

Production of Hydrogen Peroxide from Dioxygen and Hydroxylamine or Hydrazine catalysed by Manganese Complexes

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Manganese(II) catecholates complexes efficiently catalyse the production of H_2O_2 from dioxygen in the range pH 7.5–8.6 using hydroxylamine or hydrazine as substrates; concentrations of hydrogen peroxide $> 0.2 \text{ mol dm}^{-3}$ and turnover numbers $[\text{H}_2\text{O}_2]/[\text{Mn}^{\text{II}}] > 10^4$ can be obtained. The rate of production and yields are very sensitive to the electronic effect of the substituents on the catechol ring with the best results being achieved using 4,5-dihydroxybenzene-1,3-disulfonate. Deuteriation studies (using ND_2OD) indicated that the reduction of O_2 occurs *via* an electron transfer from the substrate and a mechanism is proposed whereby both O_2 and the substrate become bound to manganese and the electron transfer is mediated through the manganese catecholate complex.

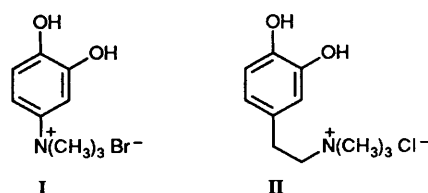
Dioxygen is extremely abundant in the environment and therefore potentially a cheap raw material. However, while it is a strong oxidant it is often kinetically inert and will not undergo many reactions under ambient conditions. In the reduction of O_2 to H_2O_2 there is the opportunity to produce an oxidising agent which is more reactive under ambient conditions and easier to manipulate. Possible *in situ* uses of the H_2O_2 generated are in synthetic organic chemistry and in the formulation of liquid laundry detergents.

A number of metal-containing enzyme systems which produce H_2O_2 are known, for example the copper-containing galactose oxidase which catalyses the oxidation of galactose and related compounds by O_2 , with the O_2 being reduced to H_2O_2 .¹ There have been a number of reports of production of H_2O_2 when O_2 reacts with systems containing transition-metal ions or complexes,² although in the majority of cases the H_2O_2 rapidly disappears by further reaction or by catalytic decomposition.³

In the presence of a reducing substrate, catalytic production of H_2O_2 is possible. It has already been reported that the manganese(II)-4,5-dihydroxybenzene-1,3-disulfonate (Tiron) system is an efficient catalyst for production of H_2O_2 from O_2 by NH_2OH in the range pH 7.5–8.6.⁴ In this study the effect of variations in the substrate and ligand on the production of H_2O_2 were investigated. The high selectivity of efficient production of H_2O_2 to one metal (Mn) and one class of ligand (the catechols) led to a more detailed investigation of the nature of the catalyst and the method of dioxygen reduction, and thereby the suggestion of a plausible mechanism for production of H_2O_2 .

Experimental

Materials.—The water used in hydrogen peroxide production experiments was purified by passage through a mixed-bed ion-exchange resin (Amberlite MB3, BDH). All reagents used were of AnalaR grade and purified, when necessary. Tiron and *N*'-2-(hydroxyethyl)piperazine-*N*-propane-3-sulfonic acid (hepps) were recrystallised from aqueous ethanol. Catechol was sublimed before use. 4-Chloro,⁵ 4,5-dichloro- and tetrachlorocatechol⁶ were prepared by standard methods. In the preparation of 3,4-⁷ and 3,5-dinitro⁸-catechol a solid CO_2 -MeOH bath was used to obtain better temperature control. 5-Nitrotropolone (2-hydroxy-5-nitrocyclohepta-2,4,6-trien-1-one),⁹ 3-formyl-4-hydroxybenzenesulfonate¹⁰ and 4-hydroxy-3-



iminomethylbenzenesulfonate¹¹ were prepared according to standard procedures. Phenylhydroxylamine was prepared by the reduction of nitrobenzene with zinc.¹² The complex $[\text{Mn}(\text{acac})_3]$ (acac = acetylacetonate) was prepared according to Bhattacharjee and Chaudhuri.¹³ Yield: 8.5 g (76%), m.p. 155 °C (decomp.) (lit.,¹³ 155 °C) (Found: C, 51.10; H, 5.95%; N, 0. Calc. for $\text{C}_{15}\text{H}_{14}\text{MnO}_6$: C, 51.15; H, 6.00%).

(3,4-Dihydroxyphenyl)trimethylammonium bromide **I**. 3,4-Dimethoxyaniline (3 g), sodium hydroxide (1.9 g), and methyl iodide (4.7 cm^3) were dissolved in water (20 cm^3) and stirred vigorously under reflux at room temperature for 3 h. The solution was cooled to 0–4 °C and the solid filtered off, washed with ice-cold water recrystallised from water with animal charcoal. The iodide was dissolved in water and converted into the bromide by passing it through an ion-exchange column which had been treated with KBr (aq.). The eluent was evaporated to dryness and dried *in vacuo*. Yield 2.5 g (51%) (Found: C, 40.6; H, 6.00; N, 5.35. Calc. for $\text{C}_9\text{H}_{14}\text{BrNO}_2 \cdot \text{H}_2\text{O}$: C, 40.65; H, 6.00; N, 5.40%).

(3,4-Dihydroxyphenethyl)trimethylammonium chloride **II**. 3,4-Dihydroxyphenethylamine hydrochloride (5g) and NaHCO_3 (6 g) were dissolved in MeOH (22 cm^3) and methyl iodide (7.5 cm^3) was added. The solution was stirred under reflux for 16 h, cooled and the residue filtered off and washed with MeOH. The filtrate and washings were combined and evaporated to dryness, and the residue recrystallised from water. The solid was washed with ice-cold water. The iodide was converted into the chloride by passing an aqueous solution down an anion-exchange column in the chloride form. Yield 4.6 g (76%), m.p. 240 °C (Found: C, 56.05; H, 7.75; N, 5.95. Calc. for $\text{C}_{11}\text{H}_{16}\text{ClNO}_2$: C, 57.00; H, 7.80; N, 6.05%).

