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Kinetics of the Decomposition of Hydrogen Peroxide Catalyzed by Ferric Ethylenediaminetetraacetate Complex

(hydroxyl radicals/metal ion catalysis/ferric complexes/catalase/peroxidase)

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ABSTRACT **Added substrates, acetone and *t*-butyl alcohol, strongly retard the decomposition of H_2O_2 brought about by ferric ethylenediaminetetraacetate (EDTA) at pH 8–9.5. Their relative effectiveness and the kinetic form of the retardation are consistent with their interruption of a hydroxyl radical chain that is propagated by HO· attack both upon H_2O_2 and on complexed and uncomplexed EDTA. Similar retardation is observed with decompositions catalyzed by ferric nitrilotriacetate and hemin, and it is proposed that such redox chains may be quite a general path for transition metal ion catalysis of H_2O_2 decomposition.**

In 1973 Walling and Goosen (1) reported a study of the retarding effect of organic substrates on the Fe^{3+}-catalyzed decomposition of hydrogen peroxide which strongly supported the redox chain mechanism developed by Barb *et al.* (2) on the basis that suitable substrates act as effective traps for hydroxyl radicals which normally propagate the chain. The reaction was considered to involve the steps

$$Fe^{3+} + H_2O_2 \xrightarrow{k_1} Fe^{2+} + H^+ + HO_2\cdot \qquad [1]$$

$$Fe^{2+} + H_2O_2 \xrightarrow{k_2} Fe^{3+} + HO^- + HO\cdot \qquad [2]$$

$$HO\cdot + H_2O_2 \xrightarrow{k_3} H_2O + HO_2\cdot \qquad [3]$$

$$HO_2\cdot + Fe^{3+} \xrightarrow{k_4} Fe^{2+} + H^+ + O_2 \qquad [4]$$

$$HO_2\cdot + Fe^{2+} \xrightarrow{k_5} HO_2^- + Fe^{3+} \qquad [5]$$

$$HO\cdot + RH \xrightarrow{k_6} H_2O + R\cdot \qquad [6]$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \xrightarrow[H^+]{Fe^{2+}} ROOH + Fe^{3+} \qquad [7]$$

where reactions **1** and **4** show an inverse dependence on $[H^+]$, presumably because they involve prior equilibria. At high enough substrate concentrations reaction **6** becomes the major termination step, leading to kinetic expressions

$$-d[H_2O_2]/dt = 2k_1[H_2O_2][Fe^{3+}](1 + (k_3[H_2O_2]/k_6[RH])) \qquad [8]$$

$$d[O_2]/dt = k_1[H_2O_2][Fe^{3+}](k_3[H_2O_2]/k_6[RH]) \qquad [9]$$

From Eqs. **8** and **9**, experiments at high $[H_2O_2]/[Fe^{3+}]$ ratios should yield second order k_{obs} that vary linearly with $[H_2O_2]/[RH]$ and intercepts of $2k_1$ and zero for H_2O_2 consumption and O_2 evolution, respectively, and with slopes differing by a factor of 2. The chief confirmation of the scheme was observation that acetone, acetic acid, and *t*-butyl alcohol all yielded such plots with similar intercepts and slopes inversely proportional to their relative reactivities towards HO· (measured independently). Further, absolute values of the slopes were in fair agreement with those calculated from literature values of k_3 and k_6†. Some other substrates, e.g., methanol, were less effective retarders than predicted and it was suggested that here radicals were not entirely trapped by O_2, but were in part oxidized by Fe^{3+} to propagate the chain.

$$\cdot CH_2OH + Fe^{3+} \rightarrow CH_2O + H^+ + Fe^{2+} \qquad [10]$$

These results apply only to aquo Fe(III) in acid solution (pH < 2). However, at higher pH a number of Fe(III) complexes are also known to catalyze the decomposition of hydrogen peroxide, and this paper describes a study of the effect of organic substrates on some of these systems, in particular the complex with ethylenediaminetetraacetic acid (EDTA).

Experimental

Reaction mixtures were prepared by combining standard solutions of sodium perchlorate (to adjust ionic strength to 0.43), EDTA, ferric perchlorate, substrate, and distilled H_2O_2 in that order. Reactions were conducted in a thermostated pH-stat, started by bringing the pH to the desired value (since H_2O_2 is unstable in alkaline solution the order of combining components is important), and followed by withdrawing aliquots, quenching with acid, and determining H_2O_2 by permanganate titration using an automatic titrator. Each determination of slope or intercept involved a series of runs with various substrate concentrations but other concentrations held constant, and values were determined by least squares fitting of the data; compare Fig. 1.

