_6](ClO_4)_2$, (c) 3.0 mM DTBQ plus 1.5 mM $[Fe^{II}(H_2O)_6](ClO_4)_2$, and (d) 3.0 mM DTBQ plus 1.0 mM $[Fe^{III}(H_2O)_6](ClO_4)_2$. The scan rate was 0.1 V s^{-1}, and a Pt electrode (area 0.23 cm^2) was used.

bination of either $Fe^{II}(ClO_4)_2$ or $Fe^{III}(ClO_4)_3$ and DTBQ in mole ratios of 1:1, 1:2, and 1:3 in 50 mL of deaerated supporting electrolyte solution. Iron(III)–catecholate solutions were prepared in situ from $Fe^{III}(ClO_4)_3$, $DTBCH_2$, and TEA(OH) in mole ratios of 1:1:2, 1:2:4, and 1:3:6 in 50 mL of deaerated supporting electrolyte or by exhaustive controlled-potential electrolysis at −0.65 V vs. SCE of iron(II)–quinone systems. The 3,5-di-*tert*-butyl-*o*-semiquinone anion radical ($DTBSQ^{-}\cdot$) was formed in CH_3CN, DMF, or Me_2SO by controlled-potential electrolysis of DTBQ at −0.65 V vs. SCE and in CH_2Cl_2 by reduction at −0.80 V vs. SCE. Synthesis of the tris(3,5-di-*tert*-butyl-*o*-semiquinonato)iron(III) complex ($Fe(DTBSQ)_3$) was accomplished by previous methods.[2,67] The complex was identified by its infrared and UV–visible spectra.[2]

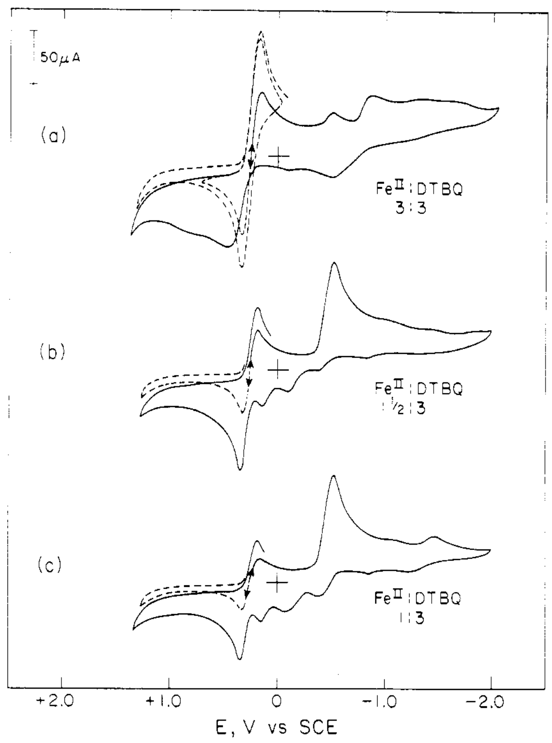


Figure 2. Cyclic voltammograms in dimethyl sulfoxide (Me_2SO) (0.1 M TEAP) of (a) 3.0 mM DTBQ plus 3.0 mM $[Fe^{II}(H_2O)_6](ClO_4)_2$, (b) 3.0 mM DTBQ plus 1.5 mM $[Fe^{II}(H_2O)_6](ClO_4)_2$, and (c) 3.0 mM DTBQ plus 1.0 mM $[Fe^{II}(H_2O)_6](ClO_4)_2$. The scan rate was 0.1 V s^{-1}, and a Pt electrode (area 0.23 cm^2) was used.

Results

Electrochemistry. Reduction of 3,5-di-*tert*-butyl-*o*-quinone (DTBQ) in the presence of equimolar, or less, quantities of $[Fe^{II}(H_2O)_6](ClO_4)_2$ provides insight to the formation of iron–catechol and –semiquinone complexes and a means to their electrosynthesis and characterization. Figure 1 illustrates the electrochemistry of 1:1, 1:2, and 1:3 mole ratios of $[Fe^{II}(H_2O)_6](ClO_4)_2$ to DTBQ in CH_3CN as well as the redox behavior of free DTBQ. The anodic peaks that result from a reverse scan for these cyclic voltammograms represent the oxidation of the bound catecholato and bound semiquinonato species of the product complexes. Controlled-potential electrolysis of 1:1 and 1:2 Fe(II)–DTBQ solutions at −0.65 V vs. SCE requires 1.5 electrons per quinone in each case.

The product solutions do not exhibit any additional reductions out to the solvent limit (about −1.8 V vs. SCE). Controlled-potential electrolysis at −0.65 V for the 1:3 Fe(II)–DTBQ solution requires 5 electrons per three DTBQ molecules, and there are no additional reduction peaks out to −2.0 V.

