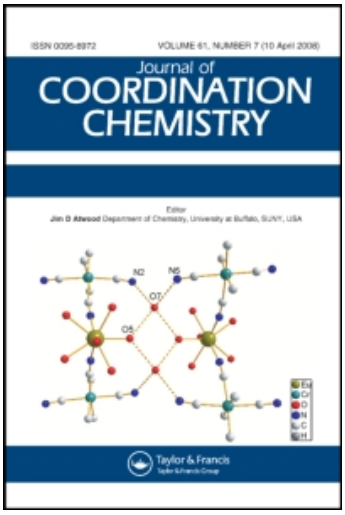

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The Effect of Triethanolamine on the Iron(III)-Catalysed Decomposition of Hydrogen Peroxide

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THE EFFECT OF TRIETHANOLAMINE ON THE IRON(III)-CATALYSED DECOMPOSITION OF HYDROGEN PEROXIDE

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The influence of triethanolamine on the iron(III)-catalysed decomposition of hydrogen peroxide was studied by manometric and spectrophotometric techniques. This ligand caused increasing inhibition with increasing concentration, attributed to the saturation of the coordination sphere of the metal, and also to its properties as a radical scavenger. Kinetic measurements indicated the formation and the subsequent breakdown of a peroxo-intermediate in the rate-determining step, for which a rate constant of $2.9 \times 10^{-2}\,s^{-1}$ was determined at 308 K. Evidence for the participation of oxygen radicals, as well as carbon-centred radicals, was obtained from ESR spectra of the radical adducts detected using the spin-trap method. Based on the pH profile for the reaction, a mechanism was proposed, suggesting the formation of different complexes with different catalytic activities, at higher pH.

Keywords: Catalysis, peroxide, iron(III), stabilizers, triethanolamine

INTRODUCTION

Many efforts have been made to understand the catalytic decomposition of hydrogen peroxide in aqueous media by iron complexes, including model compounds[1–3] and biological systems.[4,5] On one hand, there is an increasing interest in the nature of the peroxidic reactions, with the purpose of clarifying the reactivity of the peroxide, and in the reactive species formed as intermediates. Early investigations in this field, based on kinetic data, have been interpreted in terms of chain reactions involving active oxygen intermediates in a free-radical mechanism.[6] The participation of these species has been mainly supported by studies using selected scavengers,[7] or by direct pulse radiolysis methods.[8] In addition, oxidative damage in biological systems has more recently been associated with iron-mediated formation of oxygen free radicals[9] from hydrogen peroxide. However, an alternate mechanism has also been considered, involving high-valent oxoiron (FeO^{3+}) intermediates,[10] by analogy to the mechanism of action of peroxidases. Evidence for the presence of the ferryl group (Fe^{IV}=O) at the active site of heme complexes and hemoproteins was provided by spectroscopic measurements,[11] including Mössbauer data.[12] Nevertheless, some controversy still remains, since in the case of more simple iron compounds conclusive data for the presence of higher oxidation states of the metal have not been forthcoming.

On the other hand, investigations of catalase- and peroxidase-like activity of iron-containing systems are particularly important for industrial applications of peroxide,

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which demand its stabilization under usually drastic conditions of temperature and pH. The use of hydrogen peroxide as a bleaching agent[13] claimed to be enhanced by the addition of compounds capable of complexing metallic ions, thus modifying their redox and catalytic properties. Different substances have been used as stabilizers[14] of peroxide. However, only more recently have their characteristics as radical scavengers and as sequestering agents been systematically studied.

Triethanolamine is one such compound added to alkaline bleaching baths,[15] although its properties as a complexing agent for ferric ions is not yet well known.[16] The aim of this work was to study its effect on the catalysed decomposition of peroxide, and to verify the corresponding iron complexes formed, particularly in alkaline media, as well as comparing their different catalytic activities.

