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

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The Mn^{II}/4,5-dihydroxybenzene-1,3-disulphonate (Tiron) system catalyses the production of hydrogen peroxide from dioxygen and hydroxylamine in the pH range 7.5—8.6; concentrations of hydrogen peroxide >0.2 mol dm^{-3} and turnover numbers $[H_2O_2]/[Mn^{II}] > 10^4$ can be obtained.

The production of H_2O_2 when O_2 reacts with systems containing transition metal ions or complexes has been observed quite frequently,[1] although in the majority of cases the H_2O_2 rapidly disappears by further reaction or by catalytic decomposition. In the presence of a reducing substrate, catalytic production of H_2O_2 is possible. Although such a process is unlikely to compete with that used industrially (the reaction of O_2 with an alkylanthrahydroquinone)[2] it might be useful in the formulation of liquid laundry detergents, where the H_2O_2 desirable for bleaching could be generated from atmospheric O_2. A number of enzyme systems which produce H_2O_2 are known, for example the copper-containing galactose oxidase,[3] which catalyses the oxidation of galactose and related compounds by O_2, with the O_2 being reduced to H_2O_2.†

We report that the Mn^{II}/4,5-dihydroxybenzene-1,3-disulphonate (Tiron) system is an efficient catalyst for the reduction of O_2 to H_2O_2 by NH_2OH in the pH range 7.5—8.6. In strongly alkaline solutions, NH_2OH reacts with O_2 to give H_2O_2.[4] The main products formed from the NH_2OH are $OONO^-$ and NO_2^-. The reactive species is the anion NH_2O^-.[5] Since the pK_a of NH_2OH is 13.7,[5] this reaction was quite insignificant in the present work. H_2O_2 is also formed from O_2 and NH_2OH in the presence of Co^{II} tetrasulphophthalocyanine at pH 11.6—12.3.[6]

The results obtained‡ are shown in Figure 1. In the absence

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† In organisms, these enzymes are normally associated with catalase, which rapidly decomposes the H_2O_2.

‡ Solutions of $NH_2OH_2{}^+Cl^-$ (AnalaR), Tiron, and *N*-2-hydroxyethylpiperazine-*N'*-3-propanesulphonic acid buffer were adjusted to the desired pH with AristaR NaOH(aq). The water was purified by passage through a mixed-bed ion-exchange resin. The Tiron and *N*-2-hydroxyethylpiperazine-*N'*-3-propanesulphonic acid (both from B.D.H. Ltd.) were recrystallized from aqueous ethanol. O_2 was passed through the rapidly stirred solutions at *ca.* 0.7 l min^{-1}. H_2O_2 was analysed iodometrically, and NO_2^- colourimetrically using sulphanilic acid and 1-aminonaphthalene.[7] After the maximum amount of H_2O_2 had been obtained, when the concentration of NH_2OH was $<$ 0.001 mol dm^{-3} (Ni^{II}/butane-2,3-dione monoxime test paper[8]), $[NO_2^-] + [NO_3^-]$ was determined by reduction to NH_3 with Devarda's alloy.

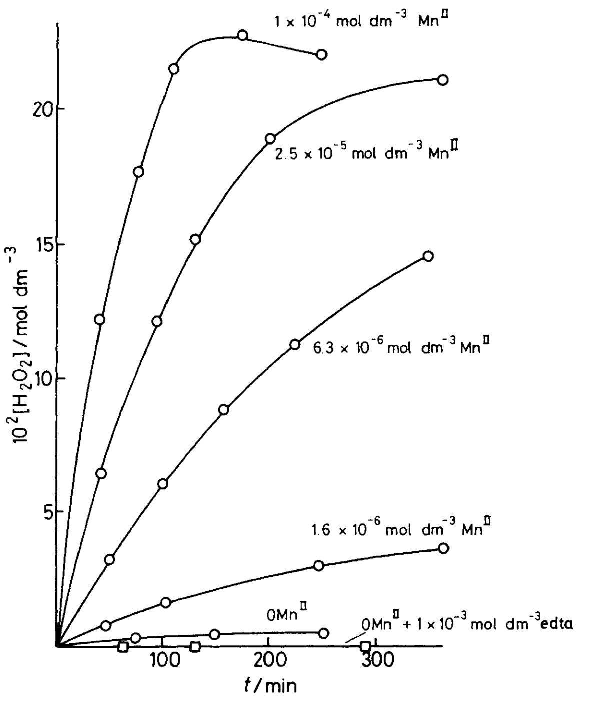

Figure 1. The production of H_2O_2 in the Mn^{II}/Tiron/NH_2OH system in the presence of O_2 at 20 °C and different concentrations of Mn^{II}. In all runs, the [Tiron] was 6×10^{-4} mol dm^{-3}, the initial [NH_2OH] was 0.5 mol dm^{-3}, and the pH was 8.0 (0.1 mol dm^{-3} *N*-2-hydroxyethylpiperazine-*N*′-3-propanesulphonate buffer).

of added Mn^{II}, slow formation of H_2O_2 was observed. This reaction was virtually quenched by the addition of ethylenediaminetetra-acetate (edta), and presumably arises from catalysis by trace metal ions. Since Cu^{II}, Fe^{II}, and Co^{II} were much less efficient as catalysts than Mn^{II}, adventitious traces of Mn^{II} may be responsible. (In the presence of Mn^{II} but without Tiron, negligible amounts of H_2O_2 were produced.) With 0.50 mol dm^{-3} NH_2OH, concentrations of H_2O_2 of > 0.2 mol dm^{-3} could be obtained. In the pH range used here, any $OONO^-$ formed would rapidly isomerize to NO_3^-.[9] However, only small amounts of NO_3^- (< 0.02 mol dm^{-3}) and NO_2^- (< 0.005 mol dm^{-3}) were produced. The main reaction product from the NH_2OH is probably N_2O. MeNHOH also produced H_2O_2, and the rate of production was appreciably faster than with NH_2OH. Tiron could be replaced by 2,3-dihydroxynaphthalene-6-sulphonic acid (sodium salt), but not by catechol.

The Mn^{II}/Tiron system, which contains 1 : 1, 2 : 1, and 3 : 1 complexes of the Tiron tetra-anion with Mn^{II},[10] is rapidly oxidized by O_2 (but not H_2O_2) to a green Mn^{III} species, which seems to be the same as that reported by Sawyer *et al.*[11] and formed from 'manganic acetate,' and Tiron in alkaline solution. Although this reaction with O_2 produces H_2O_2, it can hardly be an important feature of the catalytic process, since in an Ar atmosphere the green Mn^{III} species is only slowly reduced by NH_2OH. It seems likely that the catalytic species involves Mn^{III}. The NH_2OH (or MeNHOH) could coordinate to the metal (possibly with loss of a proton) and become activated towards reaction with O_2. The rate of formation of H_2O_2 in air was *ca.* 1/5 that in O_2, indicating that O_2 is involved in the rate-determining step. This mechanism is similar to that suggested for the action of galactose oxidase.[12]

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