The Fe(III)–EDTA–H_2O_2 system

At pH > 8, the Fe(III) EDTA complex reacts with H_2O_2 to

Abbreviations: EDTA, ethylenediaminetetraacetate; NTA, nitrilotriacetate; obs., observed; calc., calculated.

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† All rate constants throughout the paper are given in terms of molarity and seconds. A value of $k_3 = 4.5 \times 10^7$ was used in the calculations. Two more recent values are 2.25×10^7 (3) and 1.2×10^4 (4). Taking an average of the three, 2.65×10^7, greatly improves the agreement, and this value is used for calculations here.

TABLE 1. *Retardation of the Fe(EDTA)–H_2O_2 reaction*[a]

[Fe] × 10^3	[H_2O_2] × 10^2	Intercept	Slope × 10^2 Obs.	Slope × 10^2 calc. [8]	Slope × 10^2 calc. [14]
		Series 1[b]			
1.2		0.294	1.42	0.180	1.44
1.0		0.374	1.70	0.229	1.83
0.8		0.320	1.57	0.196	1.57
0.6		0.379	1.32	0.232	1.86
0.7		0.383	1.17	0.235	1.88
0.2		0.448	1.28	0.275	2.20
		Series 2[c]			
	19.5	0.0725	10.01	0.66	2.53
	33.3	0.0728	7.26	0.96	2.93
	39	0.0885	4.23	1.37	3.77
	58.5	0.0721	6.03	1.67	3.63
		Series 3[d]			
1.2		0.245	0.230	0.017	0.189
0.9		0.277	0.270	0.019	0.214
0.55		0.313	0.379	0.022	0.242
0.2		0.306	0.382	0.021	0.236

[a] All experiments at 30°; ionic strength = 0.43.

[b] pH 9.0, 0.0154 M H_2O_2, 0.00155 M EDTA, RH = acetone.

[c] pH 8.5, 0.0039 M Fe, 0.0098 M EDTA, RH = acetone.

[d] pH 9.0, 0.015 M H_2O_2, 0.0015 M EDTA, RH = *t*-BuOH.

form an intensely colored purple complex (λ_{max} 520 nm, ϵ 528) by a process corresponding to the stoichiometry

$$Fe(EDTA)OH^{2-} + HO_2^- \rightleftharpoons Fe(EDTA)O_2^{3-} + H_2O \quad [11]$$

with an equilibrium constant for the reaction as written of about 10^4 (5). The complex exists only in solution and has not been isolated. It shows both "catalase" and "peroxidase" activity, i.e., catalyzes both the decomposition of hydrogen peroxide and the oxidation of organic substrates, including both complexed and uncomplexed EDTA. Walling *et al.* (5) examined the kinetics of this catalyzed decomposition briefly, finding the reaction first order in Fe and first or higher order in H_2O_2. The rate initially increased with pH, but leveled out at above pH 9.5. At pH 10.5 decomposition was cleanly to O_2 and H_2O, but at lower pH values organic substrates were oxidized and their presence retarded the decomposition.

We have now confirmed and extended these observations. At pH 9 the H_2O_2 decomposition is first order in Fe‡ and a 20-fold increase in [H^+] decreases the rate by a factor of 10. In all experiments it is necessary to use some excess EDTA, since otherwise the complex destroys itself, Fe(III) precipitates, and the reaction stops. This excess slightly retards the reaction (with 3 × 10^{-4} M Fe and 1.54 × 10^{-2} M H_2O_2, increasing total EDTA from 7 to 26 × 10^{-4} M decreases the rate 10–15%). Experiments followed by H_2O_2 consumption give reasonable first order plots until the ligand is consumed, but reactions followed by O_2 evolution show significant induction periods, which are discussed further below. Addition of either acetone or *t*-butyl alcohol significantly retards the decomposition and the data yield linear plots of Eq. **8**. Fig. 1 shows the results of two sets of experiments. Both acetone and *t*-butyl alcohol give similar intercepts as predicted (with values indicating a kinetic chain length for the unretarded reaction of about 8), and the ratio of slopes, 6.2, is close to that calculated from the values of k_6, 5.9§.

