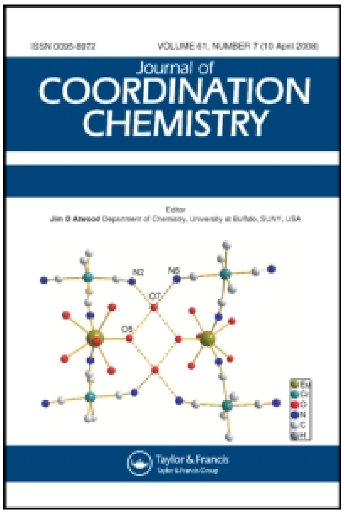

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KINETIC STUDIES OF THE OXIDATION OF bis[1-HYDROXY-2-(SALICYLIDENEAMINO)-ETHANE]MANGANESE(II) BY MOLECULAR OXYGEN

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KINETIC STUDIES OF THE OXIDATION OF bis[1-HYDROXY-2-(SALICYLIDENEAMINO)-ETHANE]MANGANESE(II) BY MOLECULAR OXYGEN

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Oxidation of the bis[1-hydroxy-2-(salicylideneamino)ethane]manganese(II) complex by molecular oxygen has been investigated in aqueous dimethylformamide and acetonitrile solutions. Kinetic EPR experiments indicated rapid oxidation of the metal to Mn(III), followed by a slower step, in which a Mn(IV) complex is formed. This final oxidation product was isolated in 90% yield, and characterized by different techniques. EPR measurements suggested the existence of an unstable binuclear intermediate $[L_2Mn(II)\ldots Mn(II)L_2]$, preceding the Mn(III) complex formation. Manometric measurements of oxygen uptake also showed two kinetic paths for formation of the Mn(III) species, both of them exhibiting a first-order dependence on the [complex], with rate constants $k_{obs} = (1.65 \pm 0.08)10^{-3}\,s^{-1}$ and $(5.57 \pm 0.28)10^{-6}\,s^{-1}$, respectively. Variation of the percentage of water in the reaction solution indicated that the rapid path is dependent on the oxygen concentration, while the slow one is almost $[O_2]$ independent. The influence of added hydroxide ions and of the solvent were also verified, suggesting competitive substitution reactions. A mechanism involving a monomeric Mn(III) intermediate is proposed and discussed, corroborated by electrochemical and EPR measurements.

Keywords: Manganese–Schiff base complexes; autoxidation; kinetic studies; mononuclear and binuclear manganese complexes

Non SI-units used: $\mu_B = e\hbar/2m_ec = 9.274 \times 10^{-24}\,J\,T^{-1}$; $1\,G = 10^{-4}\,T$

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INTRODUCTION

Manganese–Schiff base complexes have been extensively studied in recent years as models for biologically active systems, especially Mn-superoxide dismutases,[1] binuclear manganese catalases,[2] and the tetranuclear photosynthetic oxygen-evolving complex,[3] which is found in the chloroplast thylakoid membranes of higher plants and algae. Most of these studies are focused on the structural characteristics of different manganese complexes, trying to understand the assembly reactions that occur in mononuclear species or multinuclear manganese clusters with oxygen.

Spectroscopic measurements have been used to clarify the coordination sites and the many oxidation states of the metal in such clusters, although the interpretation of these data has led to considerable controversy.[4,5] Usually, mixed-valence binuclear or multinuclear clusters were used as models for those systems, but sometimes a mononuclear center was also required to explain multiline EPR signals,[6] or unusual EXAFS features.[7]

However, very few mononuclear manganese complexes containing N,O-donor ligands have been investigated,[8–10] in comparison with clusters. In addition, most of the investigations exploiting the redox capabilities, and the catalytic activities of manganese species when interacting with small molecules such as dioxygen and its reductive derivatives[11–13] are related to multicenter species.

In this paper, we describe the synthesis and reactivity of a manganese(II)–Schiff base complex toward molecular oxygen, leading to the corresponding final manganese(IV) compound. Kinetic studies were carried out in aqueous dimethylformamide or acetonitrile solutions, at (30.0 ± 0.1)°C, by monitoring the oxygen consumption. Based on the experimentally determined rate law, a mechanism is proposed involving a manganese(III) species. Evidence for this intermediate was obtained by electrochemical and EPR measurements. The final oxidized product was isolated and characterized by different techniques as a monomeric manganese(IV) complex.

EXPERIMENTAL

Materials and General Methods

Salicylaldehyde and 2-aminoethanol were purchased from Aldrich and manganese(II) chloride tetrahydrate from Merck. N,N-dimethylformamide (DMF) and acetonitrile (MeCN) (chromatographic grade) were purchased from Merck, and dried with molecular sieves for the kinetic and electrochemical measurements. All other chemicals and solvents used for synthesis were pure reagent grade. High-purity nitrogen gas was used to deaerate solutions. All the aqueous solutions were prepared in nanopure deionized water (from a Barnsted apparatus).

Preparation of the Compounds

The bis[1-hydroxy-2-(salicylideneamino)ethane]manganese(II) complex, [Mn^{II}(sal-mea)$_2$], was prepared under strictly anaerobic conditions in a glove bag with a constant flux of nitrogen. To a solution of salicylaldehyde (5.3 mL, 40 mmol) in 10.0 mL of methanol, 2-aminoethanol (3.0 mL, 40 mmol) was added, resulting in a yellow solution. Then, 1.25 g of $MnCl_2 \cdot 4H_2O$ (20 mmol) and 1.0 g of sodium acetate (10 mmol) dissolved in 25.0 mL of water were slowly added with constant stirring. Upon addition of diethyl ether (~ 30 mL), a pale yellow solid was formed. This precipitate was filtered, washed with cold water then with ethanol, and dried in a desiccator under vacuum. When dry, this solid can be exposed to air, although it has been stored under nitrogen. The yield for this reaction was 65%. Elemental analysis, yields and physical parameters for this complex are reported in Table I.

The corresponding manganese(IV) complex, [Mn^{IV}(sal-mea)$_2$]$\cdot 2H_2O$, was prepared from a previously reported procedure,[14] and observed to have identical properties to main product obtained in autoxidation of the original manganese(II) complex, with a yield of 90%. Different techniques were used in the characterization of this compound (Table I).

