Kinetic and Structural Investigations of $[Fe^{III}(edta)]^-$ [edta = Ethylenediaminetetra-acetate(4−)] Catalysed Decomposition of Hydrogen Peroxide

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A detailed kinetic analysis is given of hydrogen peroxide decomposition catalysed by $[Fe^{III}(edta)]^-$ [edta = ethylenediaminetetra-acetate(4−)]. Structural investigations have been made using n.m.r. and electronic absorption spectroscopy. It is demonstrated that the monohydroxy complex, $[Fe(edta)(OH)]^{2-}$, is the primary active catalyst and this reacts with the hydrogenperoxide ion to produce the well known purple complex $[Fe(edta)(OH)(HO_2)]^{3-}$. Decomposition of hydrogen peroxide conforms to Michaelis–Menten kinetics, the rate-determining step involving breakdown of this complex. In contrast to earlier reports, it is shown that the HO_2^- ion displaces a carboxy-group from $[Fe(edta)(OH)]^{2-}$ rather than the hydroxy group. The dihydroxy complex $[Fe(edta)(OH)_2]^{3-}$ is also shown to form a purple peroxy-complex with HO_2^-, but its breakdown occurs at a much slower rate. The results are consistent with formation of radicals upon breakdown of the peroxy-complex and in subsequent reactions.

Early kinetic investigations of metal-catalysed decomposition of hydrogen peroxide have been interpreted in terms of free radical schemes[1,2] and, accordingly, support for the participation of radicals, particularly the hydroxyl radical ($OH^\cdot$), has been presented. For example, such evidence has included (*i*) selective oxidations involving insertion of hydroxyl groups into aromatics, *i.e.* conversion[3,4] of toluene to cresol by Fenton's reagent, (*ii*) initiation of polymerisation,[5] (*iii*) the interception of radicals by organic molecules[1] or by radical traps,[6] and (*iv*) by direct detection in flow systems.[7,8] More recently, however, following the elucidation of the mechanism of action of peroxidases[9,10] and the identification of high-oxidation state intermediates,[11] there has been a move away from radical schemes[12–15] and credibility has been given to the $[FeO]^{3+}$ species proposed earlier[16,17] for peroxide systems containing Fe^{3+} and to Fe^{4+} in iron–porphyrin systems.[18,19] The purported involvement of such species, including high oxidation states of other metals, in metal-ion toxicity[20] has considerably influenced this change in emphasis. Nevertheless, considerable doubts and uncertainties remain. Whilst peroxy-complexes undoubtedly have been detected for iron compounds,[16,21,22] the major weakness of ionic mechanisms is that incontrovertible evidence for high oxidation states has not been forthcoming. Similarly, high oxidation states of other metals, $[MO]^{n+}$, have escaped detection. Another complication arises from hydrolysis of metal complexes[23,24] particularly in alkaline media, and the lack of suitable techniques for measuring it.

The aim of this work was to explore in detail the mechanism of decomposition of hydrogen peroxide catalysed by $[Fe^{III}(edta)]^-$ [edta = ethylenediaminetetra-acetate(4−)]. This complex was chosen because catalysed decomposition occurs at a reasonable rate (half-lives in the region of minutes to hours) and because the system has been partially characterised by several studies although they are of limited scope.[1,22,25–27] It forms a well known purple[22,28,29] peroxy-complex with a formation constant around 10^4 dm^3 mol^{-1} and it has been shown[22] that iron remains in the high-spin III state. Hydrolysis has been countered by addition of excess edta. Structural studies have been made primarily using the pulsed n.m.r. technique which provides information[30–32] about the structure of the peroxy-complex and about the number and type of hydroxy-species formed in alkaline media. To our knowledge, this is the first time an in-depth structural and kinetic study has been made of the mechanism of peroxide decomposition catalysed by metal ions/complexes.

Experimental

The disodium salt of ethylenediaminetetra-acetic acid (H_4edta), $Na_2(H_2edta)$, iron(III) chloride hexahydrate, sodium chloride, sodium carbonate, and sodium hydroxide were Hopkin and Williams AnalaR grade. Hydrogen peroxide (100 Vol) was Hopkin and Williams UltraR grade. The water used was doubly distilled.

A stock solution of $[Fe^{III}(edta)]^-$ was prepared by adding edta to a stirred solution of 0.2 mol dm^{-3} iron(III) chloride to give a mol ratio of 1.01:1. The pH of the solution was raised slowly to 7 with sodium carbonate, to give a stock solution which was stable over long periods.

The reaction was carried out in a double-walled glass vessel thermostatted with a Haake circulator bath. A magnetic stirrer was used to maintain homogeneity. The pH was controlled with 0.2 mol dm^{-3} sodium hydroxide using a Radiometer 26 pH meter in conjunction with a Radiometer 11 titrator. The pH electrode used was a Radiometer combined glass reference type.

Appropriate amounts of the stock solution were added to the reaction vessel and unless otherwise stated, excess edta was added to give a mol ratio of $\simeq 20:1$. Ionic strength effects were minimised by swamping with sodium chloride electrolyte (1 mol dm^{-3}). The reagents were added in the following sequence, to give a total volume of 100 cm^3: sodium chloride and edta solutions were first added to the reaction vessel, followed by addition of peroxide and pH adjustment to the desired value, and finally $[Fe(edta)]^-$, usually 9.8×10^{-4} mol dm^{-3}. Samples of the reaction mixture were removed at set time intervals using automatic pipettes and mixed with excess titanium sulphate solution in sulphuric acid. The concentration of hydrogen peroxide was determined from the absorbance at 410 nm ($\varepsilon = 753$ dm^3 mol^{-1} cm^{-1}) of the titanium peroxy-complex so formed. Absorbance measurements were made with a Perkin-Elmer 55B spectrophotometer.

Water relaxation measurements were made in the presence and absence of hydrogen peroxide. In the former case, they were carried out in parallel with the kinetic runs. Samples were removed from the reaction vessel and placed in n.m.r. tubes.

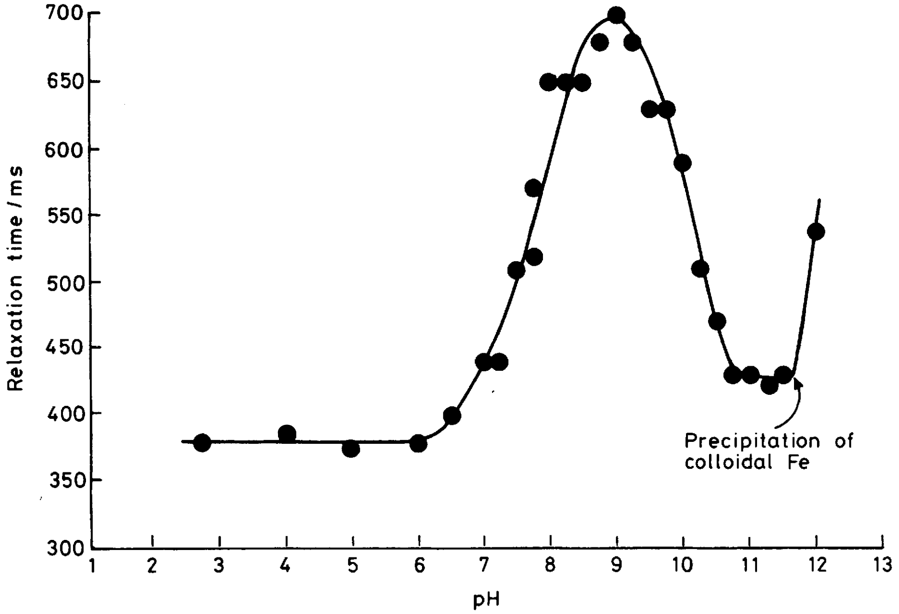


Figure 1. Water proton spin–spin relaxation times in solutions of 1 × 10^{-3} mol dm^{-3} $[Fe(edta)]^-$ as a function of pH: [edta] = 2 × 10^{-2}, [NaCl] = 1 mol dm^{-3}, 296 ± 2 K