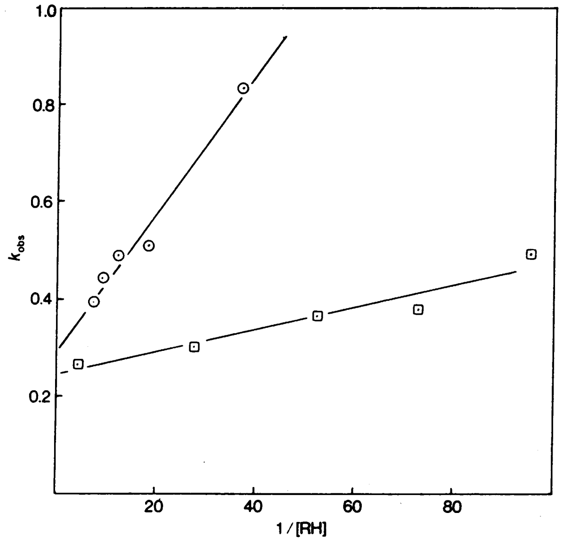
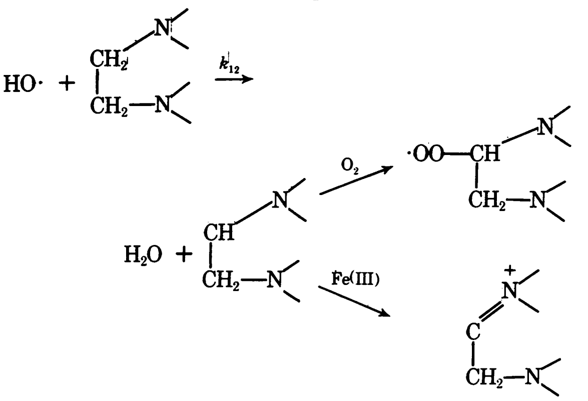


FIG. 1. Effect of substrates on the decomposition of H_2O_2 by ferric EDTA; [Fe], 1.2 × 10^{-3} M; [EDTA], 1.55 × 10^{-3} M; [H_2O_2], 1.5 × 10^{-2} M; pH 9; ionic strength, 0.435; temperature, 30°. ○, acetone; □, *t*-butyl alcohol.

On the other hand, absolute values of the slopes are about 10 times those predicted from the intercepts and k_3 and k_6's (compare Table 1).

We believe that the discrepancy arises because both complexed and uncomplexed EDTA are attacked by HO· and thus are involved in the propagation and termination steps. From our structure–reactivity studies we would anticipate predominant attack on the ethylene bridge. With uncomplexed EDTA the resulting radical would either react with O_2 (termination) or be oxidized by Fe(III) (propagation), e.g., reaction **12** indicating possible reaction paths. (Eq. **12** is only one of several alternatives. The point of HO· attack may determine whether chains are propagated or terminated.)



[12]

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‡ Under our conditions essentially all iron is complexed with EDTA, but the further complex with H_2O_2 is present in only low concentrations; accordingly the concentration of $Fe(EDTA)O_2^{3-}$, the complex that presumably decomposes to initiate redox chains, is proportional to [Fe(EDTA)][H_2O_2]/[H^+], complexed iron is understood in the reactions analogous to 1–7, and HO_2· exists chiefly as $O_2\cdot^-$ at these pH values.

§ We take k_6 (acetone) = 9.7 × 10^7, k_6 (*t*-BuOH) = 5.7 × 10^8 from our previous measurements on the Fe^{2+}–H_2O_2 substrate systems (6).

With Fe EDTA oxidation should be immediate, and the sole process, and the two steps might even be concerted. Such a formulation is consistent with the consumption of EDTA in the unretarded reaction, and the slight retardation by excess EDTA, and parallels the behavior of methanol in acid solution mentioned above. Further, in the analog of reaction **3**, HO· and Fe EDTA are produced in pairs, and the reported value (7) of k_{12} for EDTA is so large, 2.76×10^9, that (assuming a similar value for complexed EDTA) a significant amount of cage reaction could occur which could not be intercepted by added substrate.