Physical Measurements

Elemental analyses (C, H, and N) were performed at *Central Analítica IQ-USP*, using a Perkin-Elmer 2400 CHN elemental analyzer. Manganese was determined spectrophotometrically by the periodate method,[15] monitoring the formation of permanganate ions at 545 nm.

Magnetic susceptibilities were measured with a Cahn, model DTL 7500 Faraday balance at room temperature. Calibrations were made with [$HgCo(SCN)_4$] from Aldrich ($\chi = 16.44 \times 10^6$ CGS units/g, at 20°C),[16] and corrections were applied for the diamagnetism calculated from Pascal's constants. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the magnetic susceptibility per formula unit.

IR spectra were performed on KBr (Merck) pellets with a Perkin-Elmer 783 spectrometer, in the range 4000–200 cm^{-1}. UV–Vis spectra were obtained in a Beckman DU-70 instrument, equipped with a thermostatted cell compartment.

Cyclic voltammetric measurements were recorded under nitrogen in acetonitrile at (25 ± 2)°C, using a modular system of Princeton Applied

TABLE I Elemental analysis, yields and physical parameters of manganese(II) and manganese(IV) complexes with the ligand 1-hydroxy-2-(salicylideneamino)ethane

Complex	*Analysis, %*			*Yield, %*	*UV/Vis*[c] *under* N_2	λ, nm *in air*	(ε, $M^{-1}cm^{-1}$) *with* H_2O_2	μ_{eff}, μ_B (*solid*)
		Calcd.	*Found*					
[Mn^{II}(sal-mea)$_2$] or $MnC_{18}H_{20}N_2O_4$	C	56.40	56.48	65	310 (5460)	268	268	5.99
	H	5.26	5.14		394 (2155)	310 sh	310 sh	
	N	7.31	7.14		470 (574)	394	394	
	Mn	14.33	13.33			470		
[Mn^{IV}(sal-mea)$_2$] · $2H_2O$[a] or $MnC_{18}H_{18}N_2O_4 \cdot 2H_2O$	C	51.81	49.15	90			270 (19100)	4.07
	H	5.31	5.10			390 (5965)	390 (6120)	
	N	6.71	6.54			475 (2874)	475 (2634)	
	Mn	13.16	12.27			554 (1459)	554 (1337)	
[Mn^{IV}(sal-mea)$_2$] . $2H_2O$[b]	C	51.81	52.20	75				4.0
	H	5.31	5.10			396 (4846)[d]		
	N	6.71	7.00			472 (1731)		
	Mn	13.16	12.44			554 (1710)		

[a] Product obtained in the autoxidation of the corresponding Mn(II) complex, after recrystallization.
[b] Ref. 14.
[c] In Me_2SO.
[d] In Me_2SO, Ref. 14.

Research Corp., composed of a potentiostat/galvanostat model 273A, and a Hewlett-Packard plotter, model 7090A. A three-electrode configuration was employed with tetraethylammonium perchlorate (TEAP) as supporting electrolyte, an Ag/Ag^+ reference electrode (+503 mV *vs.* NHE), and platinum working and auxiliary electrodes. The ferrocene/ferrocenium couple (+560 mV *vs.* NHE) was used as an external reference.[17]

EPR spectra were performed in a Varian E-109 X-band spectrometer, equipped with a variable-temperature controller. The measurement conditions were 20 mW microwave power; 0.4 mT of amplitude modulation at 100 kHz; central magnetic field at 260.0 mT; 500 mT of scan range, and 4 min of scan time. The measurements of powder samples were made at room temperature (298 K), and at 100 K. For the kinetic EPR experiments, frozen acetonitrile solutions of the starting manganese(II) complex were used. By taking the reaction vessel out of the Dewar flask, submitting it to an ultrasonic laboratory cleaner during specified intervals of time, and finally replacing it in the Dewar flask, it was possible to follow the decay of the Mn(II) complex, and the formation of the final Mn(IV) complex by reaction with molecular oxygen.

Kinetic measurements were also carried out in aqueous-N,N-dimethylformamide or acetonitrile solutions, in a Warburg respirometer from B. Braun, model V-85, monitoring the oxygen uptake at $(30.0 \pm 0.1)°C$. The reaction was initiated by the addition of solid complex to the appropriate solutions equilibrated with air. All experiments were performed at least three times. The experimental curves of oxygen consumed *vs.* time were then analyzed by the initial rate method using standard procedures,[18] and with deviations $\leq 5\%$ for the obtained rate constants.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Manganese(II) *Complex*

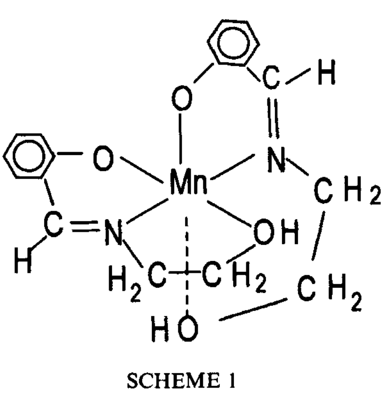
The bis[1-hydroxy-2-(salicylideneamino)ethane]manganese(II) complex was prepared under strictly anaerobic conditions as described above, and characterized by UV/Vis, infrared, and EPR spectra, and magnetic susceptibility measurements. This complex is insoluble in water, but soluble in ethanol, N,N-dimethylformamide, acetonitrile, and dimethylsulfoxide, with partial oxidation. It is also slightly soluble in ethanol/water or DMF/water mixtures (up to 20 : 80% v/v).

Characteristic infrared bands for this complex were observed at 1620–1640, 1440–1470, and 1300 cm^{-1}, attributed to imine stretching ($\nu_{C=N}$), methylene bending (δ_{CH_2}), and phenol stretching (ν_{OPh}), respectively, in agreement with the reported assignment for N-salicylideneamino acid–manganese(II) complexes,[19] and related polydentate Schiff base–Mn(III) and Mn(IV) complexes.[2(c),20] Carbon–hydrogen stretches ($\nu_{C\text{–}H}$), aliphatic and aromatic, were verified at 3050 and 2900 cm^{-1}, in addition to ν_{C-O} at 1050–1060 cm^{-1}, ν_{ring} at 1540 cm^{-1}, and ν_{Mn-O} at 560 cm^{-1}. The absence of water was indicated by the lack of a strong broad absorption band at 3300–3400 cm^{-1}. A strong band at approximately 650 cm^{-1}, indicative of Mn–OO–Mn bonds,[21] was also not observed.