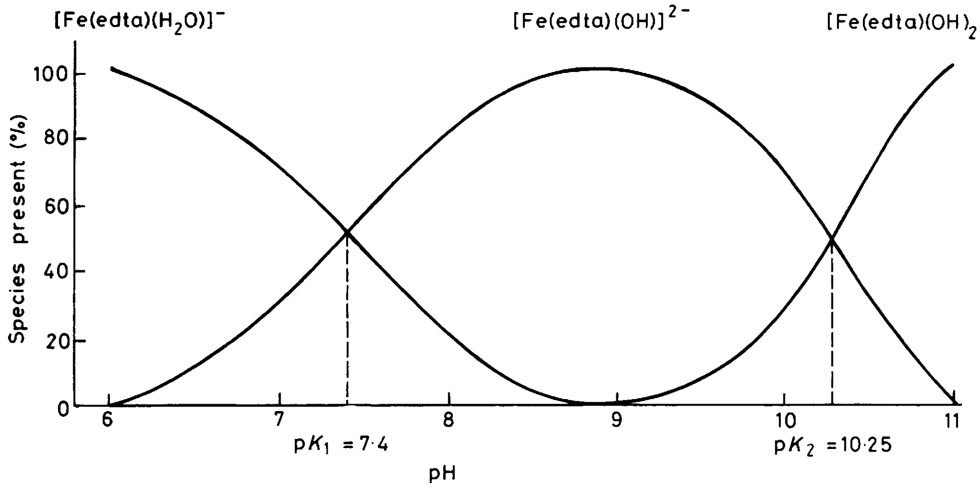


Figure 2. Distribution of species in $[Fe(edta)]^-$ solution as a function of pH calculated from water proton relaxation data

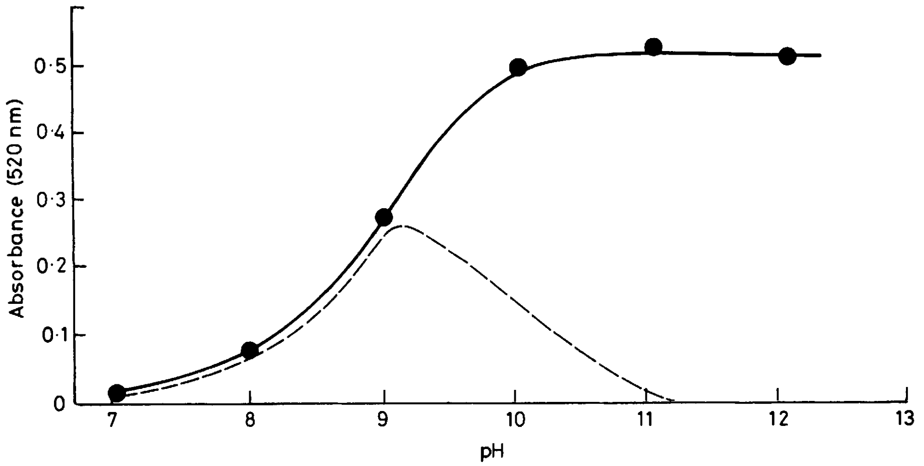


Figure 3. Absorbance of peroxy-complex of $[Fe(edta)]^-$ with pH (●). The peroxide decomposition profile (— — —) (quantified in Figure 8) is outlined for comparison: $[Fe(edta)^-]$ = 1 × 10^{-3}, [edta] = 2 × 10^{-2}, $[H_2O_2]$ = 1.78 × 10^{-2}, [NaCl] = 1 mol dm^{-3}, 298 K

These were then mounted in the magnetic field of the Bruker 322S pulse spectrometer and spin–spin relaxation times (T_2) determined. For $[\mathrm{Fe(edta)}]^-$ T_2 is equal to T_1, the spin–lattice relaxation rate, but is more conveniently measured. Details of the technique have been described previously.[30–32] All experiments were carried out at 298 ± 0.5 K except where otherwise stated.

Results and Discussion

(*a*) *Hydroxy-complexes of* $[\mathrm{Fe(edta)}]^-$.—The spin–spin relaxation time of water protons in aqueous solutions of $[\mathrm{Fe(edta)}]^-$ passes through a maximum as the pH is raised (Figure 1). Earlier investigations have established[31] that the complex is seven-co-ordinate at pH 6 and possesses a bound water molecule.* The increase in relaxation time above pH 7 has been explained[31] in terms of ionisation of the bound water molecule [equation (1)] which has a p*K* of 7.4. The subsequent

$$[\mathrm{Fe(edta)(H_2O)}]^- \rightleftharpoons [\mathrm{Fe(edta)(OH)}]^{2-} + \mathrm{H}^+ \qquad (1)$$

decrease in relaxation time above pH 9 is attributed to the introduction of a second hydroxy-group into the co-ordination sphere of iron† [equation (2)].

$$[\mathrm{Fe(edta)(OH)}]^{2-} \overset{\mathrm{H_2O}}{\rightleftharpoons} [\mathrm{Fe(edta)(OH)_2}]^{3-} + \mathrm{H}^+ \qquad (2)$$

Taking the relaxation time of water protons in $[\mathrm{Fe(edta)(H_2O)}]^-$ as 380 ms, in $[\mathrm{Fe(edta)(OH)}]^{2-}$ as 700 ms, and in $[\mathrm{Fe(edta)(OH)_2}]^{3-}$ as 400 ms,‡ the distribution of species was calculated as a function of pH (Figure 2). Good agreement is obtained with the literature[36] for the p*K* of reaction (1) and it is shown that reaction (2) has a p*K* of 10.25. Formation of a dihydroxy-species has been proposed previously but there has been some doubt[37,38] as to the precise value of its p*K*. Indeed, in a recent study[39] even the existence of this second step has been queried.

Subsequent re-examination by potentiometry has, in fact, revealed an ionisation occurring around pH 10—10.5, consistent with the formation of the dihydroxy-complex. However, (*i*) concentrations of the complex as high as 10^{-2} mol dm^{-3} were required to achieve sufficient sensitivity and (*ii*) the studies were complicated by dimer formation[35,40] and the tendency for the solutions to become thermodynamically unstable at *ca.* pH 11, producing colloidal iron.