For this more complex scheme, Eq. **8** can be generalized

$$-d[H_2O_2]/dt = (2 + \alpha)k_1[H_2O_2][\text{FeEDTA}] \times (1 + \Sigma k_x[X]/\Sigma k_y[Y])) \quad [\mathbf{13}]$$

where $\Sigma k_x[X]$ refers to all the HO· radical reactions propagating the chain, $\Sigma k_y[Y]$ represents all the reactions leading to termination, and α is the fraction of HO· radicals undergoing cage reactions with geminate Fe EDTA. At high substrate concentrations termination via attack on EDTA can be neglected, so **13** takes the form

$$-d[H_2O_2]/dt = (2 + \alpha)k_1[H_2O_2][\text{FeEDTA}] \times (1 + (k_3[H_2O_2] + k_{12}[\text{EDTA}])/k_6[\text{RH}] \quad [\mathbf{14}]$$

where $[\text{EDTA}] = [\text{EDTA}]_{\text{total}}$ and we assume k_{12} is the same for EDTA and Fe(EDTA).

For a series of experiments in which only [RH] is varied, plots of rate versus 1/[RH] should again be linear, and slopes can be calculated from intercepts, k_3, k_6, and k_{12}. Results for two sets of such series with acetone as substrate and one set with *t*-butyl alcohol are shown in Table 1 together with slopes calculated from Eqs. **8** and **14**. In all series, slopes calculated from Eq. **8** are much too small, while results using Eq. **14** give much better agreement (although there is still some scatter). In fact, comparing the contributions from $k_3[H_2O_2]$ and $k_{12}[\text{EDTA}]$, it appears that over half (54–87%) of the chains are propagating via HO· attack on EDTA and Fe(EDTA) rather than H_2O_2 under the conditions studied. (This may account in part for the sigmoid shape of O_2 evolution curves noted above. As EDTA is consumed, attack on H_2O_2, the path by which O_2 is formed, is increasingly favored.)

Returning to the unretarded reaction in the absence of added substrate, our interpretation implies the same propagation steps, but whether termination is solely via HO· attack on EDTA or involves $O_2^-\cdot$ reduction by Fe(II)EDTA, the analog of reaction **5**, is not determined. In either case, the kinetic expressions would become very complex.

Finally, at pH 10.5 and above, oxygen evolution rather than substrate attack becomes the major path of H_2O_2 decomposition (5). We have not further examined the kinetics in this region but the result seems consistent with our model. Here most Fe(EDTA) is complexed with H_2O_2, and a simple fast electron transfer is conceivable

$$\text{HO}\cdot + \text{Fe(EDTA)}O_2^{3-} \rightarrow \text{Fe(II)EDTA}^{2-} + O_2 + \text{HO}^- \quad [\mathbf{15}]$$

Further, the reaction

$$O^-\cdot + HO_2^- \rightarrow OH^- + O_2^-\cdot \quad [\mathbf{16}]$$

which is much faster than **3** (k_{16} about 5×10^8) should become increasingly important.

Other systems

At pH >5 the ferric complex of nitrilotriacetic acid (NTA) catalyzes both the decomposition of H_2O_2 and the oxidation of organic substrates (5), although there is no visible color change observed on adding H_2O_2 to the rather strongly colored complex. The decomposition is strongly retarded by acetone, and the data give good linear plots of Eq. **8**. In a typical experiment (30°, pH 5.5, 0.004 M Fe, 0.0195 M NTA, 0.39 M H_2O_2) we obtain an intercept of 0.11 and a slope of 0.209. Since k_{obs} for the unretarded reaction is 6.7, the data indicate that we are again dealing with a hydroxyl radical chain with an unretarded length of about 60. However, once again the calculated slope, 0.044, is only 20% of that observed. Since the rate constant for HO· attack on NTA is not available, Eq. **14** cannot be tested, but the results suggest HO· attack on both H_2O_2 and NTA. Consistent with this, *t*-butyl alcohol yields a similar intercept but a lower slope, indicating it is a much stronger retarder. A few other systems were investigated very briefly. Moderate concentrations of acetone had no effect on the rate of the fast decomposition of H_2O_2 by the ferric triethylene tetramine complex at pH 7, either because the process is not a HO· chain, or because attack on the amine is too rapid to intercept. However, the decomposition by hemin chloride at pH 9 is significantly retarded.

In summary, our data indicate that hydroxyl radical chain paths may be quite general mechanisms for the decomposition of H_2O_2 by a variety of iron complexes, and can account for the mixture of O_2 evolution and substrate attack observed. We suggest that observation of retardation by suitable substrates, particularly when two or more yield similar limiting rates and show effectiveness proportional to their relative reactivities towards hydroxyