Reaction of Superoxide and Hydroperoxide with a Series of Manganese Complexes

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Manganese(II) and manganese(III) complexes of polydentate Schiff base ligands have been reacted with superoxide and hydroperoxide ion. With linear pentadentate ligands, manganese(III) appears to be reduced to a 'Mn^{2+}–O$_2$°' species on reaction with superoxide. Evidence is presented in support of this formulation. No observable reaction is obtained with tetradentate ligands. All manganese(III) complexes are reduced to manganese(II) hydrated ion with hydroperoxide.

Introduction

In recent years, metalloenzymes containing manganese [1–3], and other transition metals [4–6] have been found which catalyze the disproportionation of superoxide anion, O_2^{1-}, to molecular oxygen and hydrogen peroxide [7]. Manganese has also been implicated in the photosynthetic liberation of dioxygen from water [1, 8]. No doubt the extent and nature of these manganese catalyzed reactions which involve dioxygen species are dependent on the redox properties of the manganese. For example, we have been able to correlate reactivity toward dioxygen with manganese chelate reduction potentials [9, 10]. As an extension of this work, we wish to report the reactions of O_2^{1-} and HO_2^{1-} with several of these same manganese complexes.

Experimental

All manganese complexes employed in this study have been previously characterized [9–13]. Superoxide solutions were prepared in anhydrous dimethylsulfoxide (DMSO) (Burdick & Jackson) employing dicyclohexyl-18-crown-6 [14]. Peroxide solutions were prepared by dissolving Na$_2$O$_2$ in known

amounts of deionized water. KO$_2$ was obtained from Alfa Ventron. Na$_2$O$_2$ was obtained from Fisher Scientific Company. Ultraviolet-visible spectra were recorded in anhydrous DMSO using a Cary Model 219 spectrophotometer employing 1 cm cells. Electron spin resonance spectra were obtained on solutions of manganese complexes prepared in 50/50 DMF/Toluene (V/V) and 50/50 DMSO/H$_2$O employing Varian Model 4500 and Model E-12 spectrometers.
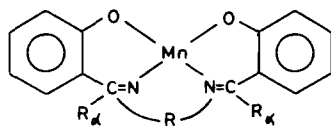
Results and Discussion

Superoxide Reactivity

In a previous study we reported on the reaction of NO with a series of Mn(III) complexes [10, 15]. From the results, we concluded that a one-electron reduction process had taken place to yield a (Mn(II)–NO$^+$) complex. Superoxide ion may function in a similar manner with transition metals. In this regard, complexes incorporating pentadentate [Mn-(ZSALDPT)NCS, Mn(SALDAPE)NCS, Mn(HBPDPT)-NCS] and hexadentate [Mn(ZSAL 1,5,8,12)NCS] ligands (Structure I) wherein Z = 5-NO$_2$, 5-H, 5-CH$_3$O, 3-NO$_2$ and 3-CH$_3$O have been successfully reacted with O_2^{1-}. Manganese(III) complexes incorporating quadridentate ligands, Mn(SALOPHEN)NCS and Mn(SALEN)Cl, appear to not react with O_2^{1-}.

Figure 1 is a trace of the visible spectrum produced when a manganese(III) complex containing either a penta- or hexadentate ligand is reacted with successive 5 μl quantities of a 0.1 M O_2^{1-} solution. The presence of an isobestic point suggests that only two species are present in solution. The spectra of the titrated solution clearly show a reduction in intensity of the Mn(III) d–d band. A shift to lower wavelength (380–360 nm) for the UV absorbing charge transfer band is also observed. Accompanying this reduction in intensity, is a color change from

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R	R_α	Abbreviation
C_6H_4	H	SALOPHEN
C_2H_4	H	SALEN
$(CH_2)_3-NH-(CH_2)_3$	H	SALDPT
$(CH_2)_3-NH-(CH_2)_3$	C_6H_5	HBPDPT
$(CH_2)_3-O-(CH_2)_3$	H	SALDAPE
$(CH_2)_3-NH-(CH_2)_2-NH-(CH_2)_3$	H	SAL 1,5,8,12

Structure I

Fig. 2. Plot of absorbance at 544 nm of 2.5 ml of 10^{-3} M Mn(5-CH$_3$OSALDPT)(NCS) titrated with 5 μl additions of 0.1 M O_2^{1-} in DMSO.