An effective magnetic moment of 5.99 μ_B was obtained for the complex in the solid state, in agreement with the spin only value for a mononuclear octahedral high-spin manganese(II) complex.[22] Results of elemental analyses (shown in Table I) were consistent with the formula $[Mn^{II}(\text{sal-mea})_2]$, in a 2 : 1 ligand to metal stoichiometry. Therefore, the complex is monomeric, with coordination of the tridentate ligands through the imine nitrogen, the phenolate and the hydroxyl oxygens, in a nearly octahedral geometry (Scheme 1). The meridional isomer is favored relative to the facial one, according to previous results for Mn(IV) complexes with related ligands, where structures were determined.[14]

Reactivity of the Manganese(II) *Complex*

Although very stable in the solid state, when dissolved in N,N-dimethylformamide, dimethylsulfoxide, ethanol, or acetonitrile, in the presence of oxygen or hydrogen peroxide, the bis[1-hydroxy-2-(salicylideneamino)-ethane]manganese(II) complex is immediately oxidized, resulting in a deep brown solution, which slowly became reddish. Figure 1 shows the UV–Vis spectra of the complex under nitrogen, in the presence of oxygen (from air), and after adding hydrogen peroxide.



SCHEME 1

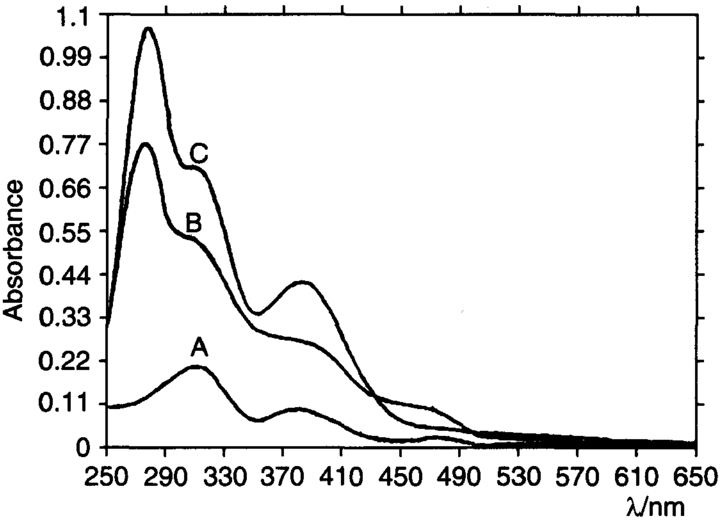


FIGURE 1 UV/Vis spectra of the bis[1-hydroxy-2-(salicylideneamino)ethane]manganese(II) complex (3.00×10^{-4} mol dm^{-3}) in dimethylformamide. A – under nitrogen; B – in air; C – with addition of $[H_2O_2] = 2.90 \times 10^{-3}$ mol dm^{-3}.

Even by dissolving the complex under nitrogen, evidence for partial oxidation was observed. The strong absorption band at 268 nm, observed only after treatment with an oxidizing agent, is assigned to π–π^* transitions of the imine groups, and the increasing band at 394 nm is probably due to a L → M electron transfer transition, with the metal in the Mn(III) or Mn(IV) oxidation state. The observed bands at 470 and 554 nm are usually attributed to d–d transitions in Mn(IV) complexes ($^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, for an octahedral environment). The abnormally large extintion coefficients for these transitions are a consequence of the intense UV tail in the visible region.[14]

The hydroxyl-rich Schiff-base ligand is a strong Lewis base and can stabilize the Mn(IV) oxidation state, as well as the Mn(II) and Mn(III). During oxidation of the starting Mn(II) complex, evidence for both oxidation states of the metal was obtained from different experimental approaches.

Electrochemical Measurements

Cyclic voltammograms in acetonitrile solutions of the bis[1-hydroxy-2-(salicylideneamino)ethane]manganese(II) complex were recorded under nitrogen, with solutions also prepared under nitrogen, and prepared in air, or with vigorous bubbling of oxygen. The complex showed strong adsorption at the electrode surface, which had to be cleaned after each voltammogram. For preparations in air, two irreversible anodic waves were observed at

$E_{pc} = +0.70$ V and $+1.24$ V *vs.* NHE, with an additional *quasi*-reversible wave at -0.20 V. This third wave was not obtained in the absence of oxygen. Under completely anaerobic conditions, only two irreversible waves were observed, at $E_{pc} = +0.60$ and $+1.04$ V *vs.* NHE. For preparations with bubbling of oxygen, the obtained voltammograms were very similar to those obtained in air.

The wave at negative potential appears only after previous oxidation of the solution, resulting from a dioxygen manganese complex formed by interaction of the starting manganese(II) complex with molecular oxygen. This compound is better described as a superoxomanganese(III) complex, involving an intramolecular electron transfer, that can be reduced electrochemically to the corresponding peroxomanganese(III) complex:

$$L_2Mn^{II} + O_2 \rightleftharpoons [L_2Mn^{III}(O_2^{\bullet -})]$$

$$L_2Mn^{III}(O_2^{\bullet -}) + e^- + H^+ \rightleftharpoons [L_2Mn^{III}(HO_2^-)]$$

A peroxo-adduct has been proposed for interaction of a similar complex, $[Mn^{III}(salen)Cl]$, where salen = N,N′-bis(salicylidene)ethylenediamine, with molecular oxygen.[23] In this case the oxidation was observed at -0.24 V *vs.* SCE (~0.02 V *vs.* NHE) under argon. In the presence of oxygen, the intensity of this peak increased two-fold.