Measurement of Hydrogen Peroxide.—(a) *In water.* In a typical experiment a solution of $\text{NH}_2\text{OH} \cdot \text{HCl}$ (3.48 g), Tiron (0.019 g) and hepps buffer (2.50 g) was adjusted to pH 8.0 with AristaR carbonate-free¹⁴ NaOH (aq.). The solution (100 cm^3) was transferred to a drechsel bottle (250 cm^3) equipped with a

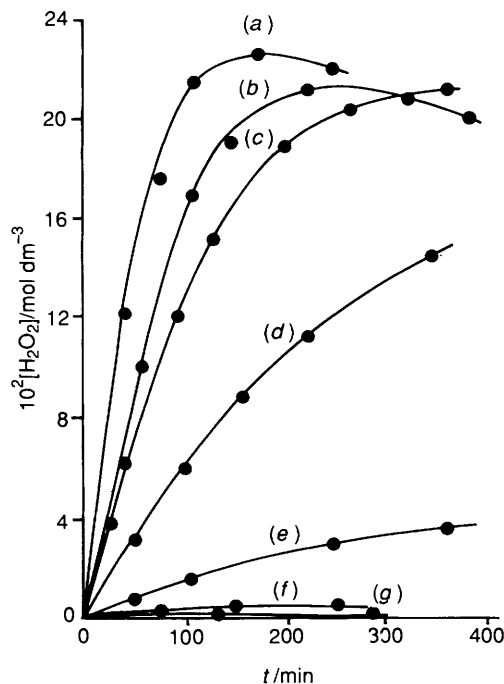


Fig. 1 Production of H_2O_2 by the Mn^{II} -Tiron catalysed oxidation of hydroxylamine. $[\text{Tiron}] = 0.0006 \text{ mol dm}^{-3}$, $[\text{NH}_2\text{OH}] = 0.5 \text{ mol dm}^{-3}$, pH 8.0, $T = 20.0^\circ\text{C}$, $0.7 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$; $[\text{Mn}^{\text{II}}] = 1 \times 10^{-4}$ (a), 2×10^{-4} (b), 2.5×10^{-5} (c), 6.3×10^{-6} (d), 1.6×10^{-6} (e), 0 and (f) 0 $\text{mol dm}^{-3} + 0.001 \text{ mol dm}^{-3} \text{ Na}_4\text{edta}$ (g)

Table 1 Production of H_2O_2 in the Mn^{II} -Tiron- NH_2OH system at different $[\text{Mn}^{\text{II}}]$. In all runs $[\text{Tiron}] = 6 \times 10^{-4} \text{ mol dm}^{-3}$, initial $[\text{NH}_2\text{OH}] = 0.5 \text{ mol dm}^{-3}$, $T = 20.0^\circ\text{C}$, pH 8.0, $0.7 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$

| $10^6 [\text{Mn}^{\text{II}}]/\text{mol dm}^{-3}$ | Relative $[\text{Mn}^{\text{II}}]$ | 10^6 Initial Rate/ $\text{mol dm}^{-3} \text{ s}^{-1}$ | $t_{\text{max}}/\text{min}$ | $[\text{H}_2\text{O}_2]/\text{mol dm}^{-3}$ |
|---|------------------------------------|---|-----------------------------|---|
| 1.6 | 1 | 2.6 | — | — |
| 6.3 | 4 | 10.4 | — | — |
| 25.0 | 16 | 25.5 | 400 | 0.212 |
| 100.0 | 64 | 60.0 | 160 | 0.228 |
| 200.0 | 128 | 27.6 | 220 | 0.212 |

sintered glass inlet and O_2 was passed through the rapidly stirred solution at *ca.* $0.7 \text{ dm}^3 \text{ min}^{-1}$ which was maintained at $20.0 \pm 0.5^\circ\text{C}$. After addition of MnCl_2 (1.0 cm^3 , $0.0025 \text{ mol dm}^{-3}$) the H_2O_2 produced was analysed iodometrically.

(b) In D_2O . A small glass tube (100 cm^3) was used and an oxygen flow rate of $0.2 \text{ dm}^3 \text{ min}^{-1}$. Deuterated hydroxylamine was prepared by dissolving $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.70 g) in D_2O (Gold label, Aldrich); rapid exchange at pH 8.0 resulted in virtually complete conversion of hydroxylamine into ND_2OD . Solid NaOH (AristaR) was added to neutralise the solution and then Tiron (0.0038 g) before adjusting the pH to 8.4 ($\text{pD} = \text{pH} + 0.4$) with NaOH (aq.). The solution was made up to 20.0 cm^3 (with D_2O) and then transferred to the reaction vessel. A concentrated solution of MnCl_2 (10.0 mol dm^{-3} in water) was prepared so that only 0.0250 cm^3 needed to be added.

Determination of Hydroxylamine.—Fiegel's reagent solution [nickel(II)-butane-2,3-dione monoxime]¹⁵ was used to indicate $[\text{NH}_2\text{OH}] < 10^{-3} \text{ mol dm}^{-3}$. As $0.5 \text{ mol dm}^{-3} \text{ NH}_2\text{OH}$ was the norm, the disappearance of the 'red ring' indicated that $>99.8\%$ NH_2OH had been used up.

Studies on the Manganese Tiron Complex.—Determination of the magnetic moment in the presence and absence of hydroxylamine. An NMR method for determination of magnetic sus-

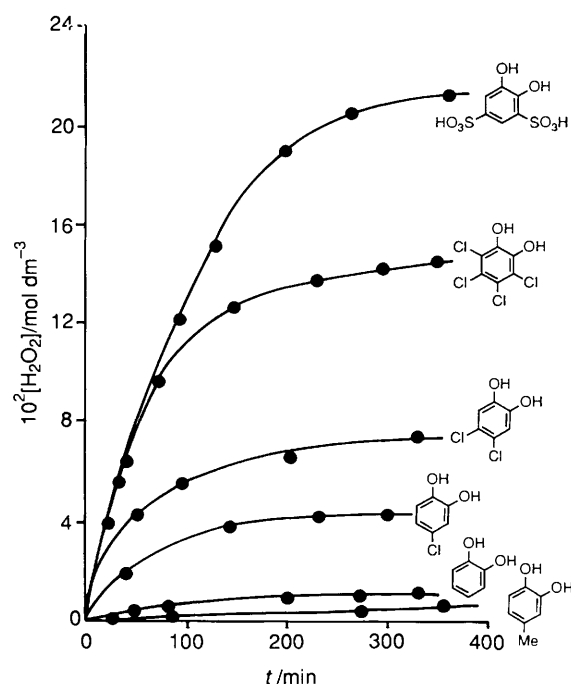


Fig. 2 Hydrogen peroxide production with catechols in the Mn^{II} - NH_2OH system. $[\text{Mn}^{\text{II}}] = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{catechol}] = 0.0006 \text{ mol dm}^{-3}$, $[\text{NH}_2\text{OH}] = 0.5 \text{ mol dm}^{-3}$, pH 8.0, $T = 20.0^\circ\text{C}$, $0.7 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$

ceptibility in solution using a split tube has been described.¹⁶ The outer segment of the split tube was filled (to a depth of 3–4 cm) with 1% Bu'OH in water containing Tiron (0.03 mol dm^{-3}) and hepps (0.1 mol dm^{-3}) at pH 8.0. The inner tube was filled to a similar depth with the same solution with in addition manganese chloride (0.01 mol dm^{-3}). This procedure was repeated with the addition of hydroxylamine (0.1 mol dm^{-3}) in the outer and inner tubes.

Instruments.—A Perkin-Elmer 683 spectrophotometer using KBr plates and samples as Nujol mulls was employed for IR spectra, a Perkin-Elmer 551 spectrophotometer for UV/VIS spectra, and a Varian E12 spectrometer for ESR spectra.

