

- (10) Sweigart, D. A.; Gower, M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.*, **1976**, *108*, C15.
- (11) Salzer, A. *Inorg. Chim. Acta* **1976**, *18*, L31.
- (12) John, G. R.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1976**, *120*, C45.
- (13) John, G. R.; Kane-Maguire, L. A. P.; Sweigart, D. A. *J. Organomet. Chem.* **1976**, *120*, C47.
- (14) Sweigart, D. A.; Wilker, C. N. *J. Chem. Soc., Chem. Commun.* **1977**, 304.
- (15) Birney, D. M.; Crane, A. M.; Sweigart, D. A. *J. Organomet. Chem.* **1978**, *152*, 187.
- (16) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807.
- (17) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458.
- (18) Walker, P. J. C.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1973**, 622.
- (19) Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta* **1973**, *7*, 621.
- (20) Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972**, *11*, 1754.
- (21) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1677.
- (22) Winkhaus, G.; Singer, H. Z. *Naturforsch., B* **1963**, *18*, 418.
- (23) Nyholm, R. S.; Snow, M. R.; Stiddard, M. H. B. *J. Chem. Soc.* **1965**, 6564.
- (24) Brown, D. A.; Sane, R. T. *J. Chem. Soc., Dalton Trans.* **1971**, 2088; Atwood, J. A.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380; Zingales, F.; Sartorelli, U. *Inorg. Chem.* **1967**, *6*, 1246; Cetini, C.; Gambino, O.; Vaglio, G. A.; Ferrari, R. P. *ibid.* **1969**, *8*, 137.
- (25) Hileman, J. C.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1962**, *1*, 933; Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844.
- (26) Kane-Maguire, L. A. P.; Thomas, G. T. *J. Chem. Soc., Dalton Trans.* **1975**, 1890.
- (27) Reimann, R. H.; Singleton, E. *J. Organomet. Chem.* **1973**, *59*, C24.
- (28) Fischer, E. O.; Strametz, H. Z. *Naturforsch., B* **1968**, *23*, 278.
- (29) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1683.
- (30) Deganello, G.; Boschi, T.; Toniolo, L.; Albertin, G. *Inorg. Chim. Acta* **1974**, *10*, L3.
- (31) Isaacs, E. E.; Graham, W. A. G. *J. Organomet. Chem.*, **1975**, *90*, 319.
- (32) Pidock, F.; Smith, J. D.; Taylor, B. W. *J. Chem. Soc. A* **1969**, 1604.
- (33) Zingales, F.; Chiesa, A.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 2707.
- (34) Brown, D. A.; Chawla, S. K.; Glass, W. K. *Inorg. Chim. Acta* **1976**, *19*, L31.
- (35) Powell, P.; Russell, L. S.; Styles, E.; Brown, A. J.; Howarth, O. W.; Moore, P. *J. Organomet. Chem.* **1978**, *149*, C1.
- (36) Al-Kathumi, K. M.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1973**, 1683.
- (37) John, G. R., personal communication.
- (38) Kane-Maguire, L. A. P., unpublished data. Sweigart, D. A.; Summers, R.; Wood, M., unpublished data.
- (39) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967.
- (40) Angelici, R. S. *Organomet. Chem. Rev.* **1968**, *3*, 173.
- (41) Angelici, R. S.; Brink, R. W. *Inorg. Chem.* **1973**, *12*, 1067.

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

Sorbitol and Related Polyol Complexes of Manganese(II), -(III), and -(IV): Redox and Oxygenation Equilibria

DAVID T. RICHENS, CECIL G. SMITH, and DONALD T. SAWYER*

Received August 17, 1978

Sorbitol, a straight-chain hexitol, complexes and stabilizes the +2, +3, and +4 oxidation states of manganese in aqueous alkaline solution in a manner analogous to that observed with D-gluconate and D-gluconate. The redox and coordination chemistry for the manganese-sorbitol complexes, as well as their reactions with molecular oxygen and hydrogen peroxide, have been studied by spectrophotometric, electrochemical, and magnetic measurements. The kinetics of their reactions with molecular oxygen have been studied by means of an oxygen membrane electrode. Molecular oxygen oxidizes the Mn(II) and Mn(III) complexes to the Mn(III) and Mn(IV) complexes, respectively, and is reduced to the peroxide anion in each case. Equilibrium constants and rate constants have been evaluated. Reaction mechanisms are proposed which are now thought to be general for the redox and oxygenation behavior of polyhydroxy complexes of manganese in aqueous alkaline solution.

Manganese is an essential component of several biological oxidation-reduction systems, including photosystem II in green plant photosynthesis¹⁻⁴ and mitochondrial superoxide dismutase.⁵ The +2, +3, and +4 oxidation states of manganese are believed to be involved in these processes,⁶⁻⁹ but this has not yet been established.

Several polarographic studies by Doležal¹⁰⁻¹⁵ have shown that polyhydroxy ligands will effectively stabilize the +3 and +4 oxidation states of manganese in aqueous, alkaline solution. These studies indicate that sorbitol, a straight-chain hexitol, has the highest stability constant, $1.94 \times 10^{16} \text{ M}^{-1}$.¹⁵

Recent studies¹⁶ also have shown that the addition of sorbitol enhances the catalytic activity¹⁷ of manganese for the oxygen-alkali pulping process in the manufacture of paper. This may be due to an effective increase in the solubilization and activation of molecular oxygen by the manganese-sorbitol complexes. The presence of sorbitol significantly increases the stability and solubility of the +3 and +4 oxidation states.

Recent studies in this laboratory have established that salts of D-gluconate and D-gluconate will also effectively stabilize the +2, +3, and +4 oxidation states of manganese in aqueous alkaline solution.^{18,19} The manganese(II) gluconate complex reacts rapidly in a bimolecular process ($k_{\text{obsd}} = 2.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) with molecular oxygen to produce the Mn(III) complex and peroxide ion and reacts in a slower reaction ($k_{\text{obsd}} = 3.9 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$) to produce the Mn(IV) complex and peroxide ion.^{20,21} The Mn(II) complex also is oxidized by peroxide ion

a much slower reaction ($k_{\text{obsd}} = 6 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$) to give the Mn(III) complex. The manganese(III)-gluconate system apparently can form both binuclear and mononuclear complexes; the relative amount depends on the ligand and hydroxide ion concentrations.^{18,19}

This paper summarizes the results of a corresponding study for the sorbitol complexes of manganese(IV), -(III), and -(II) and establishes a general scheme for the redox behavior of polyhydroxy complexes of manganese and their reactivity with molecular oxygen and hydrogen peroxide. It also includes a more detailed spectroscopic and electrochemical study of the manganese-polyol complexes.