The electrochemistry for the iron(II)–DTBQ systems in Me_2SO is significantly different from that in CH_3CN, as illustrated by Figure 2. Controlled-potential electrolysis of the 1:1 and 1:2 Fe(II)–DTBQ solutions at −0.65 V also requires 1.5 electrons per quinone, while the 1:3 Fe(II)–DTBQ solution consumes 4 electrons.

The electrochemistry for the 1:2 and 1:3 Fe(II)–DTBQ combinations in DMF is illustrated by Figure 3. The redox activity in DMF is poorly defined and represents a complex mixture of several different species. Similar electrochemistry is observed in Me_2SO if OH^- is added to a 1:3 combination of Fe(II) and 3,5-di-*tert*-butylcatechol ($DTBCH_2$). This, as well as the reduced magnetic susceptibility for such combinations in DMF, is consistent with dimerization equilibria.

If an iron(III) salt is used in CH_3CN, Me_2SO, or DMF instead of Fe(II), an additional reduction peak appears for the

---

(67) Kuz'min, V. A.; Khudyakov, I. V.; Popkov, A. V.; Karoli, L. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 2431.

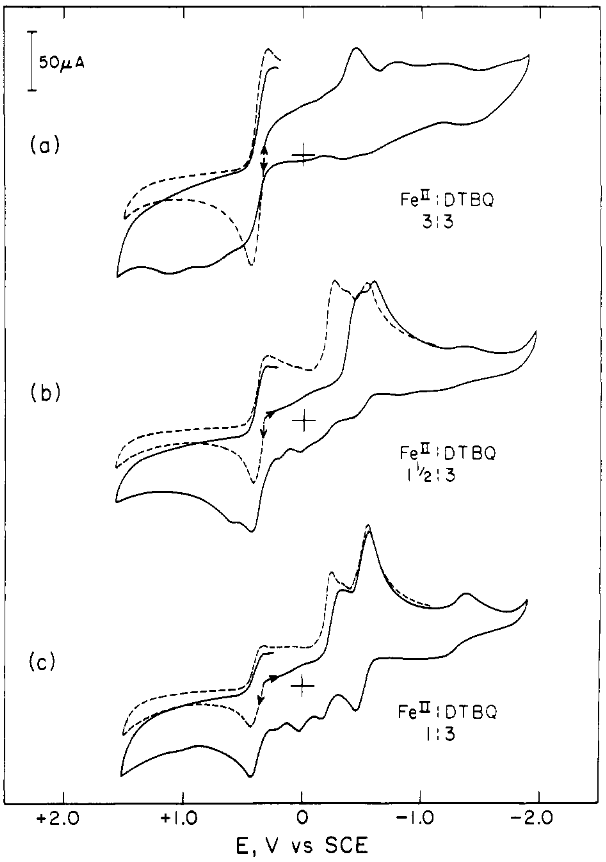


Figure 3. Cyclic voltammograms in dimethylformamide (DMF) (0.1 M TEAP) of (a) 3.0 mM DTBQ plus 3.0 mM $[Fe^{II}(H_2O)]_6(ClO_4)_2$, (b) 3.0 mM DTBQ plus 1.5 mM $[Fe^{II}(H_2O)_6](ClO_4)_2$, and (c) 3.0 mM DTBQ plus 1.0 mM $[Fe^{II}(H_2O)_6](ClO_4)_2$. The scan rate was 0.1 V s^{-1} and a Pt electrode (area 0.23 cm^2) was used.

initial negative scan; its potential becomes more negative as the ratio of DTBQ to Fe(III) is increased (about 20 mV/equiv of DTBQ). If Fe(III) is used in place of Fe(II), the controlled-potential reductions require one more electron per iron for each of the 1:1, 1:2, and 1:3 iron–DTBQ systems.

Figure 4 illustrates the cyclic voltammograms for the tris(3,5-di-*tert*-butyl-*o*-semiquinonato)iron(III) complex ($Fe^{III}(DTBSQ)_3$) in CH_2Cl_2, CH_3CN, DMF, and Me_2SO, respectively. A color change does not occur upon dissolution of $Fe^{III}(DTBSQ)_3$ in CH_2Cl_2, and this cyclic voltammogram appears to represent the electrochemistry for the intact complex. When $Fe^{III}(DTBSQ)_3$ is added to a deaerated solution of supporting electrolyte in CH_3CN, it dissolves extremely slowly. The material that does dissolve changes color and appears to be a decomposition product. Addition of $Fe^{III}(DTBSQ)_3$ to deaerated DMF or Me_2SO results in an immediate color change, and the material dissolves readily. The cyclic voltammograms for these solutions (Figure 4c,d) can be duplicated by a 2-electron controlled-potential reduction at −0.65 V of a solution that contains a 1:3 mole ratio of Fe(II):DTBQ or by the addition of 3 equiv of $DTBSQ^{-}\cdot$ to 1 equiv of $[Fe^{III}(H_2O)_6](ClO_4)_3$. When 1 equiv of $DTBSQ^{-}\cdot$ is added to Fe(II) in Me_2SO, a cyclic voltammogram similar to that of Figure 2a is obtained but without the peak at −0.50 V.