Fig. 1. Reaction of 5 μl additions of 0.1 M O_2^{1-} with 2.5 ml of 10^{-3} M Mn(5-CH$_3$OSALDPT)(NCS) in DMSO.

green to yellow. The resulting yellow solutions are insensitive to dioxygen. These factors suggest that the manganese specie in solution is not a simple manganese(II) complex which itself has been shown to be dioxygen reactive [11] under these conditions. These changes in the UV–VIS spectra upon reaction of Mn(III) with O_2^{1-} are reminiscent of those found when the same Mn(III) complexes were reacted with NO. The main difference between the two is the position of the charge transfer band of the 'Mn(II)O$_2$' and 'Mn(II)(NO)' product (O$_2$ = 360 nm; NO = 340 nm). It should be pointed out that the visible spectra of these products do not resemble that of a native Mn(II) complex (Λ_{max} = 375 nm). Consequently, it is reasonable to conclude that the O_2^{1-} reaction with Mn(III) yields a new Mn(II) complex, possibly described as a dioxygen complex.

In an attempt to determine the stoichiometry of the reaction, a plot of absorbance *versus* $N_{O_2^{1-}}/N_{Mn}$ was made, Fig. 2, for the general reaction described by Fig. 1. The curve shows a change in slope at $N_{O_2^{1-}}/N_{Mn} \cong 1$ as well as a further reaction as more O_2^{1-} is added. This secondary reaction can be ascribed to a reaction with the ligand system in the manner observed during the oxygenation of Mn(ZSALDPT). Support for this assignment comes from the fact that reaction of O_2^{1-} with several free ligands (5-NO$_2$SAL 1,5,8,12; 5-NO$_2$SALEN; 5-NO$_2$SALDPT; 5-NO$_2$-SALOPHEN) revealed minor but significant changes in each UV–VIS spectrum. ESR spectra of solutions wherein the Mn(III) is in excess are silent both at room temperature and at −150 °C. Two points are suggested by this observation: 1) the product formed with O_2^{1-} is not a simple high spin Mn(II) complex because there is no six-line pattern and 2) at −150 °C one should see the O_2^{1-} signal but it is also absent indicating reaction with Mn(III).

At least three reactions should be considered when one attempts to interpret these results. The UV–VIS data would appear to eliminate reaction
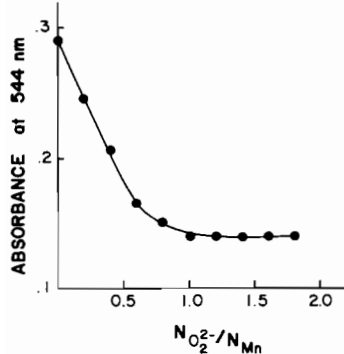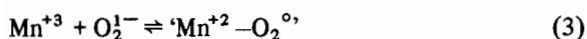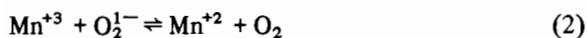
$$Mn^{+3} + O_2^{1-} \rightleftharpoons Mn^{+3}-O_2^{1-}$$
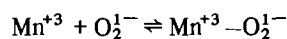
Fig. 3. Plot of absorbance at 544 nm of 2.5 ml of 10^{-3} M Mn(5-NO$_2$SALDPT)(NCS) titrated with 5 μl aliquots of 0.1 M O$_2^{2-}$ in DMSO.

$$Mn^{+3} + O_2^{1-} \rightleftharpoons Mn^{+2} + O_2 \qquad (2)$$

$$Mn^{+3} + O_2^{1-} \rightleftharpoons \text{'}Mn^{+2} - O_2^{\circ'} \qquad (3)$$

(1) because the d–d band for Mn(III) disappears. The absence of an ESR signal would rule-out reaction (2) wherein a free Mn(II) is generated. Reaction (3) appears to be implicated. Exchange broadening

between the Mn(II) and O$_2^{\circ}$ could account for the absence of an ESR signal. This is further supported by the fact that the native Mn(II) complexes, in fact, react with O$_2$ under these conditions to give Mn(III) μ-peroxo dioxygen complexes.