Results

The Mn^{II} -Tiron system catalyses the production of H_2O_2 from O_2 and NH_2OH in the range pH 7.5–8.6. The results are shown in Fig. 1; concentrations of $\text{H}_2\text{O}_2 > 0.2 \text{ mol dm}^{-3}$ and turnover numbers $[\text{H}_2\text{O}_2]/[\text{Mn}^{\text{II}}] > 10^4$ were obtained. Without Tiron negligible amounts of H_2O_2 were produced. In the absence of added Mn^{II} slow formation of H_2O_2 was observed. This reaction was virtually quenched by the addition of ethylenediaminetetraacetate (as Na_4edta) and presumably arises from adventitious traces of Mn^{II} .¹⁷ At higher $[\text{Mn}^{\text{II}}]$ the rates of production of H_2O_2 and yields fall off probably due to metal-catalysed decomposition of H_2O_2 .

This effect is seen more clearly in Table 1 where an approximately four-fold increase in $[\text{Mn}^{\text{II}}]$ between 1.6×10^{-6} and $6.3 \times 10^{-6} \text{ mol dm}^{-3}$ is accompanied by a four-fold increase in rate, but between 2.5×10^{-5} and $1 \times 10^{-4} \text{ mol dm}^{-3}$ the rate is only increased by a factor of about 2.5 and between 1×10^{-4} and $2 \times 10^{-4} \text{ mol dm}^{-3}$ there is a fall in the initial rate. The maximum yield of H_2O_2 was marked by the disappearance of hydroxylamine and by the greatest intensity in the yellow colour of the reaction solution.

Fig. 2 shows the results with Tiron, catechol and 4-methylcatechol. The rates of production of H_2O_2 are in the order Tiron \gg catechol $>$ 4-methylcatechol. Also shown are the results with three chlorocatechols. The rates of production of

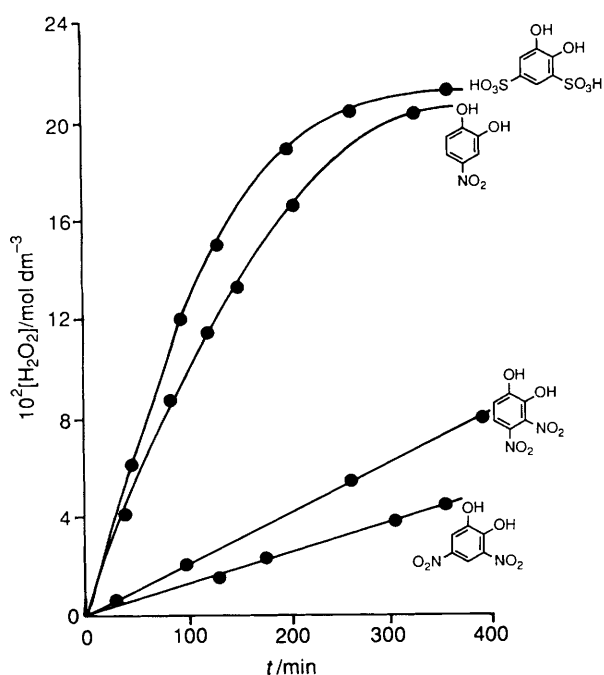


Fig. 3 Production of H_2O_2 with some nitrocatechols in the $\text{Mn}^{\text{II}}-\text{NH}_2\text{OH}$ system. Conditions as in Fig. 2

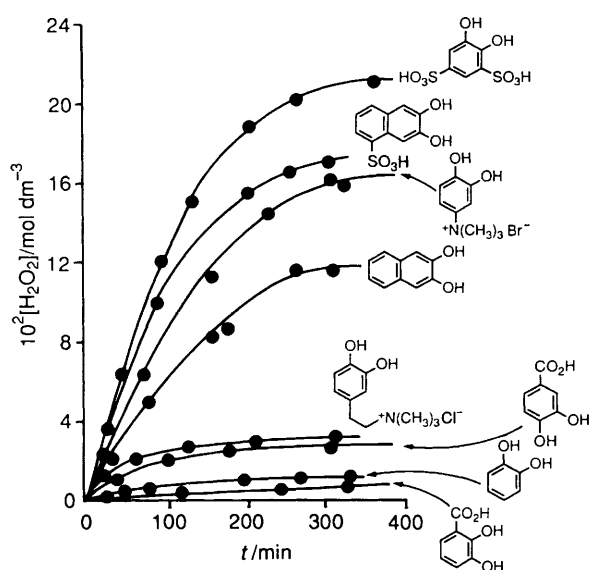
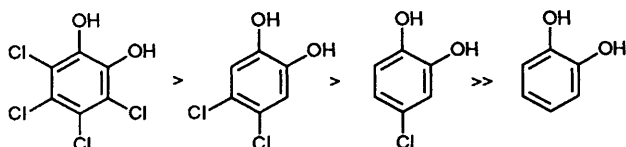


Fig. 4 Hydrogen peroxide production with dihydroxy-naphthalenes, -benzoic acids and -trimethylammonium salts in the $\text{Mn}^{\text{II}}-\text{NH}_2\text{OH}$ system. Conditions as in Fig. 2

H_2O_2 and the yields obtained are greater than those for catechol but less than those for Tiron. Furthermore, the chlorocatechols show the order below for the yields and initial rates of production of H_2O_2 . These results follow the order of increasing chlorine substitution on the catechol ring and an increasing electron-withdrawing effect on the oxygen atoms of the substituted catechol.



One factor in the low yields of H_2O_2 obtained with catechol and 4-chlorocatechol was shown to be decomposition of the

ligand, probably through oxidation, with a consequent loss of catalytic activity. Thus, in contrast to Tiron, NH_2OH was still found to be present at a time corresponding to the flat portion of the curve and H_2O_2 was again produced if a fresh sample of the ligand was added.

Nitrocatechols.—With 4-nitrocatechol (Fig. 3) the initial rates and yields of H_2O_2 were very similar to those of Tiron. When 3,4-dinitro- and 3,5-dinitro-catechol were used in place of Tiron the rate of formation of H_2O_2 was slow but constant which suggests that the nitrocatechols are stable to oxidation. The rate of production of H_2O_2 is in the order 3,4-dinitrocatechol > 3,5-dinitrocatechol.

Dihydroxy-naphthalenes, -benzoic Acids and -trimethylammonium Salts.—Fig. 4 shows the results for the above ligands together with Tiron and catechol for comparison. All except one ligand fall between the boundary of Tiron and catechol and orders such as 6,7-dihydroxynaphthalene-1-sulfonate > 2,3-dihydroxynaphthalene and (3,4-dihydroxyphenyl)trimethylammonium bromide > (3,4-dihydroxyphenyl)trimethylammonium chloride could all be explained by purely electron-withdrawing effects.