Experimental Section

Equipment. Polarography and cyclic voltammetry were performed with a three-electrode potentiostat based on the use of solid-state amplifiers.²² Both the dropping-mercury electrode and the conventional polarographic cell, with built-in calomel reference electrode, have been described previously.²³ For cyclic voltammetry a Beckman hanging-drop mercury electrode was used with the standard three-electrode cell. A Princeton Applied Research Model 173 potentiostat, with a Model 179 digital coulometer and mercury-pool working electrode, was used for controlled-potential coulometry.

The spectrophotometric measurements were performed with a Cary Model 17 recording spectrophotometer. Circular dichroic spectra were recorded by use of a Cary Model 60 spectrometer with a Cary Model 6002 CD accessory. Quartz cells were used for all measurements.

The magnetic susceptibilities were determined by the modified²⁴ NMR method that was developed by Evans.²⁵ The paramagnetic shift

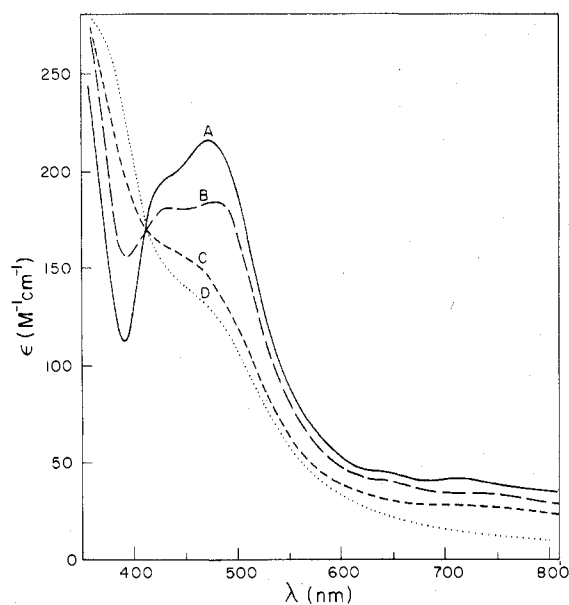


Figure 1. Visible absorption spectra for the manganese(III)-sorbitol complexes as a function of solution pH (1.0 mM manganese, 0.5 M sorbitol: A, pH >12; B, pH 11.7; C, pH 11.0; D, pH 10.0).

between the two 3-(trimethylsilyl)propanesulfonate (DSS) peaks was measured on a Varian E390 recording NMR spectrometer; the probe temperature was determined with an ethylene glycol standard. Diamagnetic corrections were made.²⁶

For the kinetics of the reactions of molecular oxygen with the manganese complexes, the concentration of dissolved oxygen in the solutions was measured with a Rank Brothers membrane oxygen electrode and oxygen detector which was connected to a Hewlett-Packard Model 7030A X-Y recorder.

Reagents. The source of manganese(II) was hexaaquamanganese(II) perchlorate (Alfa Products). The Mn(III) and -(IV) complexes were prepared from the corresponding Mn(II) complexes either by the addition of stoichiometric amounts of $K_3Fe(CN)_6$ (Mallinkrodt) or molecular oxygen or by controlled-potential electrolysis. Manganese(III) acetate, synthesized by the method of Christensen,²⁷ was also used in the preparation of the Mn(III) complexes. The source of gluconate ion was D-glucono- δ -lactone (Chas. Pfizer and Co.), which was recrystallized from ethylene glycol monomethyl ether. Solutions of sodium gluconate were prepared by addition of a stoichiometric amount of sodium hydroxide (Mallinkrodt) to the D-glucono- δ -lactone. The glucarate ion was obtained from the disodium salt of glucaric acid, prepared by an ion-exchange reaction between Na_2CO_3 (Baker and Adamson) and the calcium salt of D-glucaric acid (Sigma). Sorbitol (Matheson Coleman and Bell), meso-erythritol (Aldrich), L-tartrate (Baker and Adamson), myo-inositol (Matheson Coleman and Bell) and (+)-sucrose (Mallinkrodt) were used without further purification. The solutions were deaerated with high-purity argon. Acidification of the alkaline solutions was performed with a 5 M solution of perchloric acid (Mallinkrodt). DSS was supplied by Aldrich.

Results and Discussion

Spectroscopic and Magnetic Measurements. Combination of manganese(II) with an excess of a polyhydroxy ligand in 0.5 M NaOH (pH 13.7) results in the formation of a colorless Mn(II) complex (when protected from oxygen). For solutions of D-glucarate, D-gluconate, L-tartrate, and (+)-sucrose, the complex is soluble, whereas for polyols such as sorbitol, meso-erythritol, and myo-inositol, the complex exists as a white colloidal precipitate. Subsequent oxidation of these colloidal solutions with molecular oxygen, hydrogen peroxide, ferricyanide, or controlled-potential electrolysis results in soluble, intensely colored manganese(III) complexes.

Spectrophotometric measurements, as a function of pH and of ligand concentration, confirm that several different Mn(III) complexes are formed by each ligand. Figures 1 and 2 illustrate the effect of such variations on the spectra for the

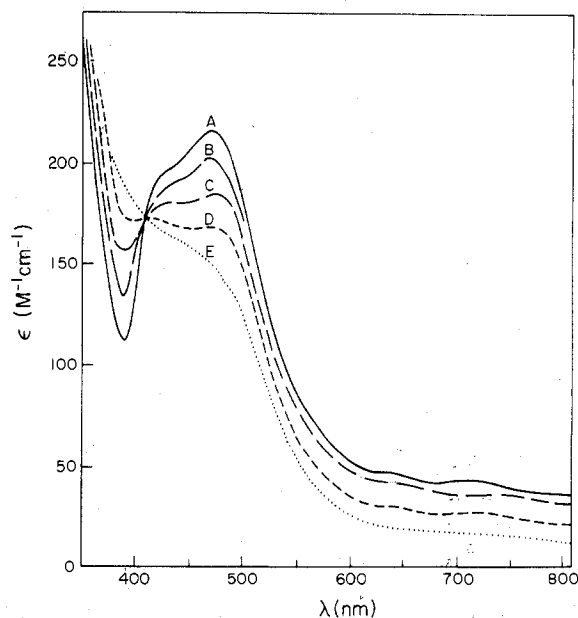


Figure 2. Visible absorption spectra for the manganese(III)-sorbitol complexes as a function of sorbitol concentration (5.0 mM Mn, 0.5 M NaOH: A, 45 mM sorbitol; B, 35 mM; C, 30 mM; D, 15 mM; E, 10 mM).