The reaction of Mn(III) complexes containing only four donor atoms with O$_2^{1-}$ was also investigated. It was found that these complexes, Mn-(SALEN)Cl and Mn(SALOPHEN)NCS, do not react with O$_2^{1-}$. Proof for this comes from the fact that no change is observed in the Mn(III) visible spectrum when O$_2^{1-}$ is added. Reasons for this difference in reactivity are not readily apparent; however, certain factors can be eliminated. Recent electrochemical data on the reduction of Mn(SALEN)Cl and Mn-(SALOPHEN)NCS [16] reveal that each potential is comparable to a related 5-coordinate complex, Mn(SALDPT)NCS, which does react with O$_2^{1-}$. Reduction potentials for Mn(SALEN)Cl, Mn-(SALOPHEN)NCS, and Mn(SALDPT)NCS are -0.297 mv, -0.153 mv and -0.245 mv respectively *versus* SCE. If reduction potentials were the main criteria, one would predict that either Mn(SALOPHEN)NCS or Mn(SALEN)Cl should react with O$_2^{1-}$. In a related study the E$_{1/2}$ for Mn(TPP)Cl
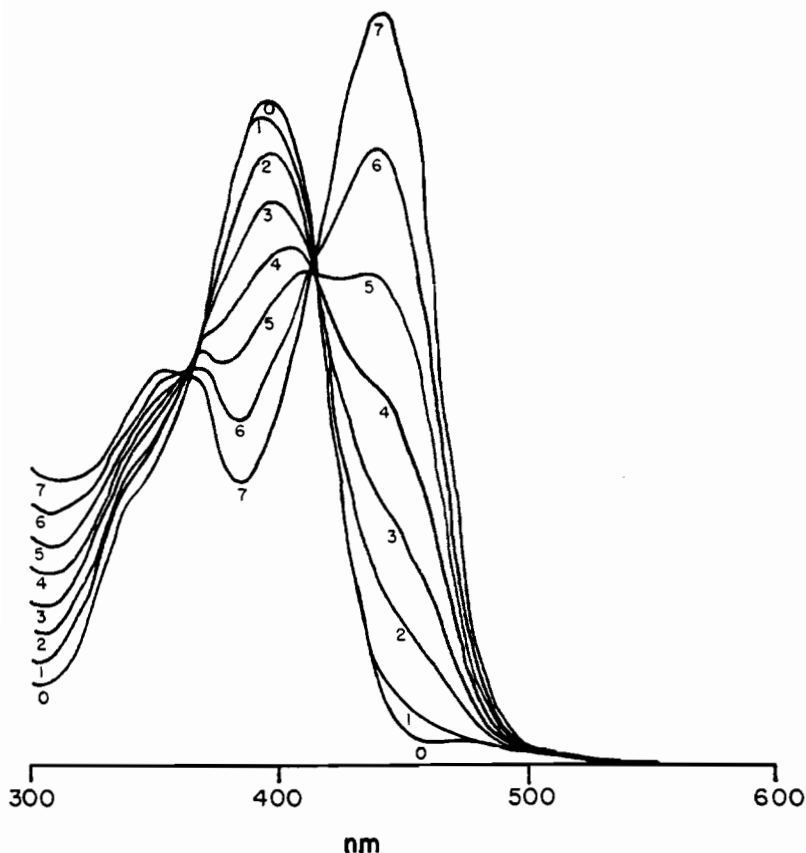

Fig. 4. Reactions of 5 μl additions of 0.1 M O$_2^{1-}$ with 2.5 ml of 10^{-4} M 5-NO$_2$SAL 1,5,8,12 free ligand in DMSO.