The very slow production of H_2O_2 with 2,3-dihydroxybenzoic acid may reflect hydrogen bonding between the hydroxyl group at the 2 position and the carboxylate group, which would increase the pK for removal of this proton.

Tropolone, Nitrotropolone and Chromotropic Acid.—The very similar structure of these compounds to catechol compounds suggested similar catalytic behaviour would be observed. However, tropolone and 5-nitrotropolone showed little catalytic activity producing only $0.005 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$. Chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulfonic acid) produced rather more H_2O_2 (0.05 mol dm^{-3}) with a constant rate very similar to that of 3,5-dinitrocatechol.

Schiff Bases and Related Compounds.—Missen¹⁸ has shown that Schiff bases produce stable manganese complexes which rapidly oxidise in air. Tests with 3-formyl- and 3-iminomethyl-4-hydroxybenzenesulfonate showed that H_2O_2 was produced initially but when the hydroxylamine was exhausted rapid oxidation of Mn^{III} to MnO_2 occurred and the H_2O_2 rapidly decomposed.

Many other bidentate ligands were also tried, e.g. salicylic acid, 2,3-dihydroxypyridine, 4-nitroanthranilic acid and 4-nitrophthalic acid. None exhibited any great catalytic activity in the manganese-hydroxylamine system and production of H_2O_2 was always $< 0.005 \text{ mol dm}^{-3}$.

The Manganese-Tiron System.—The reduction of dioxygen by hydroxylamine must proceed by one of the following processes: (a) an electron transfer to give O_2^- , (b) a hydrogen-atom transfer (H^\cdot) to give HO_2^\cdot or (c) a hydride transfer (H^-) to give HO_2^- . If one of the last two processes is occurring then an appreciable deuterium isotope effect would be expected with the rate of formation of H_2O_2 substantially less with deuteriated hydroxylamine.¹⁹

Fig. 5 shows the results of deuterium studies. The rate of formation of H_2O_2 is actually slightly greater with ND_2OD . These results show that there is no deuterium isotope effect in the expected direction for H^\cdot or H^- transfer and thus an electron-transfer process is responsible for the reduction of O_2 . The apparent increase in rate on deuteration may be due to changes in the pK values of the species present on deuteration.

Fig. 6 shows the results of repeating the $2.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ Mn}^{\text{II}}$ run at three different pH values. The rate decreased in the order $\text{pH } 8.5 > 8.0 \gg 7.5$.

The effect of added sodium carbonate (AristaR) was investigated (Fig. 7) as a possible alternative, cheaper, buffer. Low levels of carbonate disturb the production of H_2O_2 and at 0.1

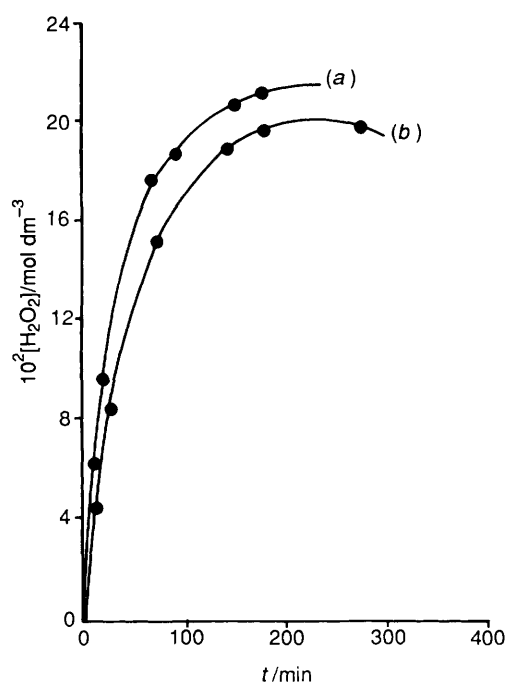


Fig. 5 Comparison of the rate of production of H_2O_2 with deuteriated (a) and undeuteriated (b) hydroxylamine. $[\text{Mn}^{\text{II}}] = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{Tiron}] = 0.0006 \text{ mol dm}^{-3}$, $[\text{NH}_2\text{OH}] = 0.5 \text{ mol dm}^{-3}$ (in D_2O), pH 8.0, $T = 20.0^\circ\text{C}$, $0.2 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$

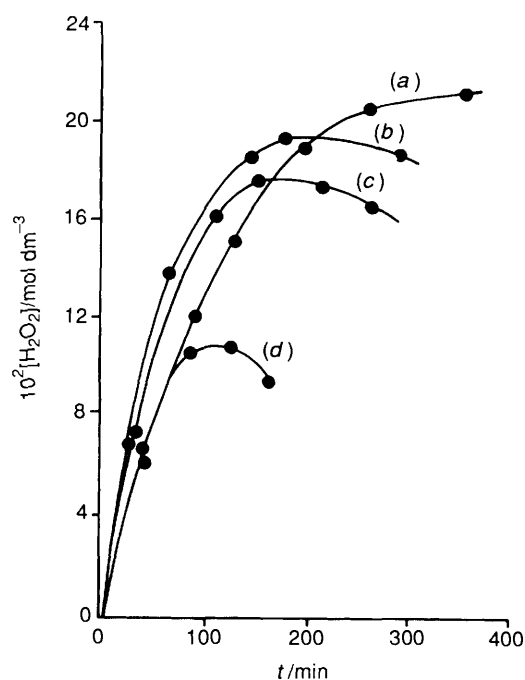


Fig. 7 The effect of added sodium carbonate on hydrogen peroxide production in the Mn^{II} -Tiron catalysed oxidation of hydroxylamine. $[\text{Mn}^{\text{II}}] = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{Tiron}] = 0.0006 \text{ mol dm}^{-3}$, $[\text{NH}_2\text{OH}] = 0.5 \text{ mol dm}^{-3}$, pH 8.0, $T = 20.0^\circ\text{C}$, $0.7 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$; $[\text{Na}_2\text{CO}_3] = 0$ (a), 0.005 (b), 0.02 (c) and 0.1 mol dm^{-3} (d)

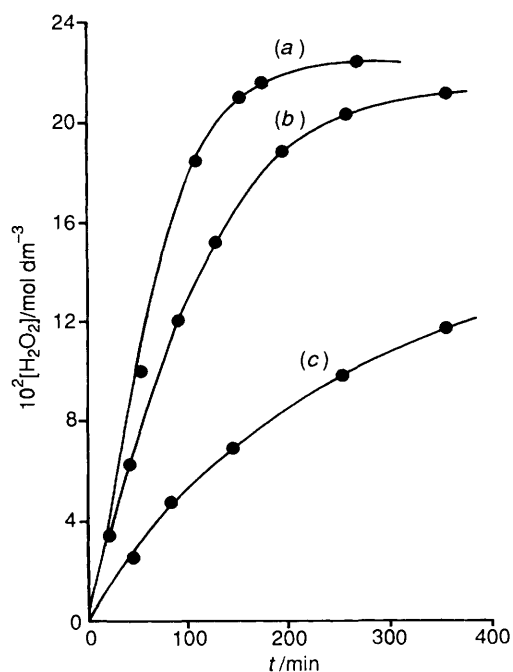


Fig. 6 Comparison of hydrogen peroxide production by the Mn^{II} -Tiron catalysed oxidation of hydroxylamine at pH 8.6 (a), 8.0 (b) and 7.5 (c). $[\text{Mn}^{\text{II}}] = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{Tiron}] = 0.0006 \text{ mol dm}^{-3}$, $[\text{NH}_2\text{OH}] = 0.5 \text{ mol dm}^{-3}$, $T = 20.0^\circ\text{C}$, $0.7 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$

mol dm^{-3} this becomes severe. This poisoning effect can be attributed to the formation of manganese carbonates. With phosphate buffer (pH 7.5) no H_2O_2 was produced, again presumably due to the formation of manganese phosphates.