The free ligand, prepared in acetonitrile solution, showed only the wave at $E_{pc} = +0.60$ V, attributed to an oxidation process of the ligand, independent of the metal. The other anodic wave, at $E_{pc} = +1.24$ V *vs.* NHE, is probably also due to a ligand-centered oxidation, but catalyzed by the metal, since it was not observed for the free ligand. It can be attributed to the conversion of the anionic ligand L to the corresponding radical ($L^{\bullet}$), which then pairs with an unpaired metal *d* electron to form a covalent bond. Similar ligand-centered processes have been described[24] for the complexes $[Mn^{II}(PA)_3]^-$ and $[Mn^{II}(PA)_2(acac)]^-$, where PA = 2-picolinate, and acac = acetylacetonate. However, in this case the free ligand PA^- was oxidized at $+1.65$ V *vs.* NHE, whereas the complex $[Mn^{II}(PA)_3]^-$ was oxidized to $[Mn^{II}(PA^-)_2(PA^{\bullet})] \equiv Mn^{III}(PA^-)_3$ at $+0.62$ V *vs.* NHE. The shift of $+1.03$ V in potential was interpreted as a measure of the covalent bond energy for the d–p bond that results from the two unpaired electrons.[24]

On the other hand, Pecoraro *et al.*[13] observed only a *quasi*-reversible cathodic wave at $E_{pc} = -542$ mV *vs.* Ag/AgCl (-0.039 V *vs.* NHE), attributed to the one-electron reduction of the corresponding Mn(IV) complex with the same ligand in dimethylsulfoxide. In our measurements, at the very beginning of the reaction this wave was not observed, probably because formation of the final manganese(IV) complex was not yet substantial.

Characterization of the Product of the Reaction

The final product of oxidation of bis[1-hydroxy-2-(salicylideneamino)-ethane]manganese(II) was isolated after 3h of reaction with molecular oxygen at 30°C. After purification by recrystallization, it was characterized as the dihydrate bis[1-hydroxy-2-(salicylideneamino)ethanoate]manganese(IV) complex by elemental analyses, UV/Vis, and IR spectroscopies, and by magnetic susceptibility measurements (see Table I). The same product can also be obtained by reaction with hydrogen peroxide. Our results were very similar to those described previously in the literature for the same compound,[14] obtained by a different procedure.

The X-band EPR spectra performed on the solid starting manganese(II) and the final manganese(IV) complexes, at 100 and 298 K, showed broad resonances for which the parameters $g = 2.037$ and 2.609 were determined, respectively (see Figure 2). No resolved hyperfine structure from ^{55}Mn was observed in the solid state or in acetonitrile solution (~0.05 mol dm^{-3}) for both complexes, indicating spin-coupling of very closed species. The EPR spectrum reported in more diluted methanol/DMF (2 : 3) solution for the Mn(IV) complex with the same ligand exhibits marked rhombic electronic distortions, with $g = 5.45$, and calculated $E/D = 0.32$.[14] Monomeric manganese(IV) complexes containing N_3O_3 donor ligands, but having predominant axial symmetry in a strong ligand field, usually show two

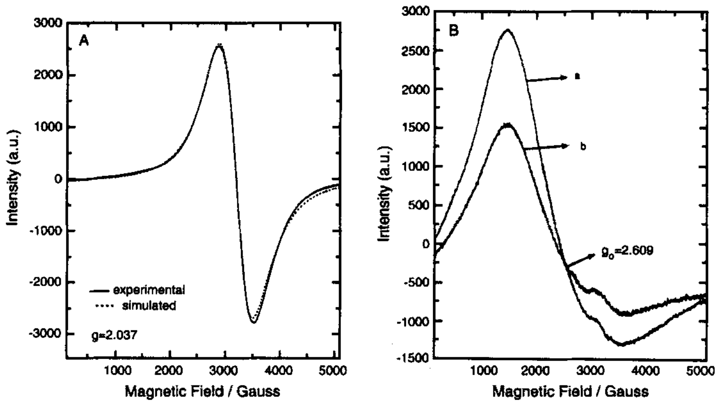


FIGURE 2 EPR spectra of solid samples: (A) the initial Mn(II) complex, at 100 K, and (B) the final Mn(IV) complex, (a) at room temperature and (b) at 100 K, with the ligand [1-hydroxy-2-(salicylideneamino)ethane].

broad signals[25] at $g=2.0$ and $g=3.6$. In our case, it seems that the axial zero-field splitting parameter is very small.

By monitoring rapid oxidation of the Mn(II) complex and slow formation of the corresponding Mn(IV) complex, in frozen acetonitrile solution as described in the Experimental section, evidence for the formation of an unstable intermediate with a zero-field splitting, at *circa* 2.0 min of reaction (Figure 3(A)), was obtained. This intermediate is probably a precursor to a