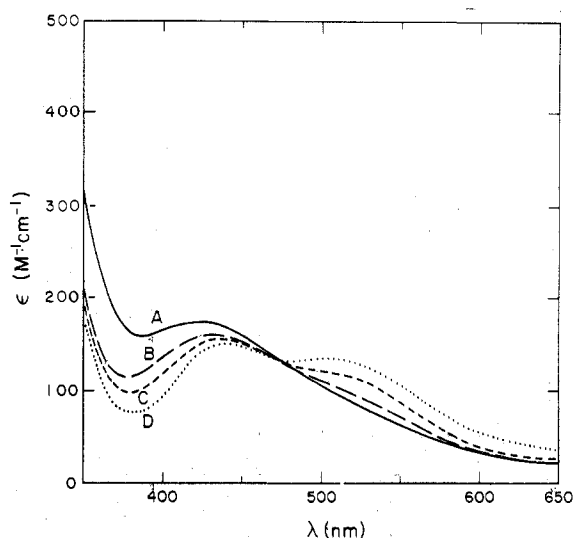


Figure 3. Absorption spectra for solutions that contain 2 mM Mn(III) and varying amounts of glucarate ion and NaOH: A, 50 mM glucarate; B, 100 mM; C, 200 mM; D, 800 mM. Base-to-ligand ratio is 2:1 (except for D, which contained 0.5 M NaOH).

Mn(III)-sorbitol system. The presence of isosbestic points in both figures indicates that two species are in equilibrium. The same is true for the Mn(III)-D-glucarate system (Figure 3) and the Mn(III)-D-gluconate system.¹⁸ A similar study of the Mn(III) complexes of L-tartrate and (+)-sucrose has shown that they also can exist in at least two distinct forms. A pink-brown manganese(III)_B complex is formed in the presence of high ligand and hydroxide ion concentrations with several absorption maxima between 410 and 520 nm. If either the ligand or hydroxide ion concentrations (or both) are lowered, a yellow-brown manganese(III)_A complex results, which only exhibits a "shoulder" between 410 and 450 nm. Table I summarizes the spectrophotometric properties of the manganese-sorbitol complexes.

In 0.5 M NaOH, the Mn(III)_A and Mn(III)_B sorbitol complexes exhibit magnetic moments (Table I) close to the spin-only value for four unpaired electrons. This is consistent with the formation of high-spin mononuclear complexes under

Table I. Magnetic Moments and Absorption Maxima for Mn(III) and -(IV)-Sorbitol Complexes^{a, b}

	μ_{eff} (cor), μ_{B}	λ , nm	ϵ , M ⁻¹ cm ⁻¹
[manganese(III _A) ₂] (A)	3.86	235	9 700
0.08 M NaOH, 0.04 M sorbitol		370 sh ^c	262
		430 sh	160
manganese(III _A) (B)	5.03	450 sh	150
0.5 M NaOH, 0.06 M sorbitol			
manganese(III _B) (C)	4.91	235	11 500
0.5 M NaOH, 1.0 M sorbitol		430 sh	180
		477	210
manganese(IV) (D)	3.85	276	15 000
B + O ₂ (40 min)		500 sh	400
manganese(IV) (E)	3.99		
B + 0.02 M K ₃ Fe(CN) ₆			
manganese(IV) (F)	4.17		
C + O ₂ (40 min)			
manganese(IV) (G)	3.91		
C + 0.02 M K ₃ Fe(CN) ₆			

^a All solutions contain 0.02 M Mn(III) from Mn^{III}(OAc)₃ and 0.05 M DSS; probe temperature 305 K. ^b Theoretical moments for high-spin Mn(III) and -(IV) complexes are 4.90 and 3.89 μ_{B} , respectively. ^c sh = shoulder.

Table II. Absorption Bands Due to d-d Transitions for Manganese(III) and -(IV)-Polyhydroxy Complexes^a

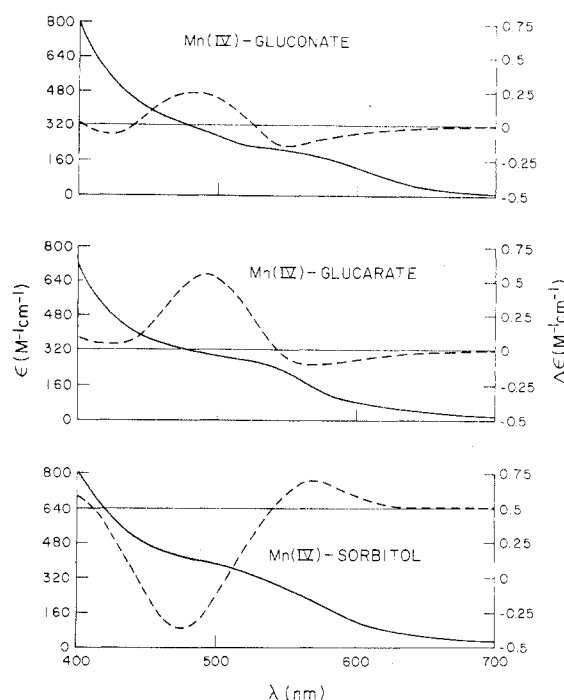
A. Mn(III _A) ₂ , Tetrakis Binuclear			
	⁵ B _{1g} → ⁵ E _g	⁵ B _{1g} → ⁵ B _{2g}	
D-glucarate	450	510	
L-tartrate	420	475	
D-gluconate	455	545	
sorbitol	410	530	
B. Mn(III _A), Bis Mononuclear			
	⁵ B _{1g} → ⁵ E _g	⁵ B _{1g} → ⁵ B _{2g}	
sorbitol	415	538	
C. Mn(III _B), Tris Mononuclear			
	⁵ B _{1g} → ⁵ E _g	⁵ B _{1g} → ⁵ B _{2g}	⁵ B _{1g} → ⁵ A _{1g}
D-glucarate	430	480	610
L-tartrate	400	475	
D-gluconate	420	505	550
sorbitol	415	482	642, 710
D. Mn(IV), Tris Mononuclear			
	⁴ A _{2g} → ⁴ T _{2g}		
D-glucarate	475, 575		
D-gluconate	480, 545		
sorbitol	480, 558		

^a Assignments given in nm.

these conditions. However, the moment for the Mn(III_A) complex is lowered significantly when both the hydroxide ion and sorbitol concentrations are decreased. Such a decrease appears to be due to spin pairing as a result of the dimerization of the Mn(III_A) complex (designated [Mn(III_A)₂]).

Analysis of the absorption and circular dichroic spectra for the manganese(III)-polyol complexes has allowed the identification of a number of optically active d-d bands for each of the Mn(III_A) and Mn(III_B) forms. These are summarized in Table II together with assignments which are reasonably consistent with those of Fackler and co-workers²⁸ and of Summers.²⁹ Because of the apparent low symmetry for the manganese center in these complexes, the assignments are tentative at best.