Optical Spectroscopy. Figure 5 illustrates the UV–visible spectra for several Fe(III)–catecholate complexes in Me_2SO. The UV–visible spectra for DTBQ,[23] $DTBCSQ^{-}\cdot$,[23] $DTBCH_2$,[23] and $Fe^{III}(DTBSQ)_3$[2] have been presented previously. Additional spectroscopic parameters for the various iron–catecholate and –semiquinonato systems in several solvents are summarized in Table I. The $Fe^{III}(DTBSQ)_3$ complex in

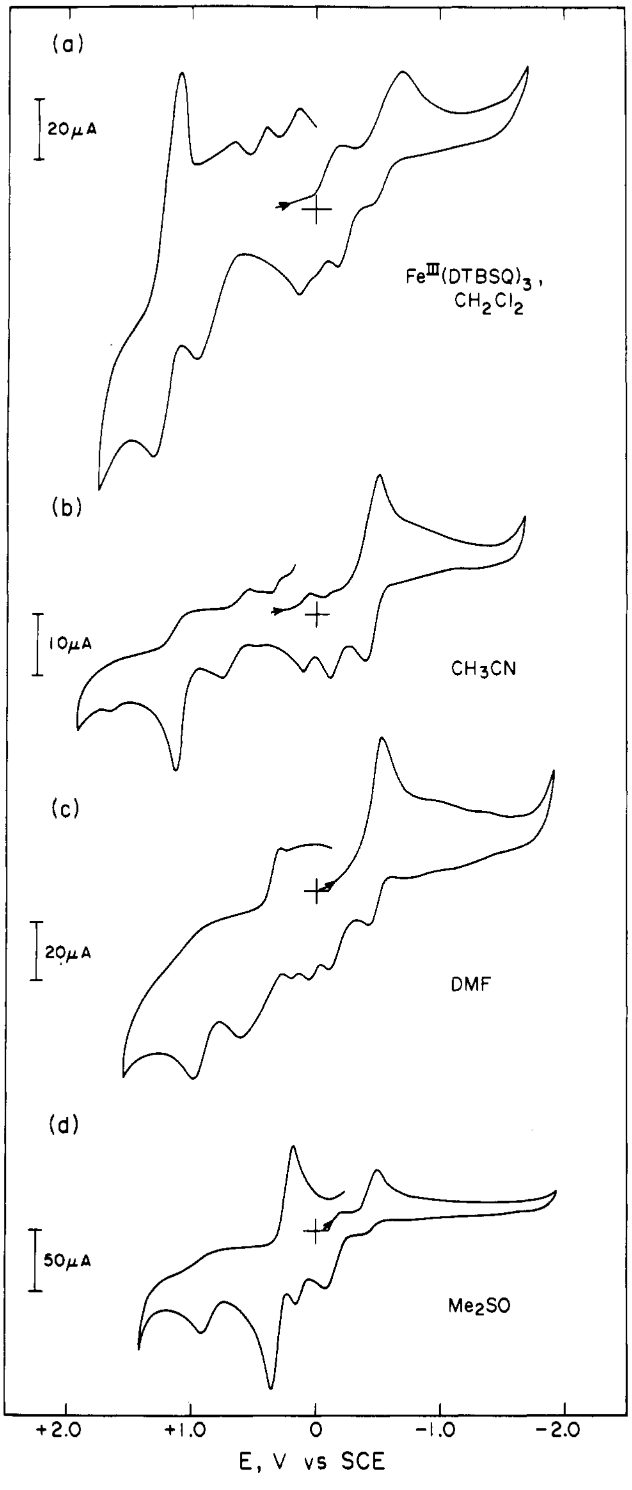


Figure 4. Cyclic voltammograms of 1.0 mM tris(3,5-di-*tert*-butyl-*o*-semiquinonato)iron(III) in (a) CH_2Cl_2 (0.1 M TBAP), (b) CH_3CN (0.1 M TEAP), (c) DMF (0.1 M TEAP), and (d) Me_2SO (0.1 M TEAP). The scan rate was 0.1 V s^{-1}, and a Pt electrode (area 0.23 cm^2) was used.