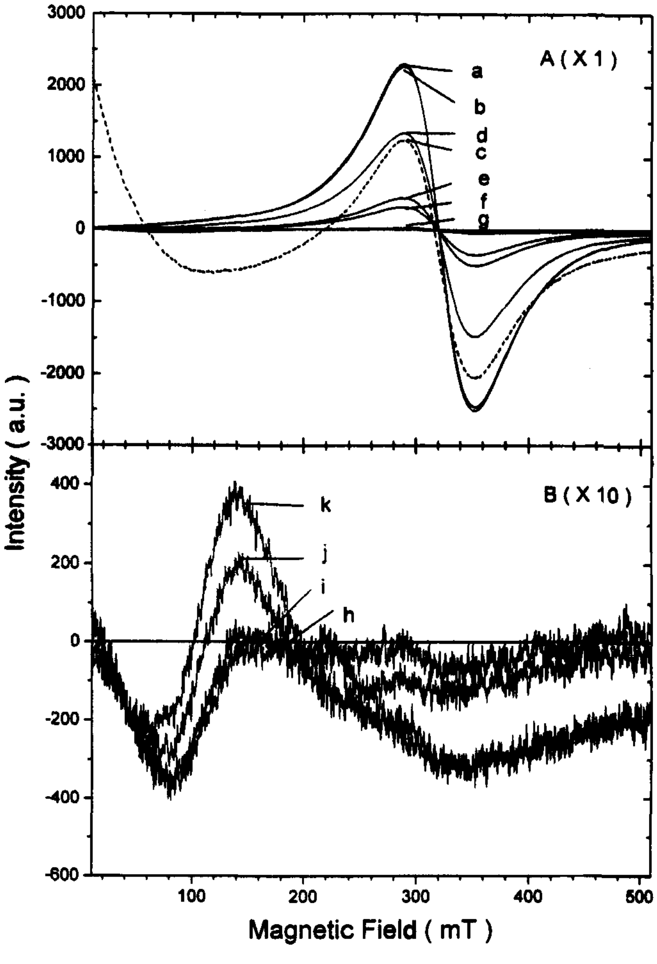


FIGURE 3 EPR spectra, at 100 K, of acetonitrile solutions of the [$Mn^{II}(sal\text{-}mea)_2$] complex, after different reaction times (controlled by using an ultrasonic cleaner, as described in Experimental section). (A) Amplifier gain = 10^3; (B) Amplifier gain = 10^4. Spectra after. (a) 30; (b) 90; (c) 110; (d) 130; (e) 160; (f) 180; (g) 240 s; and (h) 4.0; (i) 7.0; (j) 17.0; and (k) 90 min of reaction. (g) and (h) are the same spectra with different gains.

dioxygen Mn(III) complex which is EPR silent. By numerical integration of the EPR spectra in Figure 3(A), an area proportional to the concentration of the paramagnetic species was obtained, and the kinetics of disappearance of the Mn(II) species was followed, with concomitant formation of the Mn(III) species as a more stable intermediate (Figure 4). The letters in Figure 4 correspond to those in Figure 3(A). For the first two points (30 and 90 s) no significant change in the spectra was observed. At 110 s of reaction, however, the EPR spectrum changed, showing a zero-field splitting which can be attributed to an unstable binuclear species [L_2Mn(II)...Mn(II)L_2]. In this species, each manganese ion weakly interacts with the other through the alcoholic binding groups, which in this case act as bridging groups. Formation of this binuclear unstable complex (two octahedral Mn(II) species sharing a common edge) probably facilitates coordination of the oxygen molecule to the manganese center, by weakening the binding of the alcoholic groups to the metal. A similar structure has been reported for dimeric V(IV) complexes with the same ligand, exhibiting spin-coupling in

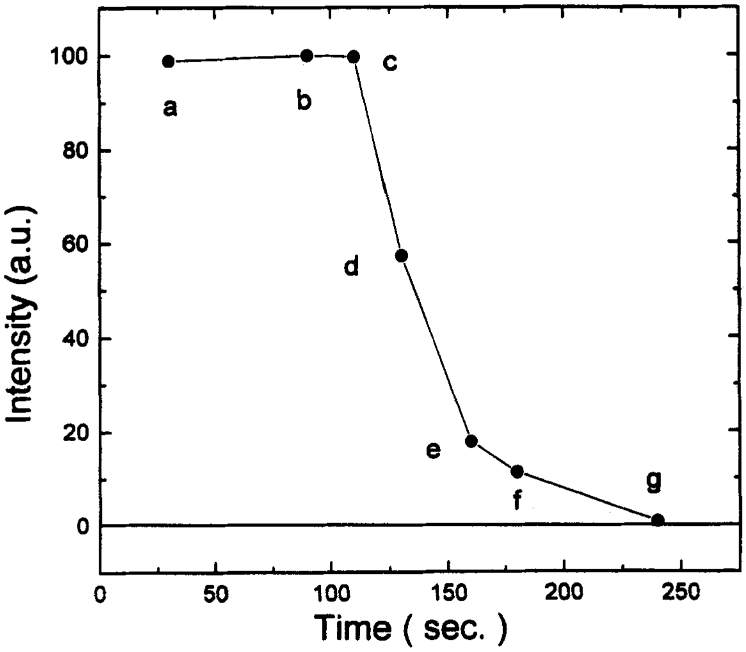


FIGURE 4 Integrated area (numerical double integration) of the EPR spectra shown in Figure 3(A) (normalized to hundred) as a function of the reaction time. It is important to note that the area corresponding to spectrum (c) is the same as those of previous time (spectra (a) and (b)).

the solid state, but yielding monomeric species in solution.[26] Probably, the observed spectrum (curve c, in Figure 3(A)) is superimposed with that of a monomeric Mn(II) complex. By area comparison, around 30–40% of the total manganese was estimated to be responsible for this zero-field splitting spectrum. The following point (150 s, spectrum d) shows loss of 44% of the total Mn(II) species, converted to a Mn(III) species which is EPR silent. It is very difficult to characterize this binuclear intermediate. After 250 s the conversion to the Mn(III) complex is complete. In Figure 3(B), spectra h, i, j, and k show a residual quantity of the binuclear intermediate and start to reveal the formation of the final Mn(IV) species as a broad line spectrum, with $g = 2.609$.

Kinetic Studies

Curves of the consumed oxygen *vs.* time showed that autoxidation of the complex occurs in two steps, an initial more rapid step, followed by a slower one, as shown in Figure 5 through the decomposition of the experimental curve. The reaction was carried out in aqueous/DMF solutions (mostly at

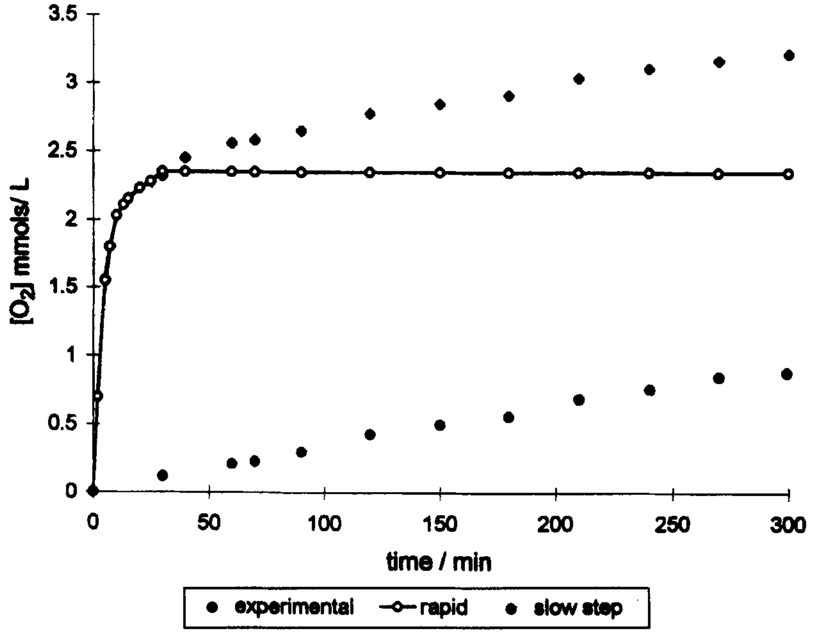


FIGURE 5 Experimental curve of the consumption of oxygen (mmols/dm^3 min), decomposed into a rapid and a slow step, for the oxidation of the bis[1-hydroxy-2-(salicylidene-amino)ethane]manganese(II) complex. Reaction at (30.0 ± 0.1)°C; [Mn^{II}(sal-mea)$_2$] = 8.70 × 10^{-3} mol dm^{-3}; [OH$^-$]$_{added}$ = 6.70 × 10^{-3} mol dm^{-3}; in aqueous DMF solution (17% water v/v).