in DMSO solution has been reported to be −0.33 mv *versus* SCE [17] which has been independently [18] indicated to react with O_2^{1-} to yield Mn(TPP). The latter was identified by its characteristic visible spectral properties. No information was provided regarding ESR characteristics of reactants and products. Hence, reduction potentials alone do not seem to afford a logical reason for the reactivity differences. Furthermore, we found no apparent substituent effects in O_2^{1-} reactivity since Z = 5-NO$_2$ and Z = 5-CH$_3$O yielded the same results. Structural differences, no doubt, exist between complexes containing tetradentate and higher polydentate ligands which may cause subtle changes in manganese d-orbital energies. For example, the bonding d-orbital on manganese(III) may match up better with the O_2^{1-} bonding orbital when 5 and 6 coordinate ligands rather than 4 coordinate ligands are involved. We cannot, of course, discount the notion that in DMSO all manganese(III) species regardless of polydentate ligand may be solvated six-coordinate structures.

Only manganese(II) complexes with 5-NO$_2$ derived ligands [Mn(5-NO$_2$SALDPT), Mn(5-NO$_2$SAL 1,5,8,12) and Mn(5-NO$_2$SALBPT)] have been shown to react with O_2^{1-}. There does not appear to be any evidence to suggest that Mn(II) is being oxidized to Mn(III) or reduced to Mn(I) by O_2^{1-}. The spectral changes observed are very similar to those which occur when the uncomplexed 5-NO$_2$ ligand [19] is reacted with O_2^{1-}, Fig. 3. In a related study, Valentine [20] has reported that Zn(TPP) reacts with O_2^{1-} to form a stable, isolable superoxo complex. The characteristics of the product from UV−Visible and ESR measurements have led the authors to conclude that the complex is highly ionic with little electron transfer from O_2^{1-} to Zn(II). In our laboratory, we have reacted Zn(SALEN) and Zn-(ZSALDPT) with O_2^{1-} but find, as in the Mn(II) case, no evidence for reaction

Hydroperoxide Reactivity

Each complex studied regardless of polydentate ligand reacts with HO_2^{1-} (5 μl amounts of 0.1 *M* aqueous solution) as shown by the disappearance of the Mn(III) d−d band. A 1:1 stoichiometry of oxidant to reductant is indicated (Fig. 4). This well behaved curve would suggest that the solvent DMSO is not reacting with peroxide to yield a sulfone. The presence of two well-defined isosbestic points suggest that reaction with HO_2^{1-} occurs with the absence of any long-lived intermediate. The above reaction was also monitored via ESR. Addition of HO_2^{1-} to those complexes containing pentadentate ligands yielded a six line ESR pattern with a coupling constant of 89 gauss. This result is reminiscent of the Mn(III) + NO reaction which we reported as a one electron reduction [13] to yield high spin Mn(II). No signal attributable to O_2^{1-} is observed at −150 °C.

Hence, we conclude that HO_2^{1-} has reduced Mn(III) to Mn(II), and since the peroxide was added as an aqueous solution, any O_2^{1-} produced would be immediately consumed.

In a related study, Stein *et al.*, [21] have examined the reactions of superoxide and peroxide with Mn(II) and Mn(III) complexes of EDTA and CyDTA in aprotic media. Using ESR, cyclic voltammetry and UV−Visible spectra, they concluded that superoxide reduced Mn(III) to Mn(II) with liberation of O_2. Results with our complexes do not give a simple Mn(II) complex since the reduced product does not exhibit the properties of our previously characterized Mn(II) complexes. We suggest only partial electron transfer from O_2^{1-} to Mn(III) has occurred. Stein also examined the reaction of O_2^{1-} with a series of Mn(II) complexes. The stoichiometry of the reaction was found to be 1 Mn:2O_2^{1-} and it was concluded that a Mn(IV)-oxo species was being produced. Again, this stands in contrast to our results wherein O_2^{1-} did not appear to react with Mn(II).

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