CH_2Cl_2 exhibits an absorption spectrum that is the same as for the known compound in pentane.[2] However, in CH_3CN, DMF, and Me_2SO the $Fe^{III}(DTBSQ)_3$ complex undergoes decomposition. The 1:3 adduct that is formed after controlled-potential electrolysis at −0.65 V appears to have the same formula and structure in all three solvent systems (CH_3CN, DMF, and Me_2SO). The absorption bands between 290 and 304 nm are due to ligand $\pi \rightarrow \pi^*$ transitions and those between 350 and 700 nm to ligand-to-metal charge-transfer bands. These assignments are similar to those for other

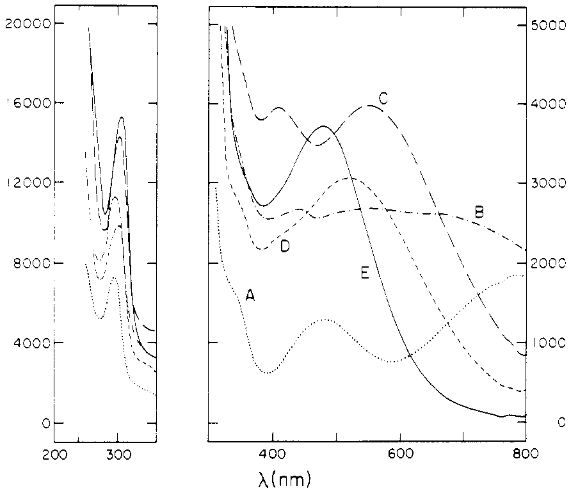


Figure 5. UV–visible spectra for the Me_2SO solutions that result when iron(II) and 3,5-di-*tert*-butyl-*o*-semiquinone (DTBSQ$^-$·) are combined in mole ratios of (A) 1:1, (B) 1:2, and (C) 1:3 (yields [Fe^{III}(DTBC)$_2^-$ + DTBQ]) and when iron(III) and 3,5-di-*tert*-butylcatechol dianion (DTBC^{2-}) are combined in mole ratios of (D) 1:2 (yields [Fe^{III}(DTBC)$_2$]$^-$) and (E) 1:3 (yields [Fe^{III}(DTBC)$_3$]$^{3-}$).

Table I. Spectroscopic Absorption Parameters for Iron(III)–Semiquinonato and Iron(III)–Catecholato Complexes in Methylene Chloride (CH_2Cl_2), Dimethyl Sulfoxide (Me_2SO), Dimethylformamide (DMF), and Acetonitrile (CH_3CN)

compd	solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})		
		I. Semiquinonato Complex		
Fe^{III}(DTBSQ)$_3$	CH_2Cl_2	300 (17 000)	378 (6170), 430 (sh)	640 (4130)
	CH_3CN	284, 296 (sh)	384	620
	Me_2SO	290	400	
	DMF	286	298	590
		II. Electrolysis Products^a		
		1:3 Fe(II)–DTBQ		
[Fe^{III}(DTBC)$_2$-DTBSQ)]$^{2-}$	CH_3CN	302 (23 000)		436 (5490)
	Me_2SO	303 (15 300)		475 (3730)
	DMF	303 (16 000)		482 (4940)
		1:2 Fe(II)–DTBQ		
[Fe^{III}(DTBC)$_2$]$^-$	CH_3CN	293		570
	Me_2SO	300, 340 (sh)		520
	DMF	295		560
		1:1 Fe(II)–DTBQ		
	CH_3CN	280		542
	Me_2SO	293		480
	DMF	285		560

^{a} From reduction at −0.65 V vs. SCE.

metal–catechol complexes.[2,3,31,36,68–72]

When 3 equiv of DTBSQ$^-$· is added to 1 equiv of Fe(III) in CH_2Cl_2, CH_3CN, DMF, or Me_2SO, they give essentially the same absorption spectra as if Fe^{III}(DTBSQ)$_3$ had been added to these solvents. The absorption peak at 400 nm for the latter three solvents is due to free DTBQ.[23] In all three cases, the peak height of 400 nm corresponds to the conversion of about 1 equiv of DTBSQ$^-$· to DTBQ.

Table II. Apparent Magnetic Moments per Iron Ion in Solid and Solution Matrices^a