When ascorbic acid (0.5 mol dm^{-3}) was used as the substrate $< 0.005 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$ was produced. In another experiment ascorbic acid (0.05 mol dm^{-3}) was added to $2.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ Mn}^{\text{II}}$ and $0.5 \text{ mol dm}^{-3} \text{ NH}_2\text{OH}$. No increase in the initial rate of production of H_2O_2 was produced and rapid de-

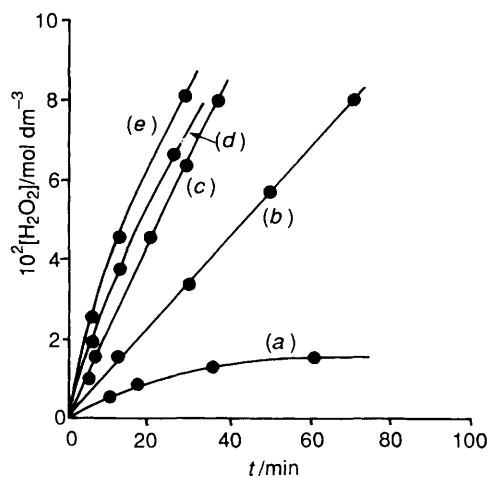


Fig. 8 The effect of $[\text{NH}_2\text{OH}]$ on the initial rate of hydrogen peroxide production in the Mn^{II} -Tiron system. $[\text{Mn}^{\text{II}}] = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{Tiron}] = 0.0006 \text{ mol dm}^{-3}$, pH 8.0, $T = 20.0^\circ\text{C}$, $0.7 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$; $[\text{NH}_2\text{OH}] = 0.1$ (a), 0.3 (b), 0.5 (c), 0.75 (d) and 1.0 mol dm^{-3} (e)

composition of H_2O_2 was observed until the ascorbic acid was nearly exhausted, this being due to the manganese-catalysed decomposition of H_2O_2 by ascorbic acid.²⁰ With glucose as substrate no production of H_2O_2 was observed.

Fig. 8 shows the effect of varying the concentration of hydroxylamine at $2.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ Mn}^{\text{II}}$. At $[\text{NH}_2\text{OH}] = 0.5 \text{ mol dm}^{-3}$ (and below) the initial rate appears to be roughly proportional to $[\text{NH}_2\text{OH}]$, thereafter 'saturation' is observed with smaller, incremental, increases on going to a 1 mol dm^{-3} solution of hydroxylamine. The yields of H_2O_2 obtained with hydrazine (N_2H_4) were about 70% of those obtained with hydroxylamine at pH 8.6. At pH 8.0 the rate of production of H_2O_2 with hydrazine was about five times lower than with hydroxylamine at a given $[\text{Mn}^{\text{II}}]$. The effect of replacing hydroxylamine with *N*-methylhydroxylamine (MeNHOH) and *N*-*tert*-butylhydroxylamine (Me_3CNHOH) was investigated.

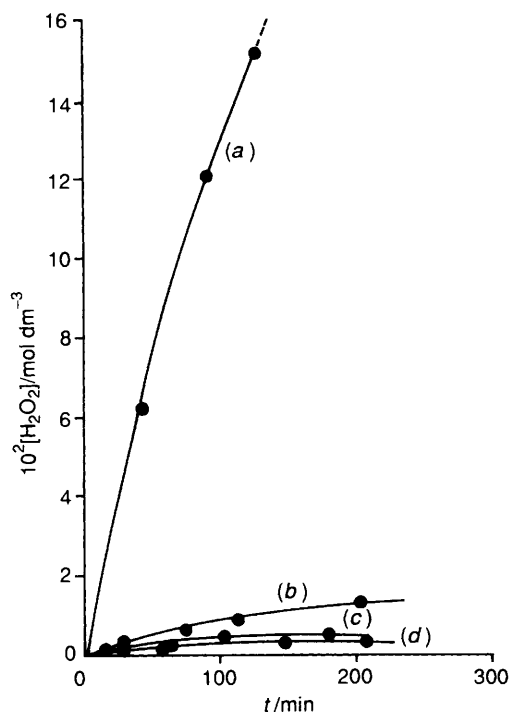


Fig. 9 Comparison of the production of H_2O_2 with Mn^{II} (a), Co^{II} (b), Cu^{II} (c) and Fe^{II} (d) in the Tiron-hydroxylamine system. $[\text{M}^{\text{II}}] = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{Tiron}] = 0.0006 \text{ mol dm}^{-3}$, $[\text{NH}_2\text{OH}] = 0.5 \text{ mol dm}^{-3}$, pH 8.0, $T = 20.0^\circ\text{C}$, $0.7 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$

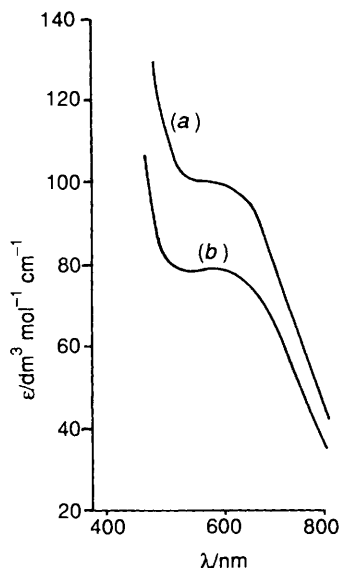


Fig. 10 Visible spectra of (a) Mn^{III} -Tiron and (b) Mn^{III} -catechol

Only slight increases in rate were found in the order $\text{Me}_3\text{C} > \text{Me} > \text{H}$.

With PhNHOH complications arose because of its insolubility in water; 0.2 mol dm^{-3} solutions had to be used and a brown-orange solid precipitated as the reaction proceeded. The yields of H_2O_2 were low and not significantly greater than for the non-metal catalysed autoxidation and probably reflect the strong electron-withdrawing benzene ring deactivating the hydroxylamine molecule.