EXPERIMENTAL

The solutions of the iron(III) catalyst were prepared by dissolving appropriate amounts of ammonium iron(III) sulfate in solutions of the ligand. Triethanolamine was obtained from Merck, and its solutions were titrated with a standard solution of CO_2-free sodium hydroxide. Hydrogen peroxide free from stabilizers was kindly supplied by Peroxidos do Brasil. The solutions were prepared by dilution and analysed by reaction with sodium metavanadate using a modified method based on literature procedures.[17,18] This method is based on the formation of a peroxo-complex of vanadium(V) in acidic solution.[19]

The pH of the reaction medium was controlled by adding perchloric acid or sodium hydroxide, and checked at the beginning and the end of the kinetic measurements with a Digimed DMPH-2 pH meter fitted with a combined glass-Ag/AgCl electrode.

Kinetic measurements of the oxygen evolved in the catalytic decomposition of hydrogen peroxide were made manometrically, in a similar manner as described elsewhere.[20] All experiments were carried out at 308 K and an ionic strength of 0.10 M ($LiClO_4$). Distilled, deionized water was used in all the experiments. Spectrophotometric monitoring of the remaining peroxide was carried out by taking aliquots of the reaction solution at different times, and analysing using the previously mentioned metavanadate method.[17]

Solutions of 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and α-(4-pyridyl-1-oxide)-*N*-*t*-butylnitrone (4-POBN) were prepared by dissolving reagents from Aldrich. DMPO was previously purified by recommended procedures.[21] Albumin and superoxide dismutase were purchased from Sigma. All other chemicals were of analytical grade and used as supplied.

The iron(III)-triethanolamine complexes, $Fe(tea)Cl_3.2H_2O$ and $Fe(tea)_2Cl_3.1.5H_2O$, were prepared in ethanolic solution by adding stoichiometric amounts of ferric chloride to solutions of the ligand, according to the method previously described in the literature.[22] The complex $Fe(tea)_3Cl_3.H_2O$ was similarly obtained, by using a 10-fold excess of the ligand. The C, N, and H analyses were consistent with the presence of the indicated molecules of water in the solid. The iron content was determined by a spectrophotometric method, using TIRON as complexing agent,[23] after dissolving the compounds in acidic solution. Chloride analyses were performed by conductimetric titrations, using a Micronal B331 apparatus.

ESR measurements of the spin adducts were recorded on a Varian E-4 spectrometer, using 20 MW microwave power, 0.5 or 1 Gauss amplitude modulation and scan rates of 0.10 or 0.21 Gauss s^{-1}.

RESULTS AND DISCUSSION

Kinetic investigations

The order of the reaction with respect to the various species present was determined from the kinetic curves (of the oxygen evolution) using the initial rate method. A pseudo-first-order was verified with respect to the catalyst concentration, as shown in Figure 1. An estimated value of $k_{obs} = 3.02 \times 10^{-3}\ s^{-1}$, at pH 11.5, was obtained from the linear plot of the initial rate (v_i) versus the total concentration of iron(III), in the range 2 to 10×10^{-4} M. However, a slight tendency to higher order was observed when the concentration of the catalyst was increased, similar to results described for related iron complexes.[2]

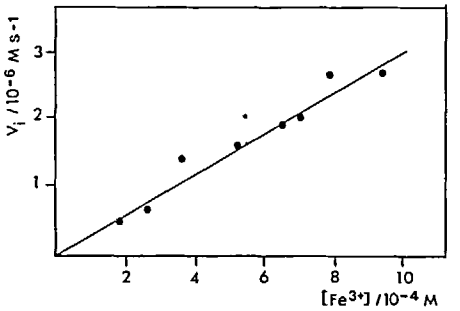

FIGURE 1 First-order dependence of hydrogen peroxide decomposition rate on total catalyst concentration; $[H_2O_2] = 7.10 \times 10^{-2}$ M, [triethanolamine] $= 6.94 \times 10^{-3}$ M, pH = 11.5, T = 35.0°C, I = 0.10 M($LiClO_4$).