compd	μ (per iron), μ_B	matrix
		A. Salts
Fe^{II}(H_2O)$_6$(ClO_4)$_2$	4.9	solid
Fe^{III}(H_2O)$_6$(ClO_4)$_3$	5.6	solid
Fe^{II}(H_2O)$_6$(ClO_4)$_2$	4.9	CH_3CN, Me_2SO, DMF
Fe^{II}(H_2O)$_6$(ClO_4)$_2$	4.8	DMF (0.1 M TEAP)
Fe^{II}(H_2O)$_6$(ClO_4)$_2$	4.7	DMF (0.1 M TEAP plus 5 mM DTBQ)
Fe^{III}(H_2O)$_6$(ClO_4)$_3$	5.7	CH_3CN
Fe^{III}(H_2O)$_6$(ClO_4)$_3$	4.8	Me_2SO
Fe^{III}(H_2O)$_6$(ClO_4)$_3$	5.6	DMF
Fe^{III}(H_2O)$_6$(ClO_4)$_3$	4.2	DMF (0.1 M TEAP)
		B. Semiquinonato and Catecholato Complexes
Fe^{III}(DTBSQ)$_3$	2.9	solid
Fe^{III}(DTBSQ)$_3$	2.9	CH_2Cl_2 (0.1 M TEAP)
Fe^{III}(DTBSQ)$_3$	4.8	Me_2SO (0.1 M TEAP)
Fe^{III}(DTBSQ)$_3$	5.2	DMF (0.1 M TEAP)
1:3 Fe^{III}–DTBC^{2-}	4.2	Me_2SO (0.1 M TEAP)
1:2 Fe^{III}–DTBC^{2-}	4.3	Me_2SO (0.1 M TEAP)
1:1 Fe^{III}–DTBC^{2-}	5.4	Me_2SO (0.1 M TEAP)
		C. Products from Controlled-Potential Electrolysis at −0.65 V vs. SCE^b
1:2 Fe^{II}–DTBQ	6.2	CH_3CN (0.1 M TEAP)
1:1 Fe^{II}–DTBQ	5.9	CH_3CN (0.1 M TEAP)
1:3 Fe^{II}–DTBQ	5.4	Me_2SO (0.1 M TEAP)
1:2 Fe^{II}–DTBQ	5.7	Me_2SO (0.1 M TEAP)
1:1 Fe^{II}–DTBQ	4.9	Me_2SO (0.1 M TEAP)
1:3 Fe^{II}–DTBQ	4.1	DMF (0.1 M TEAP)
1:2 Fe^{II}–DTBQ	4.2	DMF (0.1 M TEAP)
1:1 Fe^{II}–DTBQ	3.0	DMF (0.1 M TEAP)

^{a} These are based on the measured magnetic susceptibilities and the assumption that the complex is mononuclear in iron.[64,65]
^{b} Products of the mixtures shown.

Magnetic Measurements. The magnetic susceptibilities of iron(II) and iron(III) salts and of their semiquinonato and catecholato complexes in various solvents at room temperature are summarized in Table II. Both in the solid phase and in solution, the ferrous salt remains monomeric with a magnetic susceptibility consistent with a high-spin d^4 ion (4.9 μ_B). In contrast, the ferric salt appears to dimerize[52] when added to DMF or Me_2SO that contains electrolyte. A ferric dimer in nonaqueous solution is expected to have a magnetic moment of 2.9 μ_B.[57] Hence, the lower susceptibility values for the iron(III) salts in Table II indicate the degree of dimerization. (The apparent magnetic moments that are tabulated have been calculated on the assumption that the complex is mononuclear in iron.)

The magnetic moment of Fe^{III}(DTBSQ)$_3$ in CH_2Cl_2 does not differ from its solid-state value. Intramolecular antiferromagnetic exchange between the high-spin iron(III) and the ligand-based unpaired electrons should result in an $S = 1$ ground state with two unpaired electrons,[1] which is what is observed in both CH_2Cl_2 and pentane. Because of the insolubility of the Fe^{III}(DTBSQ)$_3$ complex in CH_3CN, a magnetic moment could not be measured. When Fe^{III}(DTBSQ)$_3$ is added to Me_2SO plus electrolyte, a rapid degeneration occurs to yield a species with a magnetic moment of 4.8 μ_B per iron. This is consistent with either some dimer formation or the presence of one bound DTBSQ$^-$· antiferromagnetically coupled to the ferric ion. The large magnetic moment that is observed for Fe^{III}(DTBSQ)$_3$ in DMF must be the result of extensive degradation to the Fe(III)–catecholate complex and free DTBQ.

The magnetic moments of the electrolysis products for the 1:1 and 1:2 Fe(II)–DTBQ combinations in CH_3CN are characteristic of high-spin d^5 Fe(III) systems. Because of the extreme air sensitivity of the 1:3 Fe(III)–DTBC complex in

---

(68) Seo, E. T.; Sawyer, D. T. *Inorg. Chem.* **1977**, *16*, 734.
(69) Wilshire, J. P.; Leon, L. E.; Bosserman, P. A.; Sawyer, D. T.; Buchanan, R. M.; Pierpont, C. G. *Chem. Uses Molybdenum, Proc. Int. Conf., 3rd* **1979**, 264.
(70) Havelkova, L.; Bartusch, M. *Collect. Czech. Chem. Commun.* **1969**, *34*, 2919.
(71) Martin, J. L.; Takats, T. *Can. J. Chem.* **1975**, *53*, 572.
(72) Tyson, C. A.; Martell, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 3379.