Hydrazine sulfate was replaced with methylhydrazine (MeNHNH_2), *trans*-1,2-dimethylhydrazine (MeNHNHMe) and 1,1-dimethylhydrazine (Me_2NNH_2). The yields of H_2O_2 obtained were in the order $\text{MeH} > \text{H} > 1,2\text{-Me}_2 \gg 1,1\text{-Me}_2$, the initial rates with the first three compounds being very similar. The yield of H_2O_2 with 1,1-dimethylhydrazine was not

very much greater than that produced by its autoxidation ($[\text{Mn}^{\text{II}}] = 0$).

Other Metal-Tiron Systems.—Fig. 9 shows the results when Mn^{II} was replaced with Cu^{II} , Fe^{II} and Co^{II} . The catalytic activity of all three metals is small when compared to that of Mn^{II} ; Co^{II} exhibits a significantly greater catalytic power than Cu^{II} and Fe^{II} and may reflect the fact that many dioxygen-carrying complexes are known for cobalt.

Manganese-Catecholate Complexes.—It is clear from the above results that the manganese-catecholate complexes are very efficient catalysts for the production of H_2O_2 from O_2 and hydroxylamine. Of particular interest was whether manganese could accommodate three Tiron molecules, if not the existence of vacant sites (for O_2 and NH_2OH) would explain the catalytic activity observed. Cooper and co-workers²¹ have suggested that the short bite distance of the oxygen atoms in catechol and the relatively large size of the manganese(III) cation (compared to the Mn^{IV} coupled with its Jahn-Teller distortion would make formation of a manganese(III) tris complex very difficult, if not impossible.

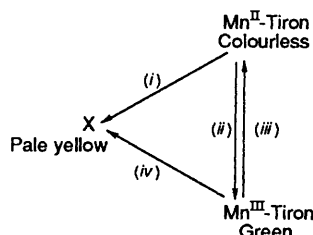
In the case of the manganese(III)-Tiron complex, isolation was found to be impossible because of the two sulfonate groups per Tiron molecule giving a tris complex a charge of -9 . This together with the powerful water-solubilising effect of the sulfonate groups did not, when attempted, produce a solid which agreed with any calculated elemental analysis for bis or tris complexes despite using the large $[\text{Co}(\text{NH}_3)_6]^{3+}$ cation.

The potassium and sodium salts of the manganese(III) tris(catechol) complex have been prepared by Weinland and Sperl;²² it was clear from the way that these solids were treated after isolation that they were far from crystalline. However, their reported analyses fitted very well for $\text{Na}_3[\text{Mn}(\text{cat})_3] \cdot 0.5\text{-NaOH} \cdot 6\text{H}_2\text{O}$ and $\text{K}_3[\text{Mn}(\text{cat})_3] \cdot 3\text{H}_2\text{O}$. The concentration of the reaction solution in catechol and base (NaOH or KOH) needed to obtain the tris solids and the presence of NaOH in one of the salts suggest that the solids are only stable at very high ligand and base concentrations. This gives some support to Cooper's assertion that the tris complex cannot be formed under less severe conditions.

Weinland and Sperl's method was repeated using NaOH , KOH and CsOH . Other variations on the method such as slow cooling, slow evaporation, use of $[\text{Mn}(\text{acac})_3]$ with aqueous MeOH-EtOH under argon, *etc.* all failed to produce crystalline material suitable for an X-ray structural determination; at best only microcrystalline material was obtained. The preparation of manganese complexes with other catecholate ligands was also attempted, especially 2,3-dihydroxynaphthalene, its sulfonate derivative and the two trimethylammonium salts mentioned before; the latter two complexes, if formed, would be neutral. In each case non-crystalline solids were obtained which did not analyse for a tris or bis complex.

Visible Spectral Studies on the Manganese-Tiron and Catechol Complexes.—When pH 8.0 buffered (0.1 mol dm^{-3} hepps) solutions of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.01 mol dm^{-3}) containing Tiron or catechol ($0.033 \text{ mol dm}^{-3}$) were exposed to air (or oxygen) olive-green solutions were produced in each case. The UV/VIS spectra of the Tiron and catechol solutions revealed (Fig. 10) similar broad shoulders at 580 nm having absorption coefficients of 101 and $78 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ respectively. This shoulder for Tiron was equivalent to that obtained when $[\text{Mn}(\text{acac})_3]$ ($0.005 \text{ mol dm}^{-3}$), in a few drops of MeOH , at pH 8.0 was degassed with argon and Tiron (0.02 mol dm^{-3}) added, the green solution obtained being transferred anaerobically to a 1 cm cell.

Magers *et al.*²³ have reported a similar spectrum which they attribute to a Mn^{III} -Tiron species. Further evidence for a manganese(III) high-spin d^4 and not a manganese(IV) d^3 complex came from the ESR spectra and solution magnetic



Scheme 1 (i) NH_2OH (or N_2H_4) + O_2 ; (ii) O_2 ; (iii) ascorbic acid; (iv) NH_2OH (or N_2H_4)

Table 2 Acidity constants and initial rates of H_2O_2 production for catechol and some substituted catechols. In all runs $[\text{Mn}^{\text{II}}] = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ligand}] = 6 \times 10^{-4} \text{ mol dm}^{-3}$, initial $[\text{NH}_2\text{OH}] = 0.5 \text{ mol dm}^{-3}$, $T = 20.0^\circ\text{C}$, pH 8.0, $0.7 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$

| Ligand | $\text{p}K_1$ | $\text{p}K_2$ | Ref. | 10^6 Initial rate/ $\text{mol dm}^{-3} \text{ s}^{-1}$ |
|---------------------|---------------|---------------|------|---|
| 4-Methylcatechol | 9.39 | 11.59 | 25 | 0.30 |
| Catechol | 9.27 | 11.49 | 25 | 1.6 |
| | 9.20 | 11.93 | 26 | |
| | 9.13 | 11.59 | 27 | |
| 4-Chlorocatechol | 8.43 | 11.54 | 5 | 10.4 |
| | 8.62 | 12.55 | 28 | |
| Tiron | 7.66 | 12.60 | 29 | 25.9 |
| | 7.57 | 12.48 | 26 | |
| 4-Nitrocatechol | 6.69 | 10.57 | 25 | 17.9 |
| | 6.59 | 10.57 | 5 | |
| | 6.78 | 10.90 | 28 | |
| 3,5-Dinitrocatechol | 3.32 | 9.86 | 30 | 2.1 |
| 3,4-Dinitrocatechol | 4.02 | 8.24 | 30 | 3.5 |
| | 4.39 | 8.27 | 8 | |

susceptibility measurements. The former gave no signal while the latter gave a value for μ of 4.97 which was very close to the value calculated (4.90) for four unpaired electrons.