Manganese(III) has a ⁵D electronic ground state which, for complexes with a "pure" octahedral symmetry, should result in a single absorption band due to the spin-allowed transitions ⁵E_g → ⁵T_{2g}. However, in view of the high-spin d⁴ configuration in these complexes, the absorption spectra for symmetrical ligand fields are subject to Jahn-Teller distortions.²⁸ This can result in as many as four d-d bands. For most Mn(III)

**Figure 4.** Absorption and CD spectra for the D-gluconate, D-glucarate, and sorbitol complexes of manganese(IV) (2.5 mM Mn, 0.5 M ligand, and 0.5 M NaOH: —, absorption; ---, CD).

complexes, the distortion is an elongation of the z axis to give D_{4h} symmetry, which should result in three absorption bands due to the transitions ⁵B_{1g} → ⁵A_{1g}, ⁵B_{1g} → ⁵B_{2g}, and ⁵B_{1g} → ⁵E_g. Thus, the two bands in the range from 410 to 520 nm are assigned to the ⁵B_{1g} → ⁵E_g (shortest wavelength) and ⁵B_{1g} → ⁵B_{2g} transitions. The bands observed above 600 nm are tentatively assigned to the ⁵B_{1g} → ⁵A_{1g} transition, although Fackler²⁸ has concluded that this transition usually occurs in the near-IR region (1042–1241 nm). Absorption bands in this range are not observed for any of the polyhydroxy complexes of Mn(III). The low symmetry in these complexes could cause distortions beyond those due to Jahn-Teller effects and may explain the increased multiplicity of bands that are observed in the visible region. A number of alternative assignments have been proposed for the low-energy bands of manganese(III) complexes, but these have been questioned.²⁸⁻³⁰

Further oxidation of the manganese(III) polyhydroxy complexes with molecular oxygen (20 min of bubbling), ferricyanide, or controlled-potential electrolysis results in the formation of soluble, intensely red manganese(IV) complexes. The latter exhibit an intense UV absorption maximum, which for sorbitol occurs at 276 nm, and a "shoulder" at about 500 nm in the visible region (Table I). For sorbitol, oxidation of either the yellow-brown (Mn(III_A)) or pink-brown (Mn(III_B)) form in 0.5 M NaOH yields the same Mn(IV) complex.

The results of a spectrophotometric titration at 276 nm for the oxidation of Mn(II) with molecular oxygen in 0.5 M NaOH as a function of sorbitol concentration establish that the predominant species in solution has a mole ratio of 3:1 (sorbitol relative to Mn(IV)). Similar studies indicate that this probably is true for the Mn(IV) complexes that are formed by D-glucarate and D-gluconate. Oxidation at stoichiometries lower than this ratio results in the formation of MnO₂ precipitates and lower concentrations of the Mn(IV) complexes.

Figure 4 illustrates the similarity between the absorption and CD spectra for the D-gluconate, D-glucarate, and sorbitol complexes of Mn(IV). These results indicate that a similar environment exists around the Mn(IV) center in these complexes³⁵ and infer that there is a common coordination structure (tris(cis alkoxo)). In 0.5 M NaOH solutions, the

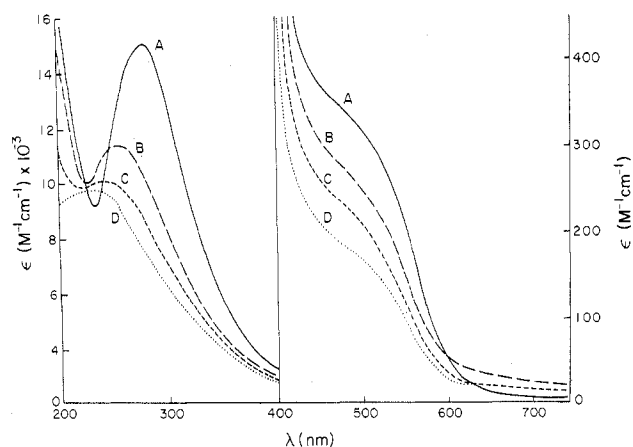


Figure 5. Absorption spectra for the Mn(IV)-sorbitol complex in the presence of oxygen at 1 atm as a function of solution pH (1.0 mM Mn, 0.5 M sorbitol): A, pH >12; B, pH 11.4; C, pH 10.9; D, pH 10.1.

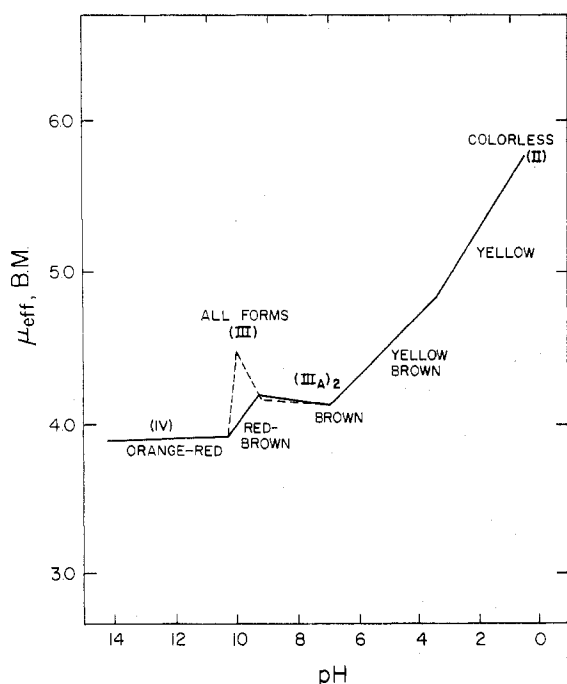


Figure 6. pH titration of the magnetic moment for the manganese(IV)-sorbitol complex in the presence of oxygen at 1 atm (--- signifies excess hydrogen peroxide added).

complexes have magnetic moments (Table I) close to the spin-only value for three unpaired electrons. When the hydroxide ion concentration is lowered, dimerization of the Mn(IV) complex does not occur; but it does cause the Mn(IV) complex to be reduced to Mn(III), as illustrated by Figures 5 and 6. In the presence of peroxide, the reduction is accompanied by evolution of molecular oxygen. In the absence of peroxide, the reduction involves an oxidation of the sorbitol ligand. In the presence of oxygen, the $[\text{Mn(III)}_2]_2$ dimeric species appears to be the dominant form between pH 9.5 and pH 7.5. When the solutions are made acidic, reduction to manganese(II) occurs accompanied by further oxygen evolution and/or ligand oxidation.