17% water v/v), and both processes were individually analyzed. A stoichiometric molar ratio of $[O_2]/[Mn]$ in the range 0.28 to 0.40 was usually observed for the rapid step under the experimental conditions.

Plots of the initial rates (V_i) *vs.* total $[Mn^{II}(sal\text{-}mea)_2]$ indicated a first-order dependence for both processes (Figure 6), with rate constants

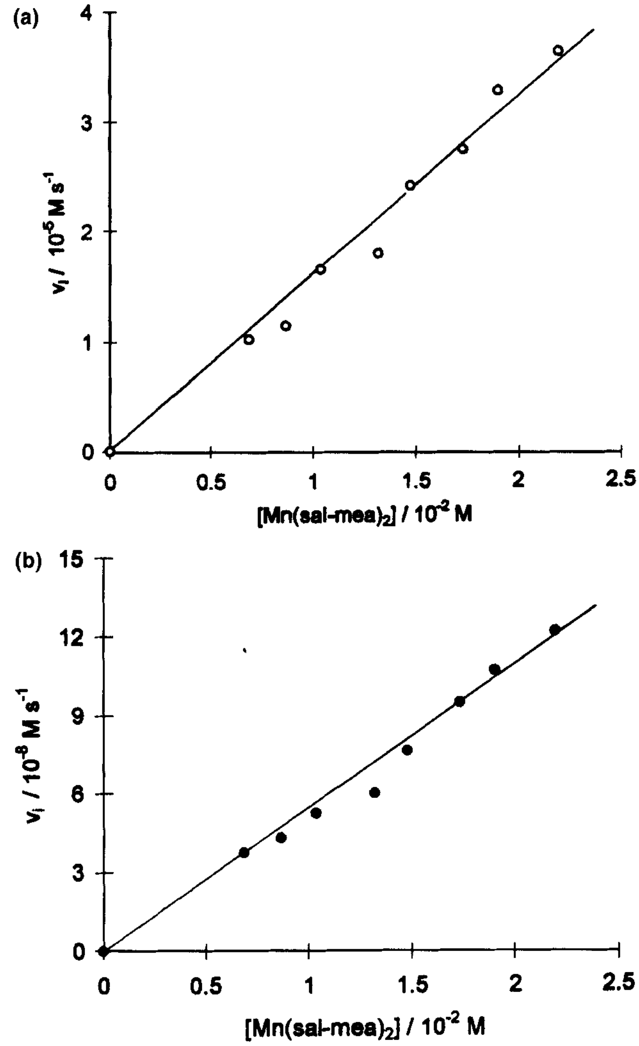


FIGURE 6 Dependence of the initial rate of the uptake of oxygen with the bis[1-hydroxy-2-(salicylideneamino)ethane]manganese(II) complex concentration: (a) rapid step; (b) slow step. Reaction in aqueous/DMF solution (3% water v/v), at $T = (30.0 \pm 0.1)$°C, and $[OH^-]_{added} = 6.70 \times 10^{-3}$ mol dm^{-3}.

$k_{obs} = (1.65 \pm 0.08)\,10^{-3}\,s^{-1}$ and $(5.57 \pm 0.28)\,10^{-6}\,s^{-1}$ for the rapid and slow steps, respectively.

Variation of the percentage of water in the organic solvent up to 23% showed a dependence of the reaction rate on the water content (Figure 7). As the solubility of molecular oxygen is higher in organic solvents than in

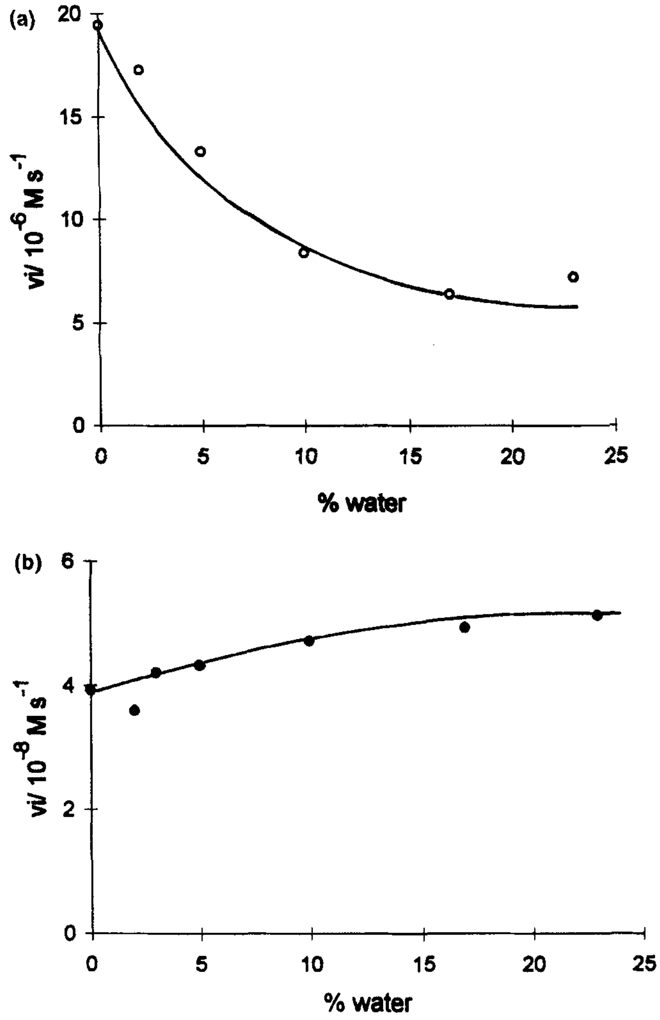


FIGURE 7 Influence of the percentage of water in the DMF solvent on the initial reaction rate for the oxidation of the bis[1-hydroxy-2-(salicylideneamino)ethane]manganese(II) complex: (a) rapid step; (b) slow step. $[Mn^{II}(\text{sal-mea})_2] = 8.70 \times 10^{-3}\,mol\,dm^{-3}$; $[OH^-]_{added} = 6.70 \times 10^{-3}\,mol\,dm^{-3}$ and $T = (30.0 \pm 0.1)°C$.