Table III. Redox Reactions for the Iron–Catechol–Semiquinone–Quinone System in Various Aprotic Solvents That Contain 0.1 M TEAP

A. Homogeneous Reactions

solvent	reacn
CH_3CN	$Fe(II) + 2DTBSQ^{-}\cdot \rightarrow Fe^{III}(DTBC)(DTBSQ)$
CH_3CN, Me_2SO	$Fe(II) + 3DTBSQ^{-}\cdot \rightarrow Fe^{III}(DTBC)_2^{-} + DTBQ$
Me_2SO	$Fe(II) + DTBQ \rightarrow Fe^{III}(DTBSQ)^{2+}$
Me_2SO	$Fe^{III}(DTBSQ)_3 \rightarrow Fe^{III}(DTBC)(DTBSQ) + DTBQ$
Me_2SO, DMF	$2Fe^{III}(DTBC)_3^{3-} + H_2O \rightarrow [Fe^{III}(DTBC)_2\text{-O-}Fe^{III}(DTBC)_2]^{4-} + 2DTBCH^{-}$

B. Electrode Reactions

		V vs. SCE		
solvent	reacn	$E^{\circ\prime}$	$E_{p,c}$	$E_{p,a}$
CH_3CN	$Fe(III) + 1e^{-} \rightarrow Fe(II)$		+0.67	
CH_3CN	$Fe(II) \rightarrow Fe(III) + 1e^{-}$			+1.90
Me_2SO	$Fe(III) + 1e^{-} \rightleftarrows Fe(II)$	+0.25		
DMF	$Fe(III) + 1e^{-} \rightleftarrows Fe(II)$	+0.39		
CH_3CN	$Fe(II) + 2e^{-} \rightarrow Fe$		−1.08	
CH_3CN	$Fe \rightarrow Fe(II) + 2e^{-}$			+0.05
Me_2SO	$Fe(II) + 2e^{-} \rightarrow Fe$		−1.26	
Me_2SO	$Fe \rightarrow Fe(II) + 2e^{-}$			−0.56
CH_3CN	$Fe(II) + 2DTBQ + 2e^{-} \rightarrow Fe^{II}(DTBSQ)_2 \rightarrow Fe^{III}(DTBC)(DTBSQ)$		+0.10	
CH_3CN	$Fe^{III}(DTBC)(DTBSQ) + 1e^{-} \rightarrow Fe^{III}(DTBC)_2^{-}$		−0.56	
CH_3CN	$Fe^{III}(DTBC)_2(DTBSQ)^{2-} + 1e^{-} \rightarrow Fe^{III}(DTBC)_3^{3-}$		−1.29	
CH_3CN	$Fe^{III}(DTBC)_3^{3-} \rightarrow Fe^{III}(DTBC)_2(DTBSQ)^{2-} + 1e^{-}$			−0.79
CH_3CN	$Fe^{III}(DTBC)_2(DTBSQ)^{2-} \rightarrow Fe^{III}(DTBC)_2^{-} + DTBQ + 1e^{-}$			−0.48
CH_3CN	$Fe^{III}(DTBC)_2^{-} \rightarrow Fe^{III}(DTBC)(DTBSQ) + 1e^{-}$			−0.33
CH_3CN	$Fe^{III}(DTBC)(DTBSQ) \rightarrow Fe^{III}(DTBC)^{+} + DTBQ + 1e^{-}$			+0.09
CH_3CN	$Fe^{III}(DTBC)^{+} \rightarrow Fe(III) + DTBQ + 2e^{-}$			+0.78
Me_2SO	$Fe(II) + 2DTBQ + 3e^{-} \rightarrow Fe^{III}(DTBC)_2^{-}$		−0.49	
Me_2SO	$Fe(II) + 3DTBQ + 4e^{-} \rightarrow Fe^{III}(DTBC)_2(DTBSQ)^{2-}$		−0.49	
Me_2SO	$Fe^{III}(DTBC)_2(DTBSQ)^{2-} + 1e^{-} \rightarrow Fe^{III}(DTBC)_3^{3-}$		−1.30	
Me_2SO	$Fe^{III}(DTBC)_3^{3-} \rightarrow Fe^{III}(DTBC)_2(DTBSQ)^{2-} + 1e^{-}$			−0.85
Me_2SO	$Fe^{III}(DTBC)_2(DTBSQ)^{2-} \rightarrow Fe^{III}(DTBC)_2^{-} + DTBQ + 1e^{-}$			−0.38
Me_2SO	$Fe^{III}(DTBC)_2^{-} \rightarrow Fe^{III}(DTBC)(DTBSQ) + 1e^{-}$			−0.07
Me_2SO	$[Fe^{III}(DTBC)(DTBSQ) + 1e^{-} \rightarrow Fe^{III}(DTBC)_2^{-}]$		−0.20	
Me_2SO	$Fe^{III}(DTBC)(DTBSQ) \rightarrow Fe^{III}(DTBC)^{+} + DTBQ + 1e^{-}$			+0.15
Me_2SO	$Fe^{III}(DTBC)^{+} \rightarrow Fe(III) + DTBQ + 2e^{-}$			+0.34

CH_3CN, the magnetic susceptibility could not be measured reliably (a value of 5.9 μ_B is a best estimate). On the bases of the magnetic moments for the electrolysis products for the 1:1, 1:2, and 1:3 Fe(II)–DTBQ systems in Me_2SO and DMF, significant dimerization appears to occur in DMF and in Me_2SO in the presence of base.