Analysis of the absorption and CD spectra for the Mn(IV) complexes has identified the presence of at least two optically active d-d bands (Table II). In view of the low symmetry surrounding these high-spin d^3 manganese centers, assignments can only be tentative. In agreement with the ligand field parameters of Jørgensen^{31,32} for high-spin d^3 ions, the two bands are assigned to components of the magnetic-dipole-

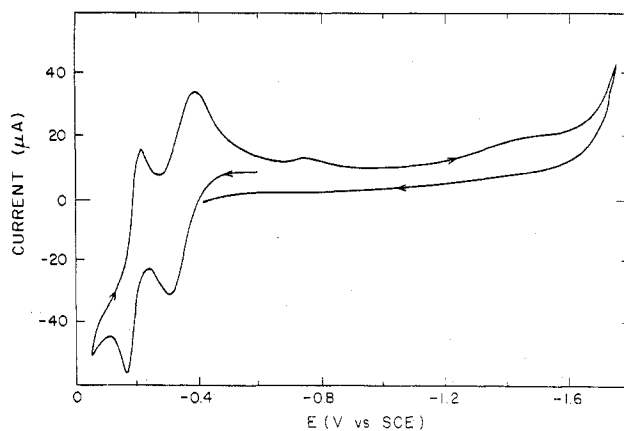


Figure 7. Cyclic voltammogram for the manganese(III_B)-sorbitol complex after oxygenation of the Mn(II) complex for 40 min and deaeration with argon for 20 min (5 mM Mn, 0.5 M sorbitol, 0.5 M NaOH; scan rate 0.05 V s⁻¹).

allowed ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition, split as a consequence of the distortion from octahedral symmetry.

Electrochemistry. Polarograms for the manganese(III)-sorbitol complex (0.5 M NaOH, 0.5 M ligand, 1.0 mM Mn(III)) exhibit a III/IV oxidation wave at -0.33 V vs. SCE, two III/II reduction waves at -0.69 and -1.1 V (designated III_A/II and III_B/II, respectively) and a II/0 reduction wave at -1.69 V.

The diffusion currents for the III/IV oxidation and the two III/II reduction waves as a function of sorbitol and hydroxide ion concentrations confirm the presence of several Mn(III) complexes, in agreement with the spectroscopic data. Similar polarographic behavior has been observed for other polyhydroxy complexes of Mn(III).¹⁹ However, complexation of Mn(III) by (+)-sucrose and *myo*-inositol results in a single III/II reduction wave, probably because of steric effects with these ligands. The IV/III reduction for the Mn(IV)-(+)-sucrose complex appears as a spontaneous wave at >0.0 V vs. SCE, which is consistent with the observation that molecular oxygen cannot oxidize the Mn(III)-sucrose complex to Mn(IV).

Polarograms for the Mn(IV)-sorbitol complex exhibit only a III_B/II reduction wave in addition to the IV/III and II/0 reduction waves. The equivalence of the half-wave potentials for the III/IV and IV/III waves and the fact that the values for $E_{3/4} - E_{1/4}$ for these waves are ~ 59 mV indicate that the III/IV redox process meets two of the criteria for electrochemical reversibility. This is further illustrated by the cyclic voltammogram (Figure 7) of the Mn(III_B)-sorbitol complex, after oxidation of the Mn(II) complex with molecular oxygen and deaeration with argon. The III/IV redox couple clearly is electrochemically reversible at the scan rates employed (0.05 V s⁻¹).

The electrochemical studies of the oxidation of the manganese(II)- and -(III)-sorbitol complexes with molecular oxygen indicate that oxygen is reduced to peroxide anion in 0.5 M NaOH (pH 13.7) at 25 °C. A reversible wave due to the HO_2^-/O_2 couple is observed at -0.18 V vs. SCE (Figure 7), as well as an irreversible reduction wave at -1.41 V. However, the reduction wave for free peroxide anion in alkaline sorbitol at pH 13.7 occurs at -1.29 V. The negative shift of 120 mV in the presence of the manganese complexes indicates that the peroxide anion has become harder to reduce to OH^- ions because of an interaction with the manganese(II) ion. However, the invariance of the oxidation wave at -0.18 V indicates that the peroxide anion does not interact significantly with the Mn(IV)-sorbitol complex.

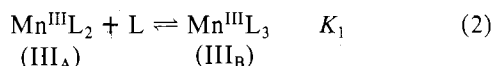
The dependence of the half-wave potentials for the III/IV oxidation wave and the two III/II reduction waves for the

manganese(III) complex as a function of the hydroxide ion and sorbitol concentrations has been determined. On the basis of the relationship²³

$$\Delta E_{1/2} = -(p - q) \frac{0.059}{n} (\Delta \log C_x) \quad (1)$$

where C_x is the concentration of the ligand, p is the number of ligands per metal ion in the oxidized complex, and q is the number of ligand species per metal ion in the reduced complex, two hydroxide ions are required for the oxidation of the Mn(II) complex to the Mn(III_A) and Mn(III_B) complexes, and two hydroxide ions also are required for the oxidation of the Mn(III_B) complex to the Mn(IV) complex. The results also indicate that the number of sorbitol molecules per manganese atom does not change for the oxidation of the Mn(II) complex to the Mn(III_A) complex and for the oxidation of the Mn(III_B) complex to the Mn(IV) complex. However, oxidation of the Mn(II) complex to the Mn(III_B) complex appears to require the acquisition of an additional sorbitol molecule per manganese atom. Velikov and Doležal¹⁵ have studied the rapid displacement reaction by sorbitol in an alkaline solution of the Mn(II)-EDTA complex and concluded that the sorbitol complex contains two sorbitol molecules per Mn(II). Hence, the Mn(III_A) complex appears to contain a sorbitol:Mn(III) mole ratio of 2:1 and the sorbitol:Mn(III_B) complex in a mole ratio of 3:1.

Further analysis of the absorption spectra as a function of sorbitol concentration (Figure 2) provides a means to estimate the equilibrium constant K_1 for the process

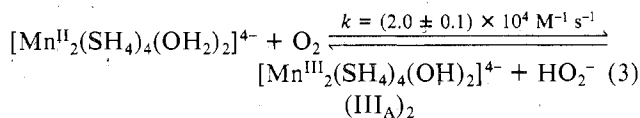


where L represents the dianion of sorbitol. In 0.5 M NaOH at 25 °C, K_1 has a value of $(1.08 \pm 0.05) \times 10^2 \text{ M}^{-1}$.

An analogous set of experiments with the D-gluconate complex of manganese(III) in 0.3 M NaOH yields a value for K_1 (gluconate) of $(1.2 \pm 0.06) \times 10^2 \text{ M}^{-1}$. The comparable values of the equilibrium constants for these two ligands provide support for the conclusion that their coordinate bonding to the Mn(III) ion is the same. Namely, complexation occurs via two vicinal hydroxyl groups of the polyhydroxy ligand.

Reaction Kinetics and Equilibria. The reactivity of molecular oxygen with both the Mn(II)- and Mn(III)-sorbitol complexes has been studied in terms of kinetics and stoichiometry. The kinetics of the reactions have been followed by means of an oxygen-membrane electrode to monitor the partial pressure of dissolved oxygen in solution (for the solution conditions the solubility of O₂ is approximately 1 mM at a partial pressure of 1 atm).