water, we determined the concentration of dissolved oxygen on different mixtures of water and DMF, equilibrated with air by polarography (data not shown). Under our experimental conditions, the determined solubility of oxygen was 0.25 mM in pure water, and 0.58 mM in dried DMF. By plotting the calculated initial rates at different percentage of water *vs.* the corresponding determined oxygen solubilities, it was verified that the rapid step is first-order on the $[O_2]$, in the range 0.4–0.8 mM, with a second-order rate constant $k = (8.62 \pm 0.34)\,M^{-1}\,s^{-1}$. On the contrary, the slow step is almost $[O_2]$ independent.

Similar studies on the reactivity of $[LMn_2^{II,II}(\mu\text{-}CH_3CO_2)](ClO_4)_2$ (L= N,N,N′,N′-tetrakis(2-methylenebenzimidazole)1,3-diaminopropan-2-ol) with hydrogen peroxide, in aqueous acetonitrile or aqueous ethanol solutions, have also shown a dependence on water content. This was interpreted as evidence of an aqua-complex intermediate, with dissociation of the bridged carboxylate group.[2(a)]

Comparative studies were carried out with our complex in acetonitrile or dimethylformamide for different percentages of water. The results are shown in Table II. Both solvents have similar dielectric constants: 38.3 and 37.5, at 20°C for DMF and MeCN, respectively. Although the solubility of oxygen in MeCN is higher than in DMF (1.6 mM *vs.* 0.58 mM), the initial rates were lower in this solvent, for both steps. As acetonitrile is a better coordinating agent than DMF, molecules of the solvent can coordinate to the metal center, acting as a Lewis base. Therefore, this competition between dioxygen and solvent molecules for the coordination center could explain the difference observed on the kinetic parameters in the two solvents.

The oxidation reaction was also favored at higher apparent pH. The influence of added hydroxide showed a first-order dependence up to 10 mM concentration, followed by a tendency to saturation (Figure 8), for both steps in aqueous DMF solutions. This can be explained by formation of a hydroxo-complex, which is also reactive toward oxygen.

TABLE II *Pseudo*-first-order rate constants for the oxidation of the complex $[Mn^{II}(salmea)_2]$ in aqueous dimethylformamide, and acetonitrile solutions, at (30.0 ± 0.1)°C, with addition of $[OH^-] = 6.70 \times 10^{-3}$ M

Solvent	*% Water in the solvent*	$k_{obs}/10^{-4}\,s^{-1}$ *Rapid step*	$k_{obs}/10^{-6}\,s^{-1}$ *Slow step*
DMF	1	23.9 ± 1.2	7.24 ± 0.36
	2	19.8 ± 1.0	4.14 ± 0.21
	5	15.3 ± 0.8	4.98 ± 0.25
MeCN	1	7.92 ± 0.39	5.84 ± 0.29
	2	7.59 ± 0.38	3.17 ± 0.16
	5	4.53 ± 0.23	1.93 ± 0.09

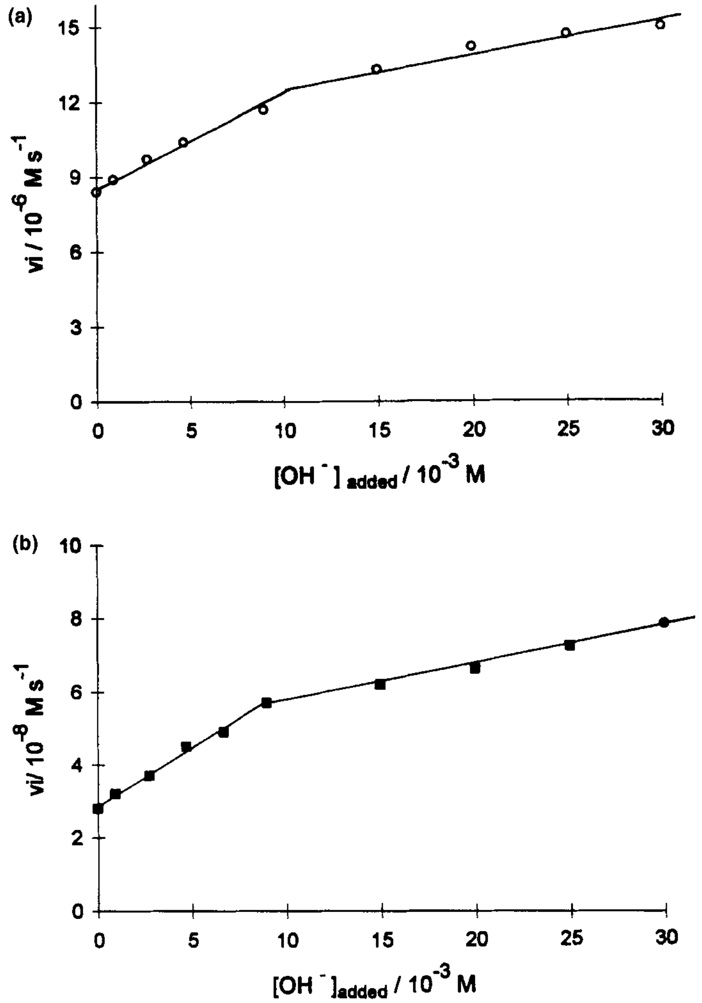


FIGURE 8 Initial rate of the uptake of oxygen by the bis[1-hydroxy-2-(salicylidene-amino)ethane]manganese(II) complex as a function of the added $[OH^-]$: (a) rapid step; (b) slow step. Reaction in aqueous/DMF solution (17% water v/v), $[Mn^{II}(sal\text{-}mea)_2] = 8.70 \times 10^{-3}\,mol\,dm^{-3}$, at $T = (30.0 ● 0.1)$°C.