Discussion and Conclusions

On the basis of the experimental results, a self-consistent set of redox and formation reactions for the iron–catechol and iron–semiquinone systems can be formulated; these are summarized in Table III. When a combination of iron(II) and DTBQ is electrolyzed, reduction of the quinone occurs first, followed by coordination of two semiquinones to one Fe(II) ion. The latter species undergoes a concerted disproportionation and metal-to-ligand electron transfer to give $Fe^{III}(DTBC)(DTBSQ)$. This is analogous to the manganese–catechol system.[28] Ferrous ion contributes 1 electron to the overall electron stoichiometry for all of the reactions that have been studied.

The redox reactions for iron and DTBQ in CH_3CN follow a simple pattern. Because the complexes remain monomeric and the $Fe^{III}(DTBSQ)_3$ complex is insoluble, the number of intermediates is limited. For the 1:1 and 1:2 combinations of Fe(II) and DTBQ in CH_3CN a reasonable reduction sequence is represented by eq 7.

$$Fe(II) + 2DTBQ \xrightarrow[2e^{-}]{+0.10\text{ V}} [Fe^{II}(DTBSQ)_2] \rightarrow Fe^{III}(DTBC)(DTBSQ) \xrightarrow[1e^{-}]{-0.56\text{ V}} Fe^{III}(DTBC)_2^{-} \quad (7)$$

Reoxidation of the product species from reduction of the 1:1 combination by cyclic voltammetry yields a broad peak that is scan-rate dependent and probably due to the excess Fe(II) that remains in solution in equilibrium with the $Fe^{III}(DTBC)_2^{-}$ complex. This also is observed for the 1:1 Mn(II)–DTBQ system.[28] The $Fe^{II}(DTBSQ)_2$ complex is short-lived because of the rapid electron transfer from Fe(II) to $DTBSQ^{-}\cdot$.

The 1:3 Fe(II)–DTBQ system in CH_3CN contains free DTBQ after the first reduction as seen by the reduction peak at −0.54 V in Figure 1d. Equation 8 outlines a mechanistic

$$Fe(II) + 2DTBQ \xrightarrow[2e^{-}]{+0.10\text{ V}} Fe^{II}(DTBSQ)_2 \rightarrow Fe^{III}(DTBC)(DTBSQ) \xrightarrow[1e^{-}]{-0.56\text{ V}} Fe^{III}(DTBC)_2^{-} \xrightarrow[DTBQ]{1e^{-},\ -0.56\text{ V}} Fe^{III}(DTBC)_2(DTBSQ)^{2-} \xrightarrow[1e^{-}]{-1.29\text{ V}} Fe^{III}(DTBC)_3^{3-} \quad (8)$$

basis for this and for the overall 5-electron reduction stoichiometry. The peak at −1.29 V is due to the reduction of a bound semiquinone and is about 0.3 V positive relative to the reduction peak for free $DTBSQ^{-}\cdot$ (see Figure 1a). The oxidation of the $Fe^{III}(DTBC)_3^{3-}$ complex (see Figure 1d) occurs in three 1-electron steps followed by a 2-electron step to the starting materials (the reverse of eq 8). Each oxidation step is distinct because it involves oxidation of bound catechol or semiquinone.

The products from reduction at −0.65 V of Fe(II)–DTBQ systems in CH_3CN contain high-spin iron(III) without evidence for antiferromagnetic ligand interactions. Hence, in this solvent only iron(III)–catechol complexes result; the Fe(III) ion provides a template for the disproportionation of two semiquinone anions. The process also is driven by the "hard acid–hard base" nature of the Fe(III)–DTBC interaction.

The catecholate complexes of iron in Me_2SO are different from those in CH_3CN and are analogous to the manganese–

catechol complexes,[28] if the solution does not contain OH^-. For a 1:1 combination of Fe(II) and DTBQ the initial reduction is due to the solvated Fe(III)/Fe(II) couple ($E^{\circ\prime}$ = +0.25 V). Approximately half of the Fe(II) is converted to Fe(III) by DTBQ; both anodic and cathodic peaks are observed for initial positive and negative scans from the rest potential (+0.25 V vs. SCE). On the basis of the spectroscopy, electrochemistry, and color of the solution, an iron–semiquinone adduct appears to be formed (eq 9).