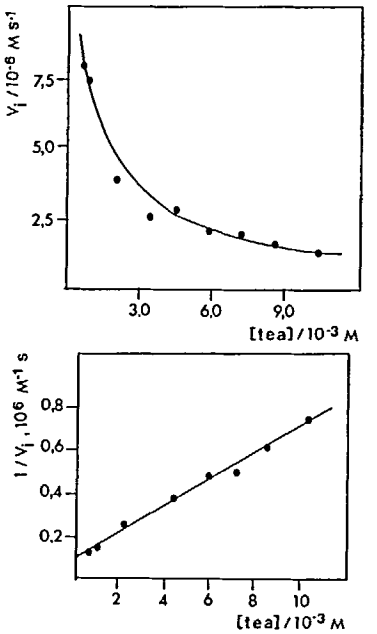

FIGURE 2 Dependence of initial rate on concentration of triethanolamine; $[H_2O_2] = 6.80 \times 10^{-2}$ M, $[Fe^{3+}] = 6.11 \times 10^{-4}$ M, pH = 11.5, T = 35.0°C, I = 0.10 M ($LiClO_4$). Inset: Reciprocal of the initial rate *versus* [triethanolamine].

The dependence of the initial rate with increasing ligand concentration showed a pronounced inhibition effect. The linear plot of the inverse of v_i *versus* the concentration of triethanolamine is shown in Figure 2. These results indicate the participation of the ligand in competitive steps, but can also be interpreted as being due to saturation of the coordination sphere of the metal. The catalytic activity of the iron complexes seems to be dependent on a coordination site being available to peroxide.

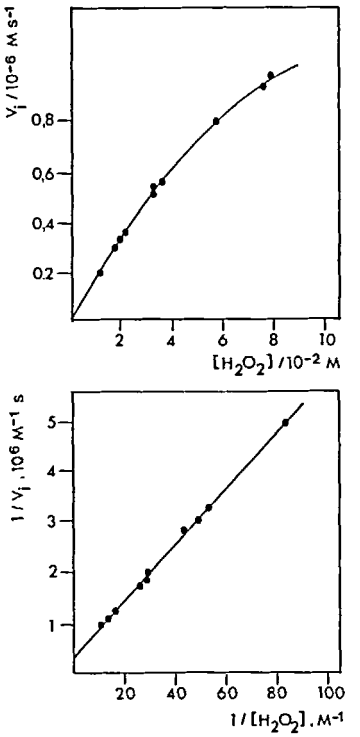

FIGURE 3 (a) Hydrogen peroxide decomposition rate as a function of hydrogen peroxide concentration; $[Fe^{3+}] = 5.30 \times 10^{-4}$ M, [triethanolamine] $= 7.00 \times 10^{-3}$ M, pH = 11.5, T = 35.0°C, and I = 0.10 M ($LiClO_4$); (b) Lineweaver–Burk plot, under the same conditions.

These results were corroborated by the observed influence of the peroxide concentration on rates of decomposition. The kinetics exhibited saturation behaviour with increasing hydrogen peroxide concentration, as shown in Figure 3. Similar results were obtained at pH 8.40, although in this case the rates are much higher, as shown in Figure 4. The linearity of the Lineweaver–Burk plot of $1/v_i$ *versus* $1/[H_2O_2]$ is consistent with the formation and subsequent breakdown of a ternary iron–triethanolamine–peroxo complex in the rate-determining step.

The pH influence on the kinetics was also investigated, in the range 1.5 to 11.5. From the pH profile for the reaction, shown in Figure 5, a maximum value in the initial rate was detected. Similar behaviour has been observed in the iron(III)-gluconate system.[24] and in others described in the literature.[2,25] For the ligand gluconate (pKa = 3.56) a maximum rate was observed at pH 4.5, while for triethanolamine (pKa = 7.88) the maximum occurred at pH 7.0. Comparative data obtained for the ligand monoethanolamine (pKa = 9.52) indicated the value of pH 8.0 under

similar experimental conditions. In this case, however, colloidal species have been observed to be present at pH values up to 8.