The determined rate law (up to $[OH^-] = 10\,mM$) was: $V_i = k_o + k[OH^-]$, where $k_o = (8.68 \pm 0.43)10^{-6}\,M\,s^{-1}$, and $k = (3.21 \pm 0.16)10^{-4}\,s^{-1}$ for the rapid step, and $k_o = (2.87 \pm 0.14)10^{-8}\,M\,s^{-1}$, and $k = (3.15 \pm 0.16)10^{-6}\,s^{-1}$ for the slow step.

As indicated by the rate constants, the second path of oxygen uptake is at least 100-fold slower than the initial one. At the beginning of the reaction it is responsible for only 1% of the total consumption of oxygen.

Mechanism of reaction

Autoxidation of bis[1-hydroxy-2-(salicylideneamino)ethane]manganese(II) to the corresponding Mn(IV) compound occurs by two steps: an initial rapid step leading to an intermediate Mn(III) species, probably a superoxo-complex, followed by a slow step in which the final stable product is formed. Peroxo-Mn(III) species, containing Schiff-base ligands, have been suggested as catalytically active complexes in epoxidation of olefins,[27] and in reactions with hydrogen peroxide[28] or molecular oxygen;[29] however, there is no chemical evidence to support this consideration.

In Scheme 2, where L = [1-hydroxy-2-(salicylideneamino)ethane], a mechanism is proposed, involving single electron-transfer paths with formation of hydrogen peroxide as a by-product. The very rapid initial formation of a binuclear species could only be detected in frozen solutions, during the kinetic EPR measurements.

$$[\mathrm{L_2Mn^{II}}] + \mathrm{O_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{L_2Mn^{III}(O_2^{\bullet-})}] \qquad (1)$$

$$[\mathrm{L_2Mn^{II}}] + \mathrm{OH^-} \overset{K}{\rightleftharpoons} [\mathrm{L_2Mn^{II}(OH)}]^- \qquad (2)$$

$$[\mathrm{L_2Mn^{II}(OH)}]^- + \mathrm{O_2} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{L_2Mn^{III}(O_2^{\bullet-})}] + \mathrm{OH^-} \qquad (3)$$

$$[\mathrm{L_2Mn^{III}(O_2^{\bullet-})}] \xrightarrow{k_3} [\mathrm{H_{-2}L_2Mn^{IV}}] + \mathrm{H_2O_2} \qquad (4)$$

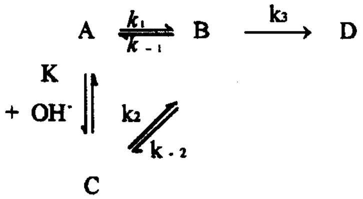
SCHEME 2

By this scheme, the total oxygen consumption involves two paths, and the rate law is given by:

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_1[\mathrm{L_2Mn^{II}}][\mathrm{O_2}] + k_2[\mathrm{L_2Mn^{II}(OH)}][\mathrm{O_2}]$$
$$- (k_{-1} + k_{-2}[\mathrm{OH^-}])[\mathrm{L_2Mn^{III}(O_2^{\bullet-})}].$$

The reaction includes formation of the intermediate $[\mathrm{L_2Mn^{III}(O_2^{\bullet-})}]$, and a path dependent on added $[\mathrm{OH^-}]$. At the beginning of the reaction, formation of the manganese(IV) complex is still small, and could be neglected.

Assuming a pre-equilibrium[30] and considering *pseudo*-first-order conditions for the oxygen consumption steps, the equations describing approximate solutions are:



SCHEME 3

$$(k_1 + k_2K[\mathrm{OH}^-])[\mathrm{A}]^{\mathrm{pe}} = (k_{-1} + k_{-2})[\mathrm{B}]^{\mathrm{pe}},$$
$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = \mathrm{d}[\mathrm{D}]^{\mathrm{pe}}/\mathrm{d}t = k_3[\mathrm{B}]^{\mathrm{pe}},$$

and

$$[\mathrm{B}]^{\mathrm{pe}} = \{(k_1 + k_2K[\mathrm{OH}^-])/(k_{-1} + k_1 + k_{-2} + k_2)\}([\mathrm{A}]_0 - [\mathrm{D}]_0^{\mathrm{pe}})\mathrm{e}^{-k_{\mathrm{pe}}t},$$

where $k_{\mathrm{pe}} = (k_1 + k_2K[\mathrm{OH}^-])k_3/(k_{-1} + k_1 + k_{-2} + k_2) =$ the effective pre-equilibrium rate constant.

Therefore, if it is assumed that $k_3 \ll k_{-1}$ (or k_{-2}) $\ll k_1$ (or k_2),

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = k_3(K_1 + K_2K[\mathrm{OH}^-])[\mathrm{L}_2\mathrm{Mn}^{\mathrm{II}}][\mathrm{O}_2],$$

where $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$.

This expression is consistent with the experimentally determined rate law, exhibiting first order on $[\mathrm{Mn}]_{\mathrm{total}}$ and $[\mathrm{OH}^-]$, and under these conditions the rate-controlling step is equation (4) in Scheme 2. The equilibria are achieved before step (4) occurs. Additionally, formation of the final $\mathrm{Mn}^{\mathrm{IV}}$ species could also explain the slow oxygen consumption by shifting of the equilibrium steps (equations 1–3). Indeed, based on data in Figure 6, an estimated value of 3.4×10^{-3} is obtained for the ratio $k_3/(k_1 + k_2)$ considering the ratio of k_{obs} for the slow and rapid steps of oxygen consumption.

In the final step (equation (4)), the coordinated ligands or water act as a proton donor for reduction of the superoxo species to hydrogen peroxide, which immediately reacts with the remaining Mn(II) and Mn(III) species. The reactivity of the studied complexes with hydrogen peroxide is the subject of a forthcoming separate report.[31]

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