(*b*) *Peroxy-complexes of* $[\mathrm{Fe(edta)}]^-$.—The absorbance of the peroxy-complex of $[\mathrm{Fe(edta)}]^-$ ($\lambda_{\mathrm{max.}} = 520$ nm) was recorded as a function of pH for solutions containing 10^{-3} mol dm^{-3} $[\mathrm{Fe(edta)}]^-$ (Figure 3). It appears that the complex is fully formed above pH 10.

It has been demonstrated thermodynamically[22,28,29] that peroxy-complex formation is a result of complexation with $\mathrm{HO_2}^-$ from the constancy of the equilibrium binding constant, *K*, with pH [equation (3)]. Consequently, it has been suggested[22,28] that a hydroxy-group is displaced by the peroxide group $\mathrm{O_2}^{2-}$ [equations (4) and (5)].

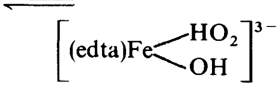
$$K = \frac{[\text{catalyst–peroxy-species}]}{[\text{catalyst}][\mathrm{HO_2}^-]} \qquad (3)$$

$$[\mathrm{Fe(edta)(OH)}]^{2-} + \mathrm{HO_2}^- \rightleftharpoons [\mathrm{Fe(edta)(O_2)}]^{3-} + \mathrm{H_2O} \qquad (4)$$

$$[\mathrm{Fe(edta)(OH)_2}]^{3-} + \mathrm{HO_2}^- \rightleftharpoons [\mathrm{Fe(edta)(OH)(O_2)}]^{4-} + \mathrm{H_2O} \qquad (5)$$

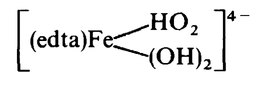
N.m.r. studies have been carried out to examine these structural possibilities. If hydroxy-groups were displaced from the hydroxy–$[\mathrm{Fe(edta)}]^-$ complexes, a marked increase in water proton relaxation time would be expected. Inspection of the Table indicates that this is not so, the relaxation time of the dihydroxy-species remaining unchanged upon formation of the peroxy-complex at pH 11, but that of the monohydroxy-complex at pH 9, in fact, decreases with time (Figure 4). The time dependence of T_2 is discussed later. The simplest explanation for the present results is that, rather than inducing displacement of a hydroxy-group, $\mathrm{HO_2}^-$ in fact, displaces a carboxy-group§ [equations (6) and (7)].

$$[\mathrm{Fe(edta)(OH)}]^{2-} + \mathrm{HO_2}^- \rightleftharpoons$$



$$\left[(\mathrm{edta})\mathrm{Fe}{<}^{\mathrm{HO_2}}_{\mathrm{OH}}\right]^{3-} \qquad (6)$$

$$[\mathrm{Fe(edta)(OH)_2}]^{3-} + \mathrm{HO_2}^- \rightleftharpoons$$



$$\left[(\mathrm{edta})\mathrm{Fe}{<}^{\mathrm{HO_2}}_{\mathrm{(OH)_2}}\right]^{4-} \qquad (7)$$

In these complexes the $\mathrm{HO_2}^-$ proton¶ is too distant from the metal ion to contribute to relaxation. The assignments are supported by resonance-Raman investigations which favour binding of the monodentate or 'end-on' $\mathrm{HO_2}^-$ group and by the apparent weakness of the charge-transfer band.[41] However, this interpretation disagrees with the recent tentative proposal[39] of a cyclic or 'side-on' peroxide structure, based principally on those structures known for peroxide complexes with the more highly charged titanium(IV) and molybdenum(VI).

It appears that the function of ionisation of the bound water molecule is simply to facilitate peroxy-complex formation by labilising the metal–carboxylate bonds. The observation[29] of higher rates of formation for the peroxy-complex formed from the dihydroxy-species (at pH 11) is consistent with this view, the addition of an extra negatively charged hydroxy-group into the co-ordination sphere of $\mathrm{Fe^{III}}$ producing additional labilisation.

Evidence has recently been provided[42] for a third peroxy-complex which contains two peroxide molecules and which is formed at very high $[\mathrm{H_2O_2}]$ (> 0.5 mol dm^{-3}). The formation of this complex ($\lambda_{\mathrm{max.}} = 480$ nm) coincides with a reduction in the

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* At low pH's the complex becomes[33,34] octahedrally co-ordinated when a carboxy-group is displaced due to protonation.

† Other structural possibilities considered were (*i*) association of $[\mathrm{Fe(edta)}]^-$ molecules, particularly dimerisation to produce the low-spin $\mathrm{Fe^{III}}$ state[35] and (*ii*) simultaneous co-ordination of two edta molecules to iron and/or hydrolysis to colloidal iron. The first was eliminated as a possibility because the present results above pH 9 can only be explained by retention of the high-spin $\mathrm{Fe^{III}}$ state. The second was discounted since n.m.r. and kinetic data (initial rates) were found to be independent of the ligand to metal ratio.

‡ This value was determined from experiments in which the pH of the $[\mathrm{Fe(edta)}]^-$ was raised rapidly to high values. The slightly higher value shown in Figure 1 is probably due to very slow time-dependent hydrolysis of the $[\mathrm{Fe(edta)}]^-$. If it is assumed that the second hydroxy-group displaces a carboxy-group, then the calculated T_2 (405 ms) is in good agreement with that observed (400 ms). The calculated T_2 for $[\mathrm{Fe(edta)(OH)}]^{2-}$ is 590 ms. The differences between experimental and calculated values could be explained either by (*i*) simultaneous elimination of a carboxy-group from the co-ordination sphere of iron, resulting in octahedral symmetry, or more probably by (*ii*) formation of 12% low-spin dimer.

§ Hydrogen bonding between the peroxidic proton and the pendant carboxy-group is implicated since neither t-butyl hydroperoxide nor peracetic acid forms complexes with $[\mathrm{Fe(edta)}]^-$.

¶ The presence of the $\mathrm{HO_2}^-$ proton is dictated by the thermodynamic requirement that $K = [\mathrm{Fe(edta)(OH)(HO_2)}^{3-}]/\{[\mathrm{Fe(edta)(OH)}^{2-}][\mathrm{HO_2}^-]\}$ is independent of pH.

Table. Determination of reaction pathway for peroxy-complex formation from water relaxation time (T_2) changes

pH	Reaction pathway[a]	Increase in T_2 (ms) on addition of H_2O_2	
		Calc.	Expt.
9	$[Fe^{III}(edta)(OH)]^{2-} + HO_2^- \xrightarrow{(i)} [Fe^{III}(edta)(OH)(HO_2)]^{3-}$	+100	<0[b]
	$\xrightarrow{(ii)} [Fe^{III}(edta)(O_2)]^{3-}$	+690	
11	$[Fe^{III}(edta)(OH)_2]^{3-} + HO_2^- \xrightarrow{(i)} [Fe^{III}(edta)(OH)_2(HO_2)]^{4-}$	+20—30	0[c]
	$\xrightarrow{(ii)} [Fe^{III}(edta)(OH)(O_2)]^{4-}$	+210	

[a] (*i*) = Displacement of carboxy-group of edta by HO_2^-; (*ii*) displacement of hydroxy-group by HO_2^-. [b] Although absorbance measurements indicate that the peroxy-complex retains integrity, the water relaxation time actually decreases with time (Figure 4). This is attributed to partial degradation of bound edta and introduction of hydroxylic protons into the co-ordination sphere of Fe^{III}. [c] No change was observed in T_2 within experimental error (±20 ms).

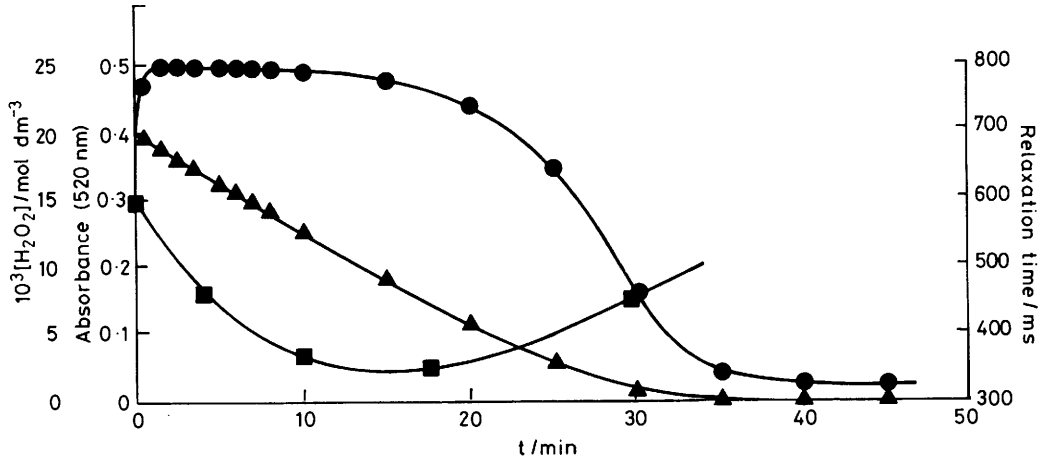


Figure 4. Interrelationship between water proton spin–spin relaxation time (■), absorbance of peroxy-complex (●), and peroxide decomposition rate (▲): $[Fe(edta)^-] = 9.9 \times 10^{-4}$, [edta] $= 2 \times 10^{-2}$, [NaCl] = 1 mol dm^{-3}, 296 ± 2 K

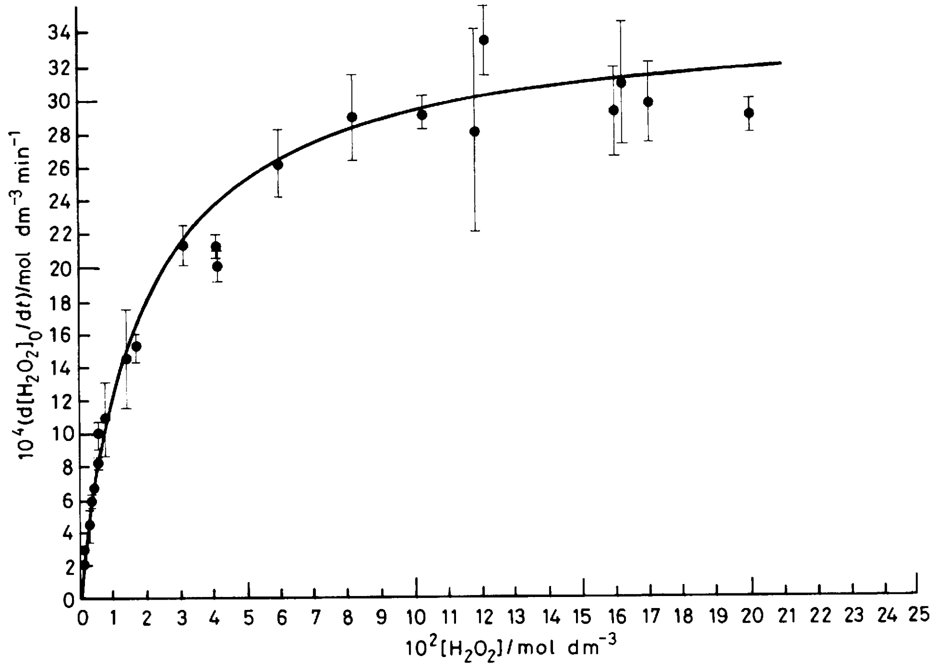


Figure 5. Hydrogen peroxide decomposition rate as a function of $[H_2O_2]_0$ at pH 9.1: $[Fe(edta)^-] = 9.9 \times 10^{-4}$, [edta] $= 1.98 \times 10^{-2}$, [NaCl] = 1 mol dm^{-3}, 298 K; (●) experimental points; (——) calculated rate

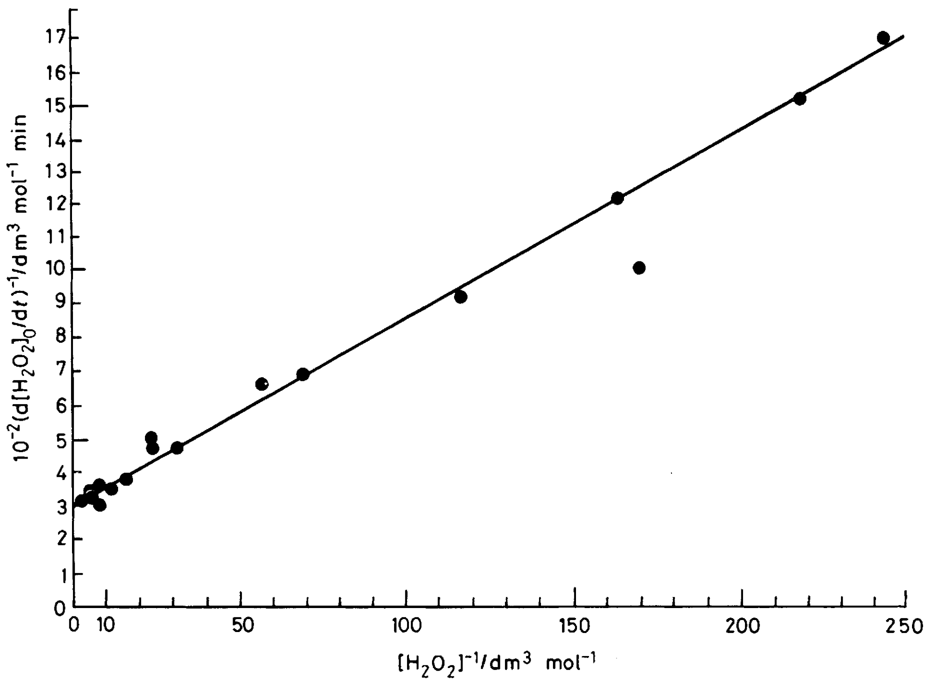


Figure 6. Lineweaver–Burk plot, conditions as in Figure 5

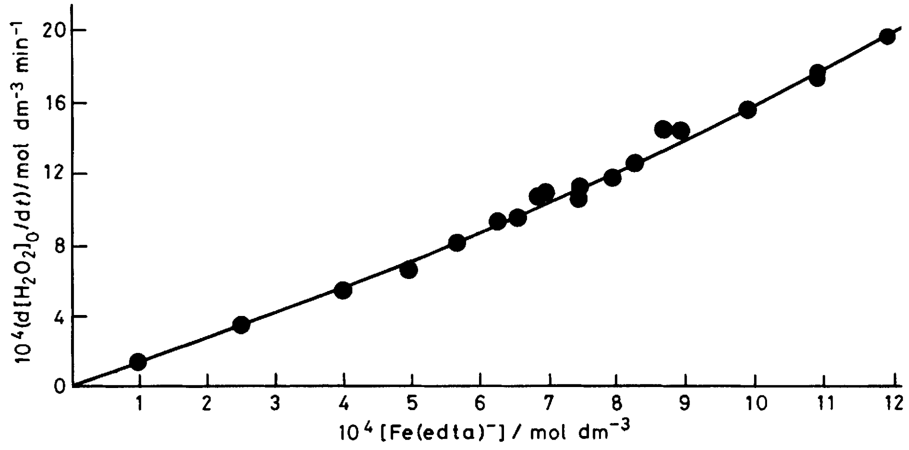


Figure 7. Hydrogen peroxide decomposition rate as a function of [Fe(edta)$^-$]: [edta] = 1.98×10^{-2}, $[H_2O_2]_0 = 1.79 \times 10^{-2}$, [NaCl] = 1 mol dm^{-3}, pH 9.1, 298 K

rate of peroxide decomposition from the maximum value, attributed to binding of a single peroxide molecule.

(*c*) *Kinetic Investigation.*—The initial rate method was used to determine the order of the reaction with respect to the various species present $\{H_2O_2$, [Fe(edta)]$^-$, and $H^+\}$. The initial rate as a function of hydrogen peroxide concentration at pH 9.1 is shown in Figure 5. At low $[H_2O_2]$, the reaction is first order in $[H_2O_2]$ changing to zero order at higher levels. Evidently, decomposition of peroxide is typical of Michaelis–Menten kinetics, with rate law (8), where V is the rate of the reaction,

$$V = \frac{k_3[\text{catalyst}][\text{substrate}]}{K_M + [\text{substrate}]} \qquad (8)$$

$K_M = (k_2 + k_3)/k_1$, and the rate constants are described by equations (9) and (10). Transformation of (8) produces the Lineweaver–Burk relationship, equation (11), where $V_{max.} = k_3$[catalyst].

$$\text{catalyst} + \text{substrate} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{catalyst–substrate complex} \qquad (9)$$

$$\text{catalyst–substrate complex} \xrightarrow{k_3} \text{products} \qquad (10)$$

$$\frac{1}{V} = \frac{K_M}{V_{max.}} \frac{1}{[\text{substrate}]} + \frac{1}{V_{max.}} \qquad (11)$$

The linearity of the plot of V^{-1} against $[H_2O_2]^{-1}$ (Figure 6) confirms that the reaction follows Michaelis–Menten kinetics and, thus, the reaction proceeds *via* formation and subsequent breakdown of a [Fe(edta)]$^-$–peroxy-complex. K_M and k_3 were determined from the slope and intercept of the plot.

As would be expected for this type of process the order of the reaction with respect to the catalyst [Fe(edta)]$^-$ is one at low [Fe(edta)$^-$] levels (Figure 7), although there is a deviation towards higher orders at higher levels of [Fe(edta)]$^-$. Such effects have previously been reported[25] and the possibility of

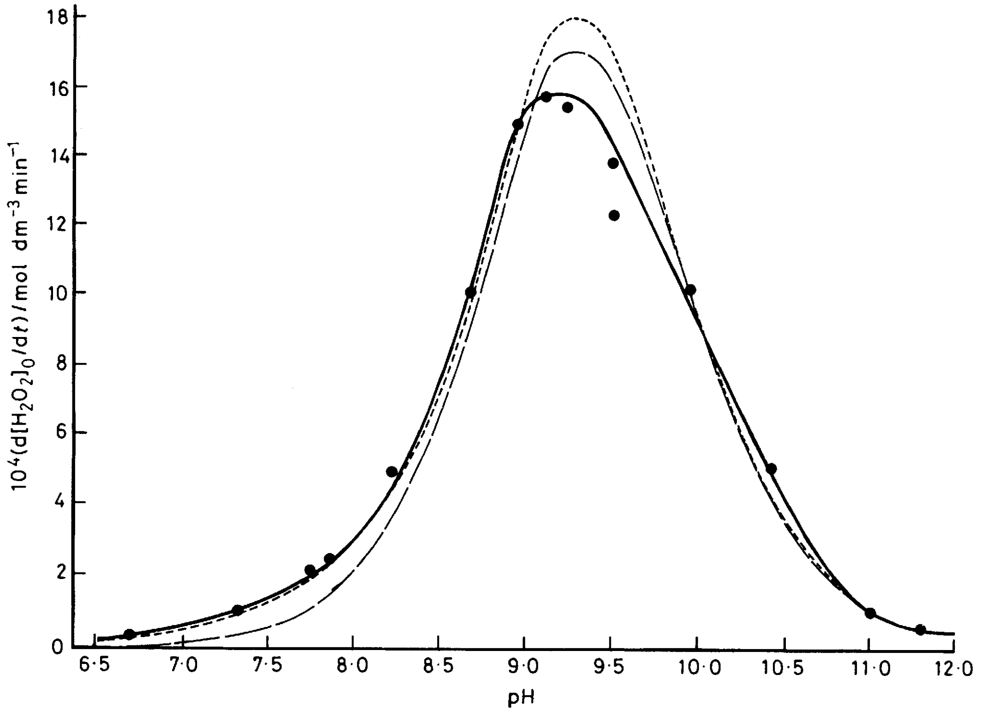


Figure 8. Hydrogen peroxide decomposition rate as a function of pH: $[Fe(edta)^-] = 9.9 \times 10^{-4}$, $[edta] = 1.98 \times 10^{-2}$, $[H_2O_2]_0 = 1.77 \times 10^{-2}$, $[NaCl] = 1\ mol\ dm^{-3}$, 298 K; (●) experimental points, (——) calculated rate, (----) improved calculated fit (see text)

an intermolecular process being involved at high $[Fe(edta)^-]$ suggested.

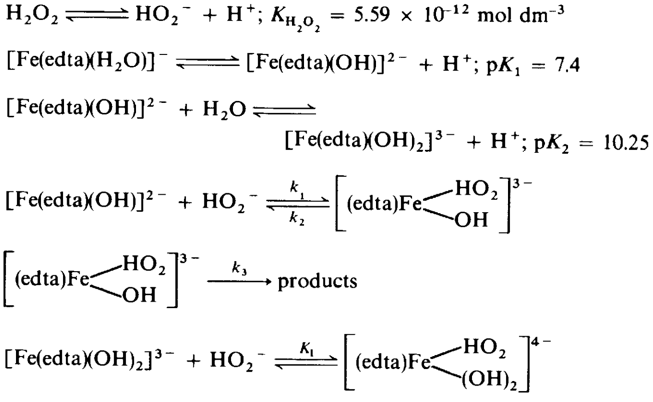
The pH profile for the reaction is given in Figure 8. The increase in the rate observed between pH 7 and 9 can only be explained if the hydrogenperoxide ion, HO_2^-, rather than undissociated hydrogen peroxide combines with the $[Fe(edta)(OH)]^{2-}$ to form the peroxo-intermediate.* Surprisingly, the rate falls with increasing concentration of the complex above pH 9. Inhibition of the decomposition could take place *via* formation of a second inactive complex at high pH or a route involving reformation of the complex after its initial breakdown. Inspection of the pH profile for speciation of $[Fe(edta)]^-$ (Figure 2) suggests the former, with $[Fe(edta)(OH)]^{2-}$ being the active species and $[Fe(edta)(OH)_2]^{3-}$ inactive. This suggestion is strengthened by the observation[42] that the diperoxy-complex which forms at very high peroxide concentrations (>0.5 mol dm^{-3}) is inactive. The reaction Scheme 1 is thus proposed.

Assuming the steady-state approximation for the peroxy-species of $[Fe(edta)(OH)]^{2-}$ the kinetic equation (12) can be derived (see Appendix), which rearranges into the Lineweaver–Burk form, equation (13), where $K_M{}^* = K_M[H^+]/K_{H_2O_2}$.

$$\frac{-d[H_2O_2]}{dt} = V = \frac{k_3[Fe]_T[H_2O_2]}{\frac{K_M[H^+]}{K_{H_2O_2}}\left\{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + \frac{[H_2O_2]K_IK_{H_2O_2}K_2}{[H^+]^2}\right\} + [H_2O_2]} \tag{12}$$

$$V^{-1} = \frac{K_M{}^*}{V_{max.}}\left\{\frac{1 + [H^+]/K_1 + K_2/[H^+]}{[H_2O_2]}\right\} + \left\{\frac{1 + (K_MK_IK_2)/[H^+]}{V_{max.}}\right\} \tag{13}$$

Values of K_M, k_3, and K_I were obtained from the slopes and intercepts of Lineweaver–Burk plots of the data at pH 9.1 (Figure 6) and pH 10 (Figure 9) using a least-squares fit program. These were then substituted into the rate equation and the initial rate as a function of pH was calculated. Very good agreement is obtained between experimental data and theoretical fit (Figure 8): K_M, K_I, and $k_3 = 2.0 \times 10^{-4}$ mol dm^{-3}, $4.1 \times 10^4\ dm^3\ mol^{-1}$, and $9 \times 10^{-2}\ s^{-1}$ respectively.



$$H_2O_2 \rightleftharpoons HO_2^- + H^+;\ K_{H_2O_2} = 5.59 \times 10^{-12}\ mol\ dm^{-3}$$
$$[Fe(edta)(H_2O)]^- \rightleftharpoons [Fe(edta)(OH)]^{2-} + H^+;\ pK_1 = 7.4$$
$$[Fe(edta)(OH)]^{2-} + H_2O \rightleftharpoons [Fe(edta)(OH)_2]^{3-} + H^+;\ pK_2 = 10.25$$
$$[Fe(edta)(OH)]^{2-} + HO_2^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[(edta)Fe\begin{smallmatrix}HO_2\\OH\end{smallmatrix}\right]^{3-}$$
$$\left[(edta)Fe\begin{smallmatrix}HO_2\\OH\end{smallmatrix}\right]^{3-} \xrightarrow{k_3} products$$
$$[Fe(edta)(OH)_2]^{3-} + HO_2^- \overset{K_I}{\rightleftharpoons} \left[(edta)Fe\begin{smallmatrix}HO_2\\(OH)_2\end{smallmatrix}\right]^{4-}$$

Scheme 1. The value of $K_{H_2O_2}$ was experimentally determined in 1 mol dm^{-3} NaCl

The value of the Michaelis constant was found to be in good agreement with the literature values[27–29] for the dissociation

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* The increase in rate with ionic strength previously reported[26] and confirmed by us is consistent with this interpretation.

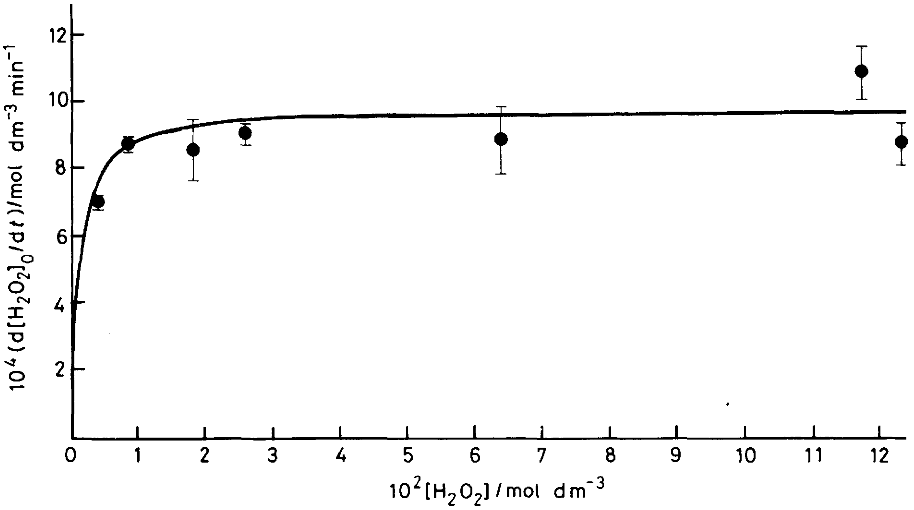


Figure 9. Hydrogen peroxide decomposition rate as a function of $[H_2O_2]_0$ at pH 10: $[Fe(edta)^-] = 9.9 \times 10^{-4}$, $[edta] = 1.99 \times 10^{-2}$, $[NaCl] = 1$ mol dm^{-3}, 298 K; (●) experimental points, (——) calculated rate

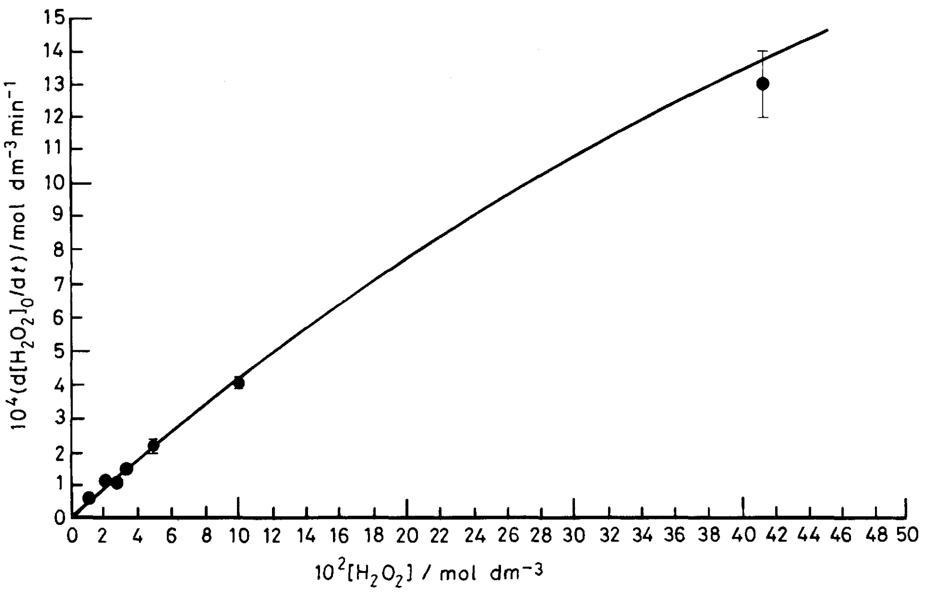
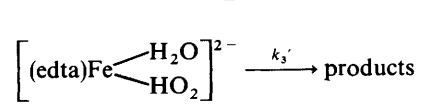


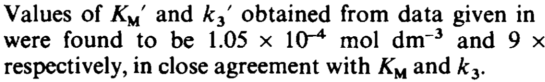
Figure 10. Hydrogen peroxide decomposition rate as a function of $[H_2O_2]_0$ at pH 7.3: $[Fe(edta)^-] = 9.9 \times 10^{-4}$, $[edta] = 1.99 \times 10^{-2}$, $[NaCl] = 1$ mol dm^{-3}, 298 K; (●) experimental, (——) calculated rate using improved scheme

constant of the peroxy-complex, hence it follows that $k_2 \gg k_3$.

An improved fit at low pH is obtained by including the reaction between $[Fe(edta)(H_2O)]^-$ and HO_2^- according to equations (14) and (15), which is also illustrated in Figure 8.



$$[Fe(edta)(H_2O)]^- + HO_2^- \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} \left[(edta)Fe{<}^{H_2O}_{HO_2}\right]^{2-} \quad (14)$$



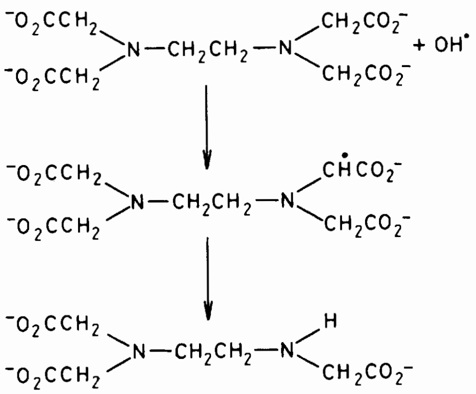
$$\left[(edta)Fe{<}^{H_2O}_{HO_2}\right]^{2-} \xrightarrow{k_3'} \text{products} \quad (15)$$

Values of K_M' and k_3' obtained from data given in Figure 10 were found to be 1.05×10^{-4} mol dm^{-3} and 9×10^{-2} s^{-1}, respectively, in close agreement with K_M and k_3.

The absorption coefficient determined for the $[Fe(edta)]^-$–peroxy-species formed at high pH, *i.e.* $[Fe(edta)(OH)_2(HO_2)]^{4-}$, is 515 dm^3 mol^{-1} cm^{-1} in reasonable agreement with literature values,[29] although its structure was previously thought to be different. The value determined for the monohydroxy-complex is 780 dm^3 mol^{-1} cm^{-1} and this was obtained using (*i*) calculated concentrations of the two peroxy-complexes at pH 9 from kinetic data, (*ii*) the measured absorption coefficient of the dihydroxy-complex, and (*iii*) the total absorbance of the two complexes at pH 9.1. The value reported for the diperoxy-complex[42] is 830 dm^3 mol^{-1} cm^{-1}.

(*d*) *Participation of Radicals.*—The time dependence of the spin–spin relaxation time (Figure 4) is attributed to degradation of edta by intermediates produced during the reaction. Catalytic destruction of edta in systems devoid of excess edta has been widely reported.[1,25,26] The purple peroxy-complex is replaced by a yellow species,[25] with concomitant increase in peroxide decomposition rate, followed by ultimate precipitation of iron(III) oxide and liberation of ammonia and carbon dioxide.[22,26] Conversely addition of excess edta suppresses both the initial rate of peroxide decomposition and hydrolysis, above ligand to metal ratios of 3:1.

Hydroxyl radicals have been implicated as the active intermediates and these are known[43] to initiate degradation by hydrogen-atom abstraction (see below).

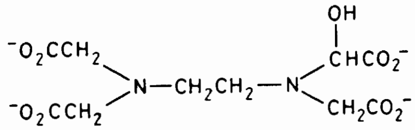


It is thought that hydrogen-atom abstraction occurs primarily[43] at the methylene carbon, as is expected on statistical grounds, leading to formation[44] of ethylenediaminetriacetate (3−) (edtra) complexes *via* peroxy-, hydroperoxy-, and hydroxy-intermediates in alkaline media. Consistent with this view is the finding[45] that edta co-ordinated to Fe^{III} is oxidised to edtra. Degradation can, and does, continue beyond[44] the stages illustrated.

The loss of a carboxy-donor from edta to form the triacetate evidently can lead to the introduction of water, hydroxylic, and amine protons into the co-ordination sphere [equation (16)].

$$OH^{\bullet} + [Fe(edta)(OH)]^{2-} \longrightarrow [Fe(edtra)(OH)(H_2O)]^{-} + CH_2O + CO_2 \qquad (16)$$

Whilst introduction of these protons could contribute to the observed decrease in n.m.r. relaxation times, it is likely that the hydroxy-intermediate shown below is primarily responsible. As



degradation continues to edtra and beyond, the ligand becomes more susceptible to displacement by edta present in excess, eliminating the relaxing protons and restoring the initial relaxation time [equation (17)].

$$[Fe(edtra)(OH)(H_2O)]^{-} + edta \rightleftharpoons [Fe(edta)(OH)]^{2-} + edtra^{3-} \qquad (17)$$

Consistent with this view it is found that the decrease in relaxation time increases with peroxide* decomposition rate, or alternatively the extent of degradation.

The production of radicals can be explained by the traditional radical Scheme 2.[1,2,23]

$$\left[(edta)Fe^{III}\begin{matrix}\diagup HO_2 \\ \diagdown OH\end{matrix}\right]^{3-} \longrightarrow [Fe^{II}(edta)]^{2-} + O_2^{\bullet -} + H_2O$$

$$[Fe^{II}(edta)]^{2-} + H_2O_2 \longrightarrow [Fe^{III}(edta)(OH)]^{2-} + OH^{\bullet}$$

$$[Fe^{II}(edta)]^{2-} + OH^{\bullet} \longrightarrow [Fe^{III}(edta)(OH)]^{2-}$$

$$[Fe^{III}(edta)(H_2O)]^{-} + O_2^{\bullet -} \longrightarrow [Fe^{II}(edta)]^{2-} + O_2 + H_2O$$

Scheme 2.