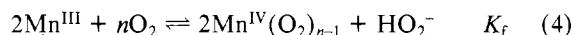
The reaction of the Mn(II)-sorbitol complex with molecular oxygen is rapid and has a stoichiometry that is first order with respect to a binuclear Mn(II) complex and first order with respect to O₂. The apparent second-order rate constant at 25 °C is $(2.0 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Detailed analysis by both polarography and spectroscopy as a function of pH indicates that the initial oxidation product is the binuclear [Mn(III_A)₂] complex which then rapidly equilibrates to the monomeric (III_A) and (III_B) complexes at higher pHs. These results indicate that the primary reaction can be represented by the expression



where SH₄ represents the dianion of sorbitol. Polarographic studies confirm that peroxide is a product of the reaction.

Although the equilibrium for eq 3 is far to the right when the basicity is greater than pH 10.0 at 25 °C, at lower pH values or for temperatures up to 80 °C at pH 10.5 the equilibrium is shifted in favor of the Mn(II) complex. For example, purging of a solution of the [Mn(III_A)₂] complex with argon for 1 h at 80 °C results in the formation of the colorless colloidal manganese(II) complex; subsequent oxygen purging causes the [Mn(III_A)₂] complex to re-form after 10 min.

The reaction of the Mn(III) complex with O₂ is much slower than that of the Mn(II) complex under similar conditions and is to some extent dependent on the initial sorbitol concentration. Solutions that contain predominantly the [Mn(III_A)₂] complex give MnO₂ as the major product after oxidation with either O₂ or ferricyanide. However, for solutions that contain predominantly the monomeric Mn(III_A) complex in 0.5 M NaOH at 25 °C, the reaction with O₂ yields the tris manganese(IV) complex and peroxide (identified by electrochemistry and spectroscopy). The reaction does not go to completion because of the comparability of the redox potentials for the IV/III couple and the O₂/HO₂⁻ couple. For a reaction stoichiometry that is expressed by



the equilibrium constant K_f for the manganese-sorbitol complex is $4.1 \pm 0.2 \text{ mM atm}^{-1}$ (with $n = 0.94$). In the case of the manganese-(+)-sucrose complex, the equilibrium of eq 4 is far to the left. Addition of peroxide causes a rapid reduction of the Mn(IV)-(+)sucrose complex to Mn(III) with evolution of molecular oxygen. This occurs because the redox potential for the IV/III couple of the (+)-sucrose complex is much more positive than that for the O₂/HO₂⁻ couple.

Because of the equilibrium situation for the Mn(III)-sorbitol-O₂ system, the initial rate method has been used to determine the reaction kinetics. The decay of P_{O₂} in solution has been measured by means of an oxygen membrane electrode. Variations of both the total Mn(III) and molecular oxygen concentrations, under pseudo-first-order conditions, confirms that the initial rate of decay of P_{O₂} for each is controlled by first-order kinetics. The exponential decay of P_{O₂} with time also confirms the first-order dependence in molecular oxygen. At a constant O₂ concentration of 1.0 mM, variations of total Mn(III) concentration from 0.07 to 0.65 mM yield an apparent first-order rate constant of $(4.1 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ (for total Mn(III)) in 0.5 M NaOH at 25 °C. The pseudo-first-order rate constant for molecular oxygen, at a total Mn(III) concentration of 3.23 mM, is $(5.3 \pm 0.3) \times 10^{-2} \text{ s}^{-1}$. Combination of these pseudo-first-order rate constants yields an average value for the second-order rate constant k_{app} (total Mn^{III}) of $(1.0 \pm 0.5) \times 10 \text{ M}^{-1} \text{ s}^{-1}$.

When the O₂ reaction is studied in the presence of a 500-fold excess of sorbitol (where the predominant form is the tris Mn(III_B) complex), the kinetics and equilibria are more complicated. The overall reaction proceeds further to favor the Mn(IV) complex. On the basis of eq 4, the equilibrium constant is calculated to be $(11.5 \pm 0.6) \text{ mM atm}^{-1}$ (with $n = 2.26$). The decay of P_{O₂} with time indicates the presence of at least two competing reactions. During the initial 10 s of the reaction, the oxidation appears to involve a Mn(III) → Mn(IV) process that obeys first-order kinetics with respect to both total Mn(III) and O₂ concentrations. At a constant O₂ concentration of 1.0 mM, variations of total Mn(III) concentration from 0.07 to 0.65 mM yield an apparent pseudo-first-order rate constant of $(3.6 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ (for total Mn(III)) in 0.5 M NaOH at 25 °C. The pseudo-first-order rate constant for molecular oxygen, at a total Mn(III) concentration of 3.23 mM, is $(6.6 \pm 0.3) \times 10^{-3} \text{ s}^{-1}$. Combination of these pseudo-first-order rate constants results in an average value for the second-order rate constant of $2.8 \pm 0.8 \text{ M}^{-1} \text{ s}^{-1}$. The second reaction involves a much slower

decay of oxygen with a half-life of several hours and involves total consumption of the dissolved oxygen in the solution. The initial rate depends upon the initial Mn(III) concentration, but the order and rate constants have not been determined. This reaction appears to involve a photocatalyzed oxidation of the excess sorbitol by peroxide in the presence of the manganese(IV) complex. A possible mechanism would involve reduction to Mn(III) or -(II) with a cyclic reoxidation to Mn(IV) by O₂.

The Mn(IV) complex evolves oxygen upon acidification in the presence of stoichiometric quantities of peroxide. At higher pHs (pH >12.0) in the presence of an excess of peroxide, O₂ is evolved at a much slower rate. In each case, reduction to the Mn(III) complex occurs, as shown in Figures 5 and 6, which is consistent with a reversal of the equilibrium given by eq 4. Further acidification to pH 1.5 results in the formation of the [Mn(H₂O)₆]²⁺ ion. An assay of O₂ evolution during acidification confirms that 0.5 mol of oxygen/mol of Mn(IV) is evolved during reduction to Mn(III) and that a further 0.5 mol of oxygen is evolved during reduction to Mn(II). When the pH is increased to pH 13.7 and the solution is bubbled with molecular oxygen at 1.0 atm, the original Mn(IV) complex is restored. Variations of the sorbitol concentration during these interchanges indicate that for stoichiometric quantities of sorbitol (relative to Mn(IV)), negligible decomposition of the complexes to MnO₂ occurs.