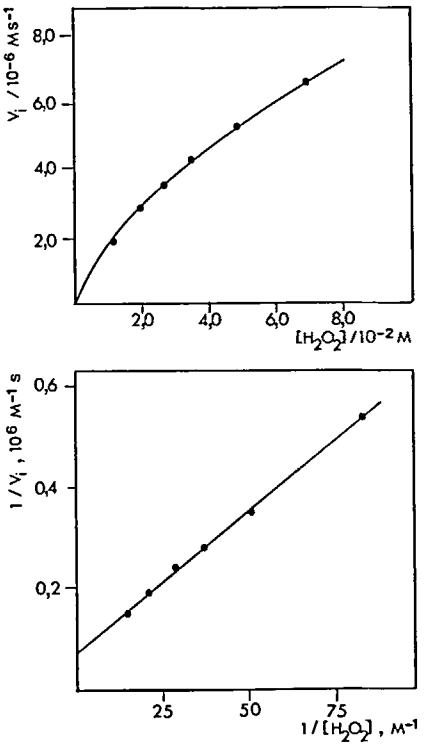

FIGURE 4 Analogous results to Fig. 3 for hydrogen peroxide decomposition rate at pH 8.40; $[Fe^{3+}] = 5.46 \times 10^{-4}$ M, [triethanolamine] = 7.23×10^{-3} M.

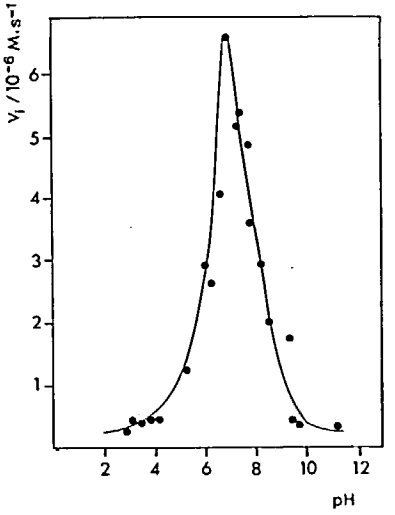

FIGURE 5 A pH profile for the catalysed hydrogen peroxide decomposition in the presence of triethanolamine; $[Fe^{3+}] = 6.11 \times 10^{-4}$ M, [triethanolamine] = 7.23×10^{-3} M, $[H_2O_2] = 6.80 \times 10^{-2}$ M, T = 35.0°C, I = 0.10 M ($LiClO_4$).

For the ligand ethylenediaminetetraacetate (edta) the pH profile[2] was associated with acidic dissociation of aqua ligands,

$$Fe(H_2O)edta^- \rightleftharpoons H^+ + Fe(OH)edta^{2-} \quad pKa = 7.4$$

$$Fe(OH)edta^{2-} \rightleftharpoons H^+ + Fe(OH)_2edta^{3-} \quad pKa = 10.25$$

with a maximum rate observed at pH 9.1. The increase in the rate between pH 7 and 9 can be explained if the reactive species is the hydrogenperoxide ion, HO_2^-, rather than undissociated H_2O_2, in the formation of the peroxo-intermediate. Inhibition of decomposition could be expected if a second inactive complex is formed at higher pH.

For the ethylenediaminetetrakis(methylenephosphonato)iron(III) complex,[25] the maximum rate occurred at a pH about 11. In this case, the substitution of coordinated water by H_2O_2 is more difficult, compared to its carboxylate analogue, due to the cumulative negative charge surrounding the metal ion, and also to hydrogen bonding between the water molecule and the free phosphonate segment.

Our kinetic results suggested that at very high pH mixed species are predominant in the iron(III)-triethanolamine system, probably involving dimeric or polymeric complexes. The lack of activity of these latter species could be attributed to the absence of labile sites in the coordination sphere of the metal ion. Evidence for such species has been obtained by studying some iron(III)-triethanolamine complexes.