The Mn^{III} -Tiron complex appears to be indefinitely stable in air at room temperature and on dilution. The corresponding catechol complex is less stable, turning blue on dilution presumably due to oxidation to Mn^{IV} or of the ligand to the semiquinone.²³ A Job's plot was carried out on the Mn^{III} -Tiron complex to determine the number of Tiron molecules per Mn in aqueous solution based on the shoulder at 580 nm. Due to the low absorption of the complex only fairly concentrated solutions could be used and the results showed an absorption maximum at $[\text{Tiron}]/[\text{Mn}^{\text{III}}] = 3:1$. This result does not rule out the possibility of lesser co-ordination in more dilute solutions and/or in the presence of a large excess of another co-ordinating species such as NH_2OH .

Scheme 1 shows the colour changes observed when the green Mn^{III} -Tiron complex ($0.005 \text{ mol dm}^{-3}$) was first formed in air and then reduced by the substrates present in a 20-fold excess. With ascorbic acid, the green Mn^{III} -Tiron species is reduced rapidly to Mn^{II} -Tiron with a complete discharge of colour. In the presence of hydroxylamine or hydrazine the situation is more complicated, with the formation of a pale yellow species 'X'. This species is not formed when hydroxylamine is added to a degassed sample of Mn^{II} -Tiron, but is formed when this solution is then exposed to air. The green Mn^{III} -Tiron colour is not regained if oxygen is bubbled through the yellow solution described and furthermore this yellow colour is not discharged on addition of ascorbic acid. It is not certain whether the species X would be formed in the more dilute solution used to produce H_2O_2 .

The appearance of six lines in the ESR spectrum confirmed the formation of the Mn^{II} -Tiron species when ascorbic acid or hydroxylamine was added to the degassed green Mn^{III} -Tiron solution. Furthermore, magnetic susceptibility studies on the Mn^{III} -Tiron + NH_2OH solution produced a value for μ of

5.95 suggesting the presence of Mn^{II} (d^5 , expected value $\mu = 5.92$).

When the green Mn^{III} -Tiron complex was formed in air at pH 8.6, degassed with argon and then a 10-fold excess of hydroxylamine, hydrazine or ascorbic acid added, the rate of discharge of the green colour was in the order ascorbic acid \gg hydroxylamine $>$ hydrazine with the reduction with ascorbic acid requiring 10 min.

Discussion

The dependence of the production of H_2O_2 on $[\text{O}_2]$ and $[\text{NH}_2\text{OH}]$ (with the possible exception of the dinitrocatechols, see below) suggests that the rate-determining step involves both O_2 and the substrate in a one-step, concerted, process.

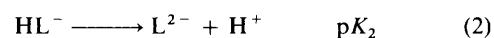
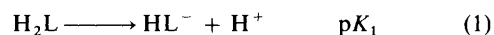
The observed slow reduction of the Mn^{III} -Tiron complex with hydroxylamine led to the conclusion that the catalytic species involves Mn^{III} -Tiron and that reduction to Mn^{II} -Tiron was unimportant. If reduction to Mn^{II} -Tiron were important then there would be an initial large rate of production of H_2O_2 with ascorbic acid before the slow decomposition. Furthermore if the mechanism involved reduction to Mn^{II} -Tiron then the results imply that this would be the rate-determining step and there then should be no dependence on $[\text{O}_2]$.

The dependence of the initial rate on $[\text{NH}_2\text{OH}]$ is consistent with hydroxylamine binding only weakly to manganese and it is bound hydroxylamine which interacts with molecular oxygen to produce H_2O_2 .

The results reveal clear trends in the yields and rates of production of H_2O_2 based on the electron-withdrawing effect of the substituents bound to the catechol ring. The lower yields with catechol and 4-chlorocatechol reflect the ready oxidation of the ligand and/or metal complex leading to a loss of catalytic activity. The evidence for this comes from the results with 4-chlorocatechol, where production of H_2O_2 was commenced if more 4-chlorocatechol was added. Catechols with weak electron-withdrawing substituents would be sufficiently electron rich to be prone to oxidation by both manganese-catalysed (due to stabilisation of Mn^{IV} relative to Mn^{III}) and uncatalysed processes.²⁴

The constant production of H_2O_2 with the dinitrocatechols suggests very slow oxidation of the ligand or independence of $[\text{NH}_2\text{OH}]$, the latter possibly due to the fact that the electron-deficient manganese would co-ordinate relatively strongly to NH_2OH .

The difference in the initial rates of production of H_2O_2 with the different ligands is a more subtle effect but is of greater chemical interest since this is related to the actual mechanism of production. The electron-withdrawing effect of the substituents is related to the acidity of the various catechols used because of their effect on the stability of the conjugate anions [equations (1) and (2) ($\text{H}_2\text{L} = \text{catechol or substituted catechol}$)]. Table



2 shows these $\text{p}K$ values and the observed initial rates of production of H_2O_2 .

The initial rates of production can be related to the electronic effect of the substituents on the catechol ring by using the acidity constants in the Hammett equation.³¹ Fig. 11 shows a graph of \log (initial rate with H_2L /initial rate with catechol) *versus* \log (K_1 for $\text{H}_2\text{L}/K_1$ for catechol); $\text{p}K_1$ was used because it is a better measure of acidity than $\text{p}K_2$. Although only an approximate treatment, this graph is revealing in that it shows how the rate of production of H_2O_2 increases from 4-methylcatechol to Tiron with an increase in the basicity of the catechol dianion and thereafter declines with the more electron-withdrawing nitrocatechols. This result suggests that the Mn^{II} - NH_2OH system is highly sensitive to the ligand environment around

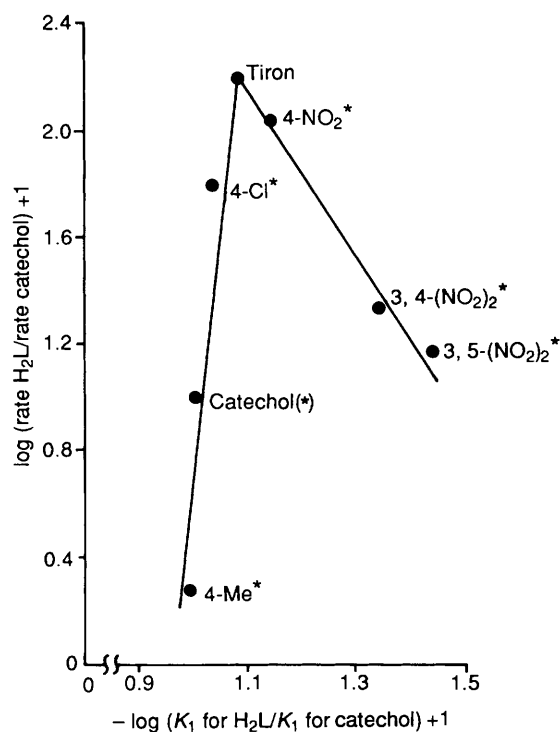
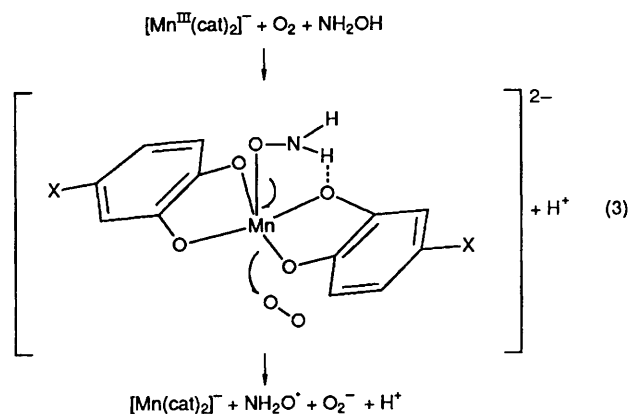