The stabilities of the manganese(III) and -(IV) complexes in the presence of excess sorbitol have been studied at temperatures up to 80 °C in 0.5 M NaOH. In the absence of oxygen, the Mn(IV) complex is slowly reduced to Mn(III), presumably by oxidation of the excess sorbitol (the presence of peroxide is not essential). The addition of peroxide accelerates the reduction to Mn(III) which indicates that the equilibrium of eq 4 is shifted to the left at elevated temperatures. On lowering the pH to 10.5 at 80 °C, only the [Mn(III_A)₂] complex is formed even in the presence of oxygen at 1.0 atm.

Conclusions

The experimental results establish that stable complexes of manganese(III) and -(IV) are formed with polyhydroxy ligands in aqueous alkaline solutions. The spectroscopic, polarographic, and magnetic measurements indicate that there is a single predominant form of the Mn(IV) complex and three forms of the Mn(III) complex. The dimeric [Mn(III_A)₂] complex appears to be the initial product from the reaction of molecular oxygen with the Mn(II) complex and is in rapid equilibrium with the apparently monomeric Mn(III_A) and Mn(III_B) complexes at higher hydroxide ion and sorbitol concentrations, which is in accord with earlier suggestions.²¹ The nature of the Mn(III) complex that is involved in the oxidation to Mn(IV) is not clear. However, the decrease in the rate of reaction with O₂ for increased sorbitol concentrations may indicate that one of the two forms of the Mn(III_A) complex is involved. The effect of the sorbitol concentrations is not simple because at higher concentrations it stabilizes the tris Mn(IV) complex.

A reasonable mechanism for the formation and reaction pathways of the various manganese-sorbitol complexes and their interaction with O₂ is presented in Figure 8. The formation of a peroxo-bridged intermediate, [Mn^{IV}₂(O₂²⁻)], is consistent with the shifts in equilibrium with acidification and addition of peroxide to form Mn(III) and O₂. Such an intermediate provides a pathway by which molecular oxygen can be reduced initially to peroxide by manganese(III).

The kinetic data relate only to the overall reaction of the total Mn(III) concentration with molecular oxygen and give little insight into which of the various Mn(III) complexes is involved in the reaction.

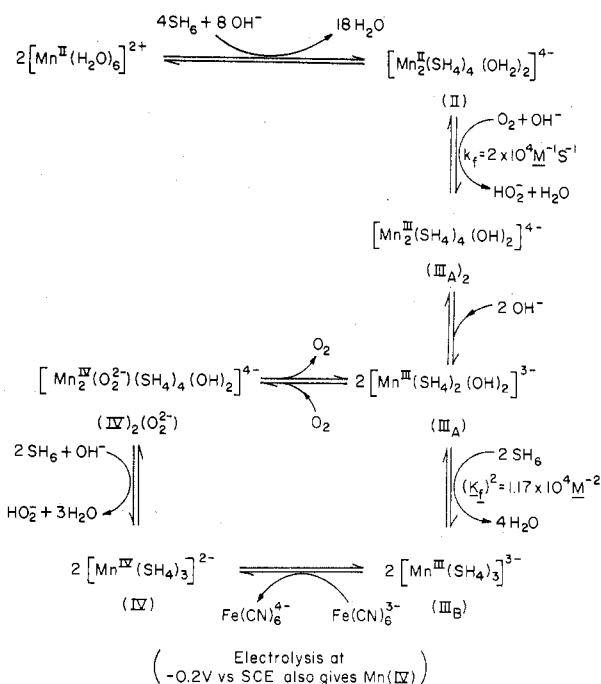
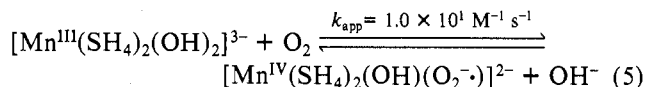
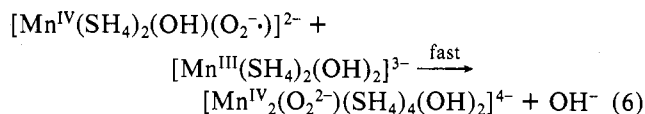


Figure 8. Redox and solution equilibria for the manganese(II), -(III), and -(IV) complexes that are formed by polyhydroxy ligands in aqueous alkaline solution (SH₆ = sorbitol).

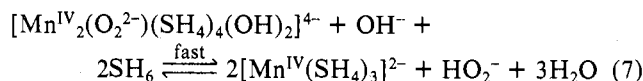
One possibility is that the monomeric Mn(III_A) complex reacts with molecular oxygen to produce a reactive Mn(IV)-superoxide ion complex in the rate-determining step



Such a superoxide ion complex could then react rapidly with another Mn(III_A) complex to produce the peroxo-bridged Mn(IV) complex in a mechanism analogous to those established in the reactions of several cobalt(II) complexes.³³



The peroxo-bridged species would then be in rapid equilibrium with the mononuclear tris Mn(IV) complex



The mechanisms of Figure 8 also provide an alternative route to the tris Mn(IV) complex through oxidation by ferricyanide ion or by controlled-potential electrolysis at -0.2 V vs. SCE of the tris Mn(III_B) complex. Apparently these two species are involved in the reversible III/IV couple at -0.33 V vs. SCE in 0.5 M NaOH and 0.5 M sorbitol. The irreversibility of the III/II reduction wave is consistent with the considerable structural rearrangements that accompany this redox change.

The increased stability of the Mn(III) and Mn(IV) oxidation states in the complexes that are formed by sorbitol, D-gluconate, and D-glucarate vs. the complexes formed by (+)-sucrose, triethanolamine,³⁴ allosane,¹³ and myo-inositol¹⁴ may reflect the inability of the latter ligands to form stable tris-bidentate complexes. The results of the present study indicate that the carboxylate groups of D-gluconate and D-glucarate are not involved in coordinate bonding to Mn(III)

and -(IV), but rather two vicinal hydroxyls in a manner analogous to sorbitol.

The enhancement of the catalytic effect of manganese for oxygen pulping in alkaline solution by the addition of sorbitol may be due to the increased solubilization of the Mn(III) and Mn(IV) oxidation states. This, in turn, would allow the manganese ions to function as more efficient oxygenation catalysts and electron transfer agents for selective delignification.

The manganese-polyhydroxy complexes appear to provide an efficient method for the generation of peroxide anion in alkaline solution from molecular oxygen. However, the ability of these complexes to act as efficient oxygenation catalysts remains to be established.

Acknowledgment. This work was supported by the U.S. Public Health Service-NIH under Grant No. GM 22761 and by the USDA-Forest Service Forest Products Laboratory, Madison, WI, under Agreement No. 12-75. We are grateful to Professor R. T. Wedding and the Biochemistry Department for the use of their CD instrument.

Registry No. Sorbitol, 50-70-4; D-gluconic acid, 526-95-4; D-glucaric acid, 87-73-0; L-tartaric acid, 87-69-4; (+)-sucrose, 57-50-1; Mn, 7439-96-5.

References and Notes

- R. L. Heath, *Int. Rev. Cytol.*, **34**, 49 (1973).
- G. M. Cheniae, *Annu. Rev. Plant Physiol.*, **21**, 467 (1970).
- R. Radmer and G. M. Cheniae in "Primary Processes", in press.
- R. E. Blankenship, Ph.D. Dissertation, University of California, Berkeley, CA, 1974.
- B. B. Keele, J. M. McCord, and I. Fridovich, *J. Biol. Chem.*, **245**, 6176 (1970).
- M. Pick, J. Rabani, F. Yost, and I. Fridovich, *J. Am. Chem. Soc.*, **96**, 7329 (1974).
- R. Radmer and G. M. Cheniae, *Biochem. Biophys. Acta*, **253**, 182 (1971).
- T. Wydrzynski, N. Zumbulyadis, P. G. Schmidt, and G. Govindjee, *Biochem. Biophys. Acta*, **408**, 349 (1975).
- T. Wydrzynski, N. Zumbulyadis, P. G. Schmidt, H. S. Gutowski, and G. Govindjee, *Proc. Natl. Acad. Sci. USA*, **73**, 1196 (1976).
- J. Doležal and F. J. Langmyhr, *Anal. Chim. Acta*, **61**, 73 (1972).
- N. Chughtai, J. Doležal, and J. Zýka, *Microchem. J.*, **20** (1975).
- G. Donoso, J. Doležal, and J. Zýka, *J. Electroanal. Chem. Interfacial Electrochem.*, **49**, 461 (1974).
- J. Doležal, E. Juláková, M. Černý, and M. Kapanica, *J. Electroanal. Chem. Interfacial Electrochem.*, **52**, 261 (1974).
- J. Doležal and H. Kekulova, *J. Electroanal. Chem. Interfacial Electrochem.*, **69**, 239 (1976).
- B. L. Velikov and J. Doležal, *J. Electroanal. Chem. Interfacial Electrochem.*, **71**, 91 (1976).
- J. L. Minor, unpublished results, Forest Products Laboratory, U.S. Department of Agriculture, Madison, WI, 1978.
- L. L. Landucci and N. Sanyer, *Tappi*, **57**, 97 (1974).
- M. E. Bodini, L. A. Willis, T. L. Riechel, and D. T. Sawyer, *Inorg. Chem.*, **15**, 1538 (1976).
- K. D. Magers, C. G. Smith, and D. T. Sawyer, *Inorg. Chem.*, **17**, 515 (1978).
- M. E. Bodini and D. T. Sawyer, *J. Am. Chem. Soc.*, **98**, 8366 (1976).
- D. T. Sawyer, M. E. Bodini, L. A. Willis, T. L. Riechel, and K. D. Magers, *Adv. Chem. Ser.*, No. **162**, 330-49 (1977).
- A. Goolsby and D. T. Sawyer, *Anal. Chem.*, **39**, 411 (1967).
- D. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists", Wiley-Interscience, New York, 1974.
- M. F. Rettig, private communication, University of California, Riverside, CA, 1975.
- D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
- B. N. Figgis and J. Lewis in "Progress in Inorganic Chemistry", Vol. 6, F. A. Cotton, Ed., Interscience, New York, 1964, pp 37-240.
- G. Brauer, "Handbook of Preparative Inorganic Chemistry", Vol. 2, 2nd ed., Academic Press, New York, 1965, p 1469.
- T. S. Davis, J. P. Fackler, Jr., and M. J. Weeks, *Inorg. Chem.*, **7**, 1994 (1968).
- J. Summers, Ph.D. Dissertation, University of Florida, 1968.
- R. Dingle, *Acta Chem. Scand.*, **20**, 33-44 (1966).
- C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Addison-Wesley, Reading, MA, 1962.
- C. K. Jørgensen, *Acta Chem. Scand.*, **12**, 1539 (1958).
- E. I. Ochiai, *J. Inorg. Nucl. Chem.*, **35**, 3375 (1973).
- J. Klepetář and K. Stulik, *J. Electroanal. Chem.*, **55**, 255 (1974).
- P. Crabbé, "ORD and CD in Chemistry and Biochemistry. An Introduction", Academic Press, New York, 1972.

Contribution from the CNR Laboratory,
Consiglio Nazionale delle Ricerche, 00131 Roma, Italy

Interaction of Iron(II) Phthalocyanine with Molecular Oxygen in Concentrated Sulfuric Acid: Kinetics and Mechanism

C. ERCOLANI,* F. MONACELLI,*¹ and G. ROSSI

Received August 8, 1978

The reaction of iron(II) phthalocyanine, FePc, with O₂ in concentrated (96%) sulfuric acid has been studied kinetically. The overall reaction is a two-step process. The first step is reversible and follows a kinetic law of the type rate = $a[O_2][FePc]/(1 + b[O_2])$, while the second step is irreversible and takes place with a rate constant $k_{II} = k_{II}' + k_{II}''[O_2]$. The experimental data can be satisfactorily explained by assuming that FePc, presumably tetraprotonated and with HSO₄⁻ ions coordinated at the axial positions of Fe(II), generates a pentacoordinate intermediate (by loss of HSO₄⁻) which then reacts with dioxygen. The 1:1 O₂:FePc adduct then gives a 1:2 species through a fast reaction with an additional FePc molecule. The 1:2 adduct is unstable and decomposes slowly with oxidation of Fe(II) and the phthalocyanine ligand, via two simultaneous processes, one of which requires the intervention of a dioxygen molecule. There are no clear-cut indications, however, to state that dioxygen is also consumed in this process. The occurrence of an induction period, sometimes observed, is discussed.

Iron(II) phthalocyanine, FePc,² has been widely studied as a model system for heme proteins such as hemoglobin and myoglobin. Although easily accessible as a stable iron(II) species in the solid state,³ like many other metal phthalocyanines, FePc is sparingly soluble in common nondonor solvents (solubility in water $\leq 10^{-4}$ M) and somewhat more soluble in N-donor solvents, with implied coordination of the N base at the axial sites of the central metal atom.⁴ FePc and several other metal phthalocyanines dissolve appreciably (ca. 10^{-2} M) in 96% H₂SO₄,³ probably owing to proton affinity of

the outer N atoms of the phthalocyanine ring. Hence, extensive studies for these complexes have been carried out in 96% H₂SO₄ concerning methods of purifying phthalocyanines,³ different crystal modifications,⁵ protonation,⁶ and interaction with small molecules.⁷

We recently described some preliminary results on the interaction of FePc with CO, NO, and O₂ in 96% H₂SO₄.⁸ Interaction with CO and NO has also been dealt with elsewhere.^{7,9} In our report,⁸ however, it was shown for the first time that a reversible oxygenation process occurs for FePc with