The kinetic results are consistent with the following rate law, at constant pH,

$$d[O_2]/dt = k_3[Fe^{3+}]_T[H_3O_2]/(K^* + [H_2O_2])$$

where $k_3 = 2.9 \times 10^{-2}\,s^{-1}$ and $K^* = 8.3 \times 10^{-1}$, for pH = 11.5, and $[Fe^{3+}]_T$ represents the total ferric ion concentration.

Based on these results, and supplemented by other measurements discussed below, a mechanism can be proposed, involving the coordination of the peroxide to a mixed triethanolamine complex predominant in the pH range considered in the present investigation. This peroxo–iron complex is therefore decomposed in the rate-determining step. The presence of a readily dissociable water ligand seems to be a stringent requirement for catalytic activity of iron complexes in reactions of hydrogen peroxide.[26]

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \quad K_H$$

$$[Fe(tea)_3]^{3+} \rightleftharpoons tea + [Fe(tea)_2(H_2O)_2]^{3+} \quad K$$

$$[Fe(tea)_2(H_2O)_2]^{3+} \rightleftharpoons H^+ + [Fe(tea)_2(H_2O)(OH)]^{2+} \quad K_1$$

$$[Fe(tea)_2(H_2O)(OH)]^{2+} \rightleftharpoons H^+ + [Fe(tea)_2(OH)_2]^+ \quad K_2$$

$$[Fe(tea)_2(H_2O)(OH)]^{2+} + HO_2^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [(tea)_2Fe\begin{matrix}O_2H\\OH\end{matrix}]^+ + H_2O$$

$$[(tea)_2Fe(O_2H)(OH)]^+ \xrightarrow{k_3} \text{Products}$$

$$[Fe(tea)_2(OH)_2]^+ + HO_2^- \overset{K''}{\rightleftharpoons} [Fe(tea)_2(OH)_2(HO_2)]$$

The deprotonation of a second coordinated water gives rise to a very stable and ess labile species, which lacks catalytic activity, as the substitution of a hydroxyl nion by perhydroxyl is much more difficult.

By considering the influence of pH, and assuming the steady state approximation or the intermediate peroxo species, a rate law was determined,

$$[O_2]/dt = k_3 [Fe^{3+}]_T [H_2O_2]/[K_m[H^+]f(H^+)/KK_1K_H + \{1 + (K_MK''K_2/[H^+]\} [H_2O_2]$$

/here

$$f(H^+) = \{[tea] [H^+] + K[H^+] + KK_1 + K K_1K_2/[H^+]\}$$

nd $K_M = (k_2 + k_3)k_1$.

This expression is very similar to others described in the literature for different gands, such as edta[2] and phosphonate,[27] which show similar pH profiles. In the ase of the triethanolamine ligand, reliable values for K, K_1 and K_2 are not yet nown.

The effect of triethanolamine in the reaction rate arises from its properties as an on ligand and as a scavenger of hydroxyl radicals, forming carbon-centred ones, as iscussed below. As a consequence, a remarkable inhibiting effect is observed, with ncreasing triethanolamine concentrations. The presented scheme can also support he participation of oxygen radicals in more rapid, non-rate-determining steps, since oth hydroxyl and superoxide radicals have been detected by using specific scavengers or by ESR measurements. Comparative data for other complexing agents howed that triethanolamine is a suitable ligand for applications of peroxide in lkaline bleaching baths. For example, the specific rate k_3 for the edta ligand[2] is $\times 10^{-2}\,s^{-1}$, showing an increase in rate between pH 8 and 10.5, while the pH rofile for triethanolamine shows a sharper increase in the rate, around pH 7, with $_3 = 3 \times 10^{-2}\,s^{-1}$.

ron(III)-triethanolamine complexes

he iron(III)-triethanolamine system has not been greatly studied, as equilibrium eactions involve hydrolysis and mixed complexes which are not yet well understood. arlier potentiometric studies indicated[16] that at pH < 3 the ligand coordinates only % of the ferric ions available in solution. The estimated value for the stability onstant of the 1:1 complex was log $\beta_{1,1} < 7$, at 25°C and I = 1M ($NaClO_4$).

Spectrophotometric and solubility methods have also been used[28] to study this ystem. At pH < 2.2 the predominant complexes are the hydrolysed iron species. In ne pH range 2.2 to 3.6, the species $[Fe_2(OH)_2]^{4+}$ has been reported, with a naximum absorption at 335 nm. A mixed species, $[Fe(tea)(OH)]^{2+}$, has also been escribed,[28] with log $\beta = 3.5$. Another complex, $[Fe(tea)_2(OH)_4]^-$, has been detected etween pH 7.3 and 9.2, for which the related global constant was log $\beta = 44.6$.

With the aim of providing supplementary data for the kinetic studies, the omplexes described in the experimental section have been prepared and character-

ized. Their solubilities, either in water or in non-aqueous solvents, are low, and increase with the number of ligands. On the other hand, the effective magnetic moments for these compounds obtained by the Gouy method,[29] using $Hg[Co(SCN)_4]$ as standard, decrease with increasing ligand : metal ratios. The experimental values, respectively 4.03, 3.69 and 2.96 B.M. for the 1:1, 1:2, and 1:3, were lower than the expected for high-spin iron(III) in an octahedral environment. The results suggest the presence of interaction between neighbouring paramagnetic sites, in dimeric or polymeric structures probably involving bridged chloride ligands. Conductimetric measurements of aqueous solutions of the compounds were consistent with the structural formulae $[Fe(tea)Cl_2]Cl.2H_2O$, $[Fe(tea)_2Cl]Cl_2.1.5H_2O$, and $[Fe(tea)_3]Cl_3.H_2O$. In the case of the 1:3 complex, measurements of a 10^{-3} M solution in dimethylformamide ($\Lambda_M = 220.7\,cm^2\ ohm^{-1}\ cm^{-1}$, at 25°C) corroborated these results.

Titrations of aqueous solutions of these complexes with sodium hydroxide, potentiometrically monitored, have shown the formation of insoluble brown species, in the pH range from 4.5 to 8.5. However, at higher pH, all were soluble, and a yellow solution has been obtained in each case.

Thermogravimetric curves for both the 1:2 and 1:3 complexes indicated[30] the formation of an intermediate species, Fe(tea)Cl, obtained by the loss of both tea ligands and chloride ions. The curves are shown in Figure 6. Initially, the loss of hydration water was observed. While for the 1:2 complex the two chloride ions and one triethanolamine ligand were lost at 380°C, for the 1:3 complex, the corresponding loss of two chlorides and two triethanolamines occurred at 338°C. At higher temperatures decomposition of the remaining triethanolamine ligand occurred.

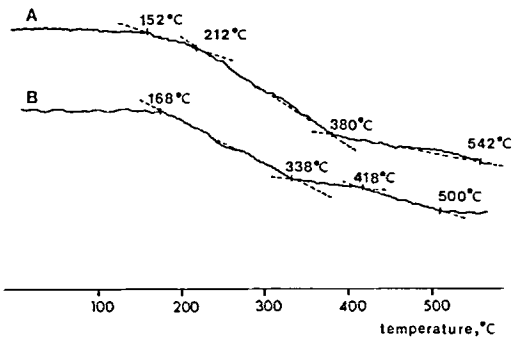

FIGURE 6 Thermogravimetric curves for the iron(III)-triethanolamine complexes under nitrogen (100 cm^3/min); heating rate 5°C/min; (A): $Fe(tea)_2Cl_3.1.5H_2O$; (B): $Fe(tea)_3Cl_3.H_2O$.

Based on all the results, it is concluded that the coordination of ferric ions by triethanolamine occurs substantially only at pH > 4. At pH around 7, the species $[Fe(tea)_2(H_2O)_2]^{3+}$ and $[Fe(tea)_2(H_2O)(OH)]^{2+}$ are probably predominant, and are those responsible for the catalytic decomposition of hydrogen peroxide. At higher pH, with the subsequent deprotonation of coordinated water molecules or even of triethanolamine ligands, much less active complexes are formed.

Participation of radicals

Evidence for the presence of radical species in the reaction has been obtained from studies of the inhibition of reaction rate with addition of scavengers.

Superoxide dismutase (SOD), which catalyses the dismutation of superoxide radicals to hydrogen peroxide and oxygen,[31] causes a slight inhibition, indicating the participation of those radicals in the reaction (Figure 7). A control experiment was carried out in the presence of albumin, in order to consider the coordinative properties of the enzyme. Inhibition of reaction rate has also been observed in the presence of scavengers of hydroxyl radicals,[32] such as ethanol, benzoate, glucose, and pyrocatechol. These experiments were performed at pH 8, and with a scavenger concentration of 4×10^{-3}M.

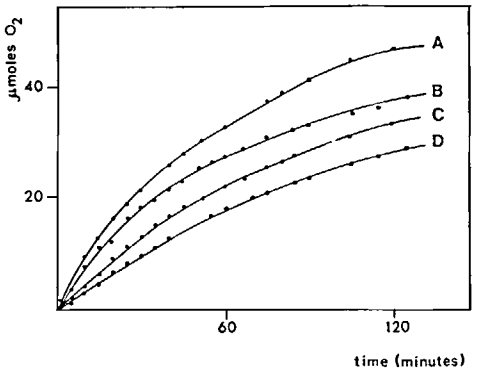

FIGURE 7 Influence of addition of superoxide dismutase (SOD) on the catalysed decomposition of hydrogen peroxide; $[Fe^{3+}] = 5.36 \times 10^{-4}$ M, $[H_2O_2]_3 = 5.05 \times 10^{-2}$ M, [triethanolamine] = 8.37×10^{-3} M, pH = 8.15, T = 35°C, I = 0.10 M ($LiClO_4$); (A): no addition; (B): with albumin, 1.12 µM; (C): with SOD, 1.37 µM; (D): with SOD, 2.75 µM.

Stronger evidence for the participation of such radicals has been obtained by electronic paramagnetic resonance studies, by using the spin-trap method.[21] Adducts with DMPO and 4-POBN were formed and their spectra analysed. With DMPO, the characteristic spectrum of the species DMPOX has been observed, as shown in Figure 8. This adduct is only formed in strongly oxidizing systems. The experimentally determined constants, $a_N = 7.25$ G and $a_H = 4.0$ G, are very close to the values described in the literature[33] for the DMPOX species, 7.2 G and 4.1 G, respectively.

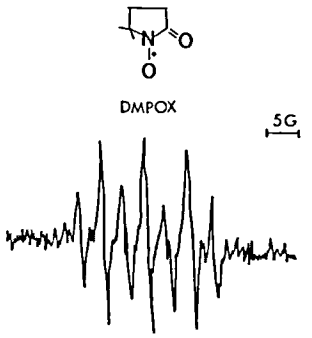

FIGURE 8 EPR spectrum of DMPOX obtained after 5 minutes of reaction in the presence of the spin-trap DMPO (0.12 M); $[H_2O_2] = 5.10 \times 10^{-2}$ M, $[Fe^{3}] = 1.64 \times 10^{-4}$ M, [triethanolamine] = 4.21×10^{-3} M, pH = 7.0, T = 25°C, I = 0.10 M ($LiClO_4$).

When the experiment was repeated in the presence of 4-POBN, different spectra were obtained with different concentrations of triethanolamine. At low concentration, the radical adduct formed was very similar to that of the hydroxyl radical, with $a_N = 15.00$ G and $a_H = 1.75$ G. However, at higher concentrations of the ligand, the adduct obtained was more related to that of carbon-centred radicals, with $a_N = 15.50$ G and $a_H = 3.00$ G, as shown in Figure 9. The reported values in the literature[34] for the adduct 4-POBN-CH_3CHOH are, respectively, 15.50 and 2.59 G, while for the adduct 4-POBN-OH the analogous values are 14.97 and 1.68 G.

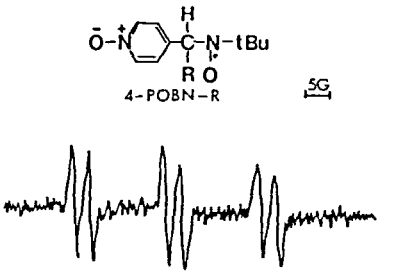

FIGURE 9 EPR spectrum of a spin-adduct observed after 50 minutes of reaction in the presence of the spin-trap 4-POBN (0.10 M); $[H_2O_2] = 5.10 \times 10^{-2}$ M, $[Fe^{3+}] = 1.85 \times 10^{-4}$ M, [triethanolamine] = 4.82×10^{-3} M, pH = 7.0, $I = 0.10$ M $LiClO_4$, T = 35°C.

Evidence for an intermediate with higher oxidation state

The reaction of acidic solutions of iron(III) ions and hydrogen peroxide were extensively studied by Kremer,[10,35] who observed a maximum in absorbance of solutions around 440 nm at the very beginning of the reaction. This was attributed to the intermediate species $[Fe(O_2H)^{2+}]$ and $[FeO^{3+}]$. As the latter rises very sharply in concentration, it causes the appearance of an inflection point in the $[H_2O_2]$ *versus* time curve. Some experiments have been realized in our system in order to obtain evidence for the formation of similar species.

The decomposition of hydrogen peroxide has been monitored spectrophotometrically, by analysing the remaining peroxide in solution as a vanadium species. At the start of the reaction, an increase in absorbance at 450 nm was detected, as shown in Figure 10, suggesting the formation of another absorbing species, in addition to $[VO(O_2)]^+$. We interpret these data as being due to the presence of a peroxo-iron complex, yielding $[FeO^{3+}]$ or related species. More recently, the formation of a ferryl species, $[FeO(OH)_n]^{2-n}$, and an iron(V) complex, $[FeO_4]^{3-}$, in alkaline solutions of $[Fe^{III}(OH)_4]^-$ and $[FeO_4]^{3-}$, in alkaline solutions of $[Fe^{III}(OH)_4]^-$ and $[FeO_4]^{6-}$, respectively, has been described in experiments using pulse radiolysis.[36] A ferryl species has also been suggested[37] in the reaction of ferric chloride and hydrogen peroxide in acetonitrile. Other evidence for the formation of such species, is the observation of the characteristic DMPOX spectrum in the ESR experiments, using the spin-trap DMPO, instead of the DMPO-OH adduct. The rapid formation of DMPOX from DMPO, which is formally a three electron oxidation, indicates a very oxidizing system, as would be the case with ferryl or analogous states.[38]

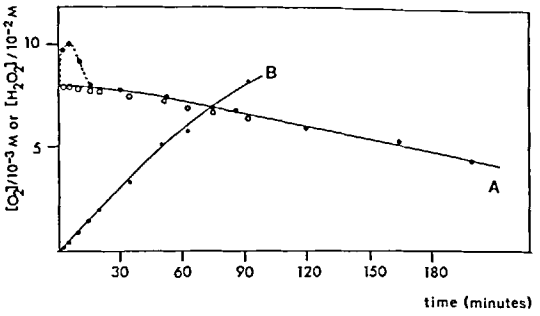

FIGURE 10 Curves obtained for the catalysed decomposition of hydrogen peroxide in the presence of triethanolamine; $[H_2O_2] = 8.10 \times 10^{-2}$ M, $[Fe^{3+}] = 4.84 \times 10^{-4}$ M, [triethanolamine] = 7.03×10^{-3} M, pH = 11.2, T = 35°C, and I = 0.10 M ($LiClO_4$); (A): $[H_2O_2]$ *versus* time; (B): oxygen evolved *versus* time; (o) calculated values of remaining $[H_2O_2]$ from the results of curve B.

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