The present investigations would support the case for participation of radicals in the decomposition reaction. This view is reinforced by the detection of hydroxyl radicals by spin trapping.[46] Whilst there is mounting evidence for the involvement of radicals, the present investigations differ from those of Walling[1] in that the kinetics can be explained by a single rate-determining step involving breakdown of the peroxy-complex; thus, k_3 need not be a composite quantity. A radical scheme can be derived with pre-equilibrium binding of peroxide and chain propagating steps. The kinetic expression for such a scheme is complex and as a consequence the individual rate constants cannot be uniquely determined from experimental data. In addition, slope and intercept terms from the appropriate Lineweaver–Burk plot are inconsistent with the measured dissociation constant of the $[Fe(edta)]^{-}$–peroxy-complex. In contrast the model presented here is simple and produces a Michaelis constant in good agreement with that expected from literature values. Thus, there is little doubt that breakdown of the peroxy-complex of $[Fe(edta)]^{-}$ is rate determining even at high peroxide concentrations and pH. The effect of added organic molecules on the rate of reaction observed by Walling remains unexplained but one obvious possibility is the suppression of hydrolysis. The organic molecules investigated, ethylenediamine, ethylene glycol, and glycine are potential ligands for Fe^{III} and may thus counter hydrolysis accordingly.

These investigations are not consistent with high-oxidation state ionic mechanisms previously proposed. Theoretical predictions suggest a build-up of such high-oxidation state species during the course of the reaction with approach to a maximum value.[16,17] We observe that the peroxy-complex of $[Fe(edta)]^{-}$ decays as the reaction proceeds but no spectroscopically high-oxidation state species were detected as this occurred.

One of the main problems with previous interpretations is that peroxy-complex formation has been taken as synonymous with ionic mechanisms by some workers and the observation of radicals with the rate-determining radical scheme by others. These studies leave little doubt that neither a rate-determining radical scheme, nor a high-oxidation state mechanism is capable of explaining the kinetics of peroxide decomposition catalysed by $[Fe(edta)]^{-}$.

Appendix

The reaction scheme for the $[Fe(edta)]^{-}$ catalysed decomposition of hydrogen peroxide is summarised in Scheme 3.

The peroxide decomposition rate is given by equation (i).

$$d[H_2O_2]/dt = k_3[\mathbf{D}] \qquad (i)$$

Assuming a steady state in **D**, $d[\mathbf{D}]/dt = k_1[\mathbf{B}][HO_2^{-}] - k_2[\mathbf{D}] - k_3[\mathbf{D}] = 0$, $[\mathbf{D}]$ is given by equation (ii), where $K_M = (k_2 + k_3)/k_1$.

$$[\mathbf{D}] = \frac{k_1[\mathbf{B}][HO_2^{-}]}{k_2 + k_3} = \frac{[\mathbf{B}][HO_2^{-}]}{K_M} \qquad (ii)$$

Rearranging the equilibrium equations for the various reactions the equations (iii)—(v) can be derived. Now the total Fe

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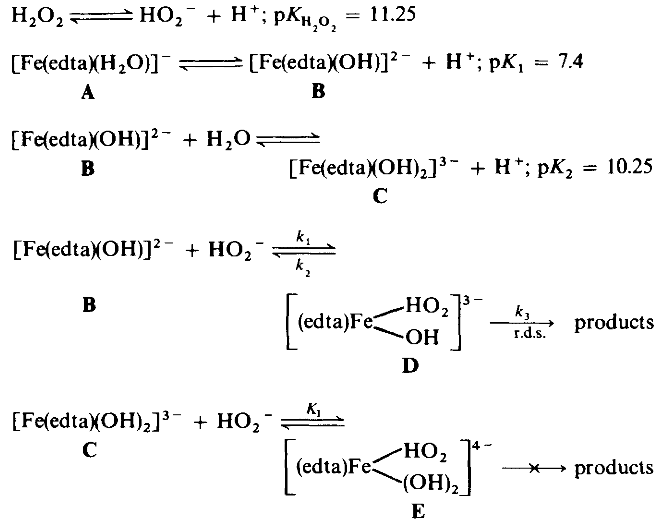
* Dissolution of evolved oxygen was eliminated as a major contribution to relaxation by carrying out control experiments in which oxygen was bubbled through a solution of $[Fe(edta)]^{-}$.



Scheme 3. r.d.s. = Rate-determining step

$$[\mathbf{B}] = [\mathbf{A}]K_1/[\mathrm{H}^+] \qquad \text{(iii)}$$

$$[\mathbf{C}] = ([\mathbf{A}]K_1K_2)/[\mathrm{H}^+]^2 \qquad \text{(iv)}$$

$$[\mathbf{E}] = (K_{\mathrm{I}}[\mathrm{HO_2}^-][\mathbf{A}]K_1K_2)/[\mathrm{H}^+]^2 \qquad \text{(v)}$$

concentration is given by equation (vi) and substituting for [**D**], [**B**], [**C**], and [**E**] in equations (vi) and (ii) yields equations (vii) and (viii).

$$[\mathrm{Fe}]_{\mathrm{T}} = [\mathbf{A}] + [\mathbf{B}] + [\mathbf{C}] + [\mathbf{D}] + [\mathbf{E}] \qquad \text{(vi)}$$

$$[\mathrm{Fe}]_{\mathrm{T}} = [\mathbf{A}] + \frac{[\mathbf{A}]K_1}{[\mathrm{H}^+]} + \frac{[\mathbf{A}]K_1K_2}{[\mathrm{H}^+]^2} + \frac{K_{\mathrm{I}}[\mathrm{HO_2}^-][\mathbf{A}]K_1K_2}{[\mathrm{H}^+]^2} + \frac{[\mathrm{HO_2}^-][\mathbf{A}]K_1}{K_{\mathrm{M}}[\mathrm{H}^+]} \qquad \text{(vii)}$$

$$[\mathbf{D}] = K_1\frac{[\mathbf{A}][\mathrm{HO_2}^-]}{K_{\mathrm{M}}[\mathrm{H}^+]} \qquad \text{(viii)}$$

Substituting the value of [**A**] from equation (vii) into equation (viii) and rearranging gives equation (ix). Substituting the value for [**D**] into equation (i) yields the final rate equation (x), which is mathematically identical to equation (12) but can be more suitably rearranged into equation (13).

$$[\mathbf{D}] = \frac{[\mathrm{Fe}]_{\mathrm{T}}[\mathrm{H_2O_2}]}{\dfrac{K_{\mathrm{M}}[\mathrm{H}^+]}{K_{\mathrm{H_2O_2}}}\left\{1 + \dfrac{[\mathrm{H}^+]}{K_1} + \dfrac{K_2}{[\mathrm{H}^+]}\right\} + [\mathrm{H_2O_2}]\left\{1 + \dfrac{K_{\mathrm{M}}K_{\mathrm{I}}K_2}{[\mathrm{H}^+]}\right\}} \qquad \text{(ix)}$$

$$\frac{-\mathrm{d}[\mathrm{H_2O_2}]}{\mathrm{d}t} = \frac{k_3[\mathrm{Fe}]_{\mathrm{T}}[\mathrm{H_2O_2}]}{\dfrac{K_{\mathrm{M}}[\mathrm{H}^+]}{K_{\mathrm{H_2O_2}}}\left\{1 + \dfrac{[\mathrm{H}^+]}{K_1} + \dfrac{K_2}{[\mathrm{H}^+]}\right\} + [\mathrm{H_2O_2}]\left\{1 + \dfrac{K_{\mathrm{M}}K_{\mathrm{I}}K_2}{[\mathrm{H}^+]}\right\}} \qquad \text{(x)}$$

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