$$\mathrm{Fe^{II} + DTBQ \xrightarrow{Me_2SO} Fe^{III}(DTBSQ)^{2+}} \tag{9}$$

For the 1:2 and 1:3 Fe(II)–DTBQ systems in Me_2SO a single multielectron reduction peak is observed at −0.49 V; a second 1-electron reduction at −1.30 V is observed for the 1:3 system (see Table IIB). Addition of 3 equiv of $DTBSQ^{-}\cdot$ to 1 equiv of Fe(II) yields $Fe^{III}(DTBC)_2^-$ and free DTBQ. The latter is reduced at −0.49 V to give $Fe^{III}(DTBC)^{3-}$. Disproportionation also occurs if the $Fe^{III}(DTBSQ)_3$ complex is added to Me_2SO. Figure 4d indicates that a 1-electron reduction is followed by a 2-electron reduction (on the basis of peak heights). Again, the visible spectrum confirms that 1 equiv of free quinone is formed, and the magnetic susceptibility is consistent with the formation of a ferric semiquinone complex. A reasonable reaction scheme is represented by eq 10. The

$$\mathrm{Fe^{III}(DTBSQ)_3 \xrightarrow{Me_2SO} Fe^{III}(DTBC)(DTBSQ) + DTBQ \xrightarrow[1e^-]{-0.20\ V} Fe^{III}(DTBC)_2^- + DTBQ} \tag{10}$$

free DTBQ is reduced by 2 electrons at −0.49 V. Oxidation of $Fe^{III}(DTBC)_3^{3-}$ in Me_2SO occurs by the reverse of eq 8. Each of the 1-electron oxidation steps is distinctly resolved in the reverse scan of Figure 2c, which indicates that the intermediate species are transiently stable.

Although mechanisms other than those proposed in eq 7–10 are possible, the reactions take into account the stability of known intermediates and the redox chemistry of quinone–semiquinone–catechol systems with and without metal ions.[23,28]

For alkaline conditions in Me_2SO, the $Fe^{III}(DTBC)_3^{3-}$ complex is hydrolyzed to $[Fe^{III}(DTBC)_2–O–Fe^{III}(DTBC)_2]^{4-}$ plus $DTBCH^-$ (see Table IIIA). The electrochemical shoulder at −0.25 V appears to be due to the μ-oxo dimeric complex; the presence of OH^- is indicated by the oxidation peak at +0.84 V (Figure 4).

The smaller apparent magnetic moments in Me_2SO for the products from controlled-potential electrolysis at −0.65 V (see Table IIC) indicate that the iron(III) centers are dimeric. The coupling probably occurs via a μ-oxo bridge or a catecholato bridge. Such catechol bridging has been observed for other metal systems[73,74] and for aromatic bound-oxygen systems.[75] However, for the present systems coupling through a μ-oxo bridge is believed to dominate the equilibria on the basis of the spectroscopic evidence. A bridging catechol $\pi \rightarrow \pi^*$ transition should be shifted somewhat from that of the nonbridging catechols; this is not observed. Also, the magnetic susceptibility is lowered by the addition of supporting electrolyte (Table II), which is consistent with the behavior of Fe(III) ions and their tendency to form μ-oxo bridges.[50]

The present study confirms that Fe(III) forms stable mixed-ligand complexes with $DTBC^{2-}$ and $DTBSQ^{-}\cdot$ in CH_2Cl_2, CH_3CN, DMF, and Me_2SO. Although CH_2Cl_2 stabilize the neutral tris(semiquinone) complex of iron(III), the solvents with higher dielectric constants promote disproportionation. The catecholato complexes of iron(II) and iron(III) in CH_3CN and Me_2SO clearly resemble the analogous complexes of manganese.[28] Many of the same mechanisms have been proposed on the basis of the similar electrochemistry, spectroscopy, and magnetic susceptibility data.

The interconversion of Fe(II) and Fe(III) complexes in the absence of OH^- (which competes for metal coordination sites) and in an aprotic medium that resembles certain physiological conditions provides an interesting model for iron-transport and electron-transfer systems. The enhanced stability for catecholato complexation of Fe(III) relative to Fe(II) is consistent with the "hard acid–hard base" interaction between the higher oxidation state metal ions and the oxo anions of the catechol ligand. The formation of stable iron–semiquinone complexes may indicate that stable O_2^- complexes of iron can be formed. Likewise, the tendency of tris- and bis(semiquinonato)iron complexes to disproportionate would be expected for the analogous complexes by the "semiquinone-like" superoxide ion, O_2^-. Such studies are in progress.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE79-22040.

Registry No. DTBQ, 3383-21-9; $[Fe^{II}(H_2O)_3](ClO_4)_2$, 15305-57-4; $[Fe^{III}(DTBSQ)_3]$, 64020-89-9; $DTBSQ^{-}\cdot$, 34515-66-7; $DTBC^{2-}$, 65767-24-0; $[Fe^{III}(DTBC)_2]^-$, 82555-48-4; $[Fe^{III}(DTBC)_3]^{3-}$, 82555-49-5; $[Fe^{III}(H_2O)_6(ClO_4)_3]$, 32963-81-8; $[Fe^{III}(DTBC)(DTBSQ)]$, 82555-47-3; $[Fe^{III}(DTBC)_2(DTBSQ)]^{2-}$, 82555-50-8.

---

(73) Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1616.

(74) Wilshire, J. P.; Leon, L. E.; Bosserman, P. A.; Sawyer, D. T. *J. Am. Chem. Soc.* **1979**, *101*, 3379.

(75) Holm, R. H.; Everett, G. W., Jr.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 82.