Fig. 11 Plot of \log (initial rate of H_2O_2 production with substituted catechol/initial rate of H_2O_2 production with catechol) versus $\log(K_1$ for substituted catechol/ K_1 for catechol). $[\text{Mn}^{\text{II}}] = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ligand}] = 0.0006 \text{ mol dm}^{-3}$, $[\text{NH}_2\text{OH}] = 0.5 \text{ mol dm}^{-3}$, pH 8.0, $T = 20.0^\circ \text{C}$, $0.7 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$

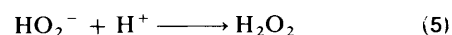
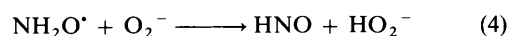
manganese, not only being specific to one class of ligands the catechols, but also to the electronic effects of the substituents on the catecholate ring. Clearly manganese plays a central role in the H_2O_2 production process, and the electron density at manganese determines at what rate the reduction of dioxygen will occur.

Both hydroxylamine and hydrazine consist of two electro-negative atoms bonded together with at least one (acidic) proton at each end of the molecule. The poor yield of H_2O_2 obtained with 1,1-dimethylhydrazine indicates that the presence of a hydrogen atom at each end of the substrate molecule is essential and that the binding of the substrate to manganese at one or both ends is important. Clear evidence has been shown that manganese(III) catecholate complexes, especially on dilution, contain vacant sites which could accommodate not only a substrate molecule but also dioxygen. A mechanism for production of H_2O_2 similar to that reported by Wagnerova *et al.*³² can now be visualised where the manganese catecholate complex containing bound substrate and dioxygen would allow electron transfer through the central manganese atom. The difference in initial rates of production of H_2O_2 with the different substituted catechols clearly shows that the manganese catecholate complex is acting as an 'electron sink' through which electrons are being transferred from NH_2OH to O_2 . This would explain the sensitivity of the system to the substituents around the catechol ring.

There are a number of reasons why catecholate ligands, in particular, would be suitable for such a pathway: (a) the reluctance to form a tris complex as mentioned earlier due to the short bite of the oxygen atoms; (b) the 'non-innocence' of the ligands in that they can exist not only as catecholate species but also as *o*-semiquinone species and yet still remain bound to manganese³³ (this would enable the manganese to delocalise charge transfer); and (c) the fact that catecholate ligands hold manganese in a rigid square-planar configuration²⁵ and hence enable the substrate and O_2 to bind above and below the plane, which would facilitate the electron transfer.



Due to the high polarisation of Mn^{III} , it is likely that binding of the hydroxylamine would be followed by loss of a proton [equation (3)]. Once formed, $\text{NH}_2\text{O}^\bullet$ can react with O_2^- [equations (4) and (5)]. Alternatively, the hydroxylamine



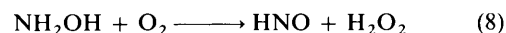
radical may react with O_2 [equations (6) and (7)] followed by



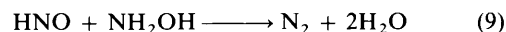
protonation as in (5) to give H_2O_2 .

The faster observed rates of production of H_2O_2 with methyl- and *tert*-butyl-hydroxylamine can be explained in terms of these substituents making the substrate more electron rich and hence facilitating the electron transfer to manganese. This effect is predictably smaller than that found by Hughes and Nicklin³⁴ at pH 12–13 where the hydroxylamine anion is involved. The slower rate with 1,2-dimethylhydrazine is probably due to the inability of the substrate to bind effectively to manganese because of steric factors.

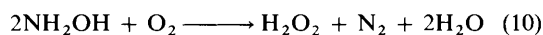
The probable initial oxidation product of NH_2OH is HNO [equation (8)]. Bonner *et al.*³⁵ found N_2 as the product of the



reaction between HNO and excess of NH_2OH in the range pH 6–8 [equation (9)]. Preliminary studies, details of which will be



published later, suggest that N_2 is the major oxidation product of the hydroxylamine in our system. At lower $[\text{NH}_2\text{OH}]$ at the end of the production of H_2O_2 , HNO could be oxidised to peroxonitrite which would account for the intense yellow colour of the reaction solution at $[\text{H}_2\text{O}_2]_{\text{max}}$. Since half of the hydroxylamine is used up in reducing HNO to N_2 the maximum efficiency of production of H_2O_2 found for the $\text{Mn}^{\text{II}}\text{-NH}_2\text{OH}$ system [combining equations (8) and (9)] is $>80\%$ based on NH_2OH [equation (10)].



Conclusion

Manganese(II) catecholate complexes uniquely and efficiently catalyse the production of H_2O_2 from O_2 in the physiological pH range 7.5–8.6 using hydroxylamine or hydrazine as substrates.

Best results were obtained with Mn^{II} -Tiron using hydroxylamine as substrate when $[H_2O_2] > 0.2 \text{ mol dm}^{-3}$ and turn-overs $> 10^4$ were obtained.

Evidence from deuterium studies, the slow reduction of Mn^{III} -Tiron by hydroxylamine and the requirement of one hydrogen atom at each end of the substrate molecule imply that the production of H_2O_2 results from an electron transfer from the substrate to O_2 in a one-step, concerted process in which both O_2 and substrate become bound to manganese. This is further supported by the dependence of the rate of production on $[O_2]$ and $[NH_2OH]$; also if an 'electron sink' was required for this process this would place severe restrictions on the metal and the nature of the ligands complexed to it as was observed.

Two remarkable features of the Mn^{II} -Tiron- NH_2OH or N_2H_4 system are the compatibility of the H_2O_2 formed with the substrate and the high selectivity of the reaction. With regard to the former, H_2O_2 and NH_2OH or N_2H_4 are used as rocket fuels.³⁶ These reactions are, however, catalysed by 'free metal ions' which were not present in this system. The high selectivity of the above system is analogous to natural systems. The mechanism postulated here could be similar to that of galactose oxidase since this copper(II)-containing enzyme is known to produce H_2O_2 very efficiently but no change in the oxidation state of the copper is thought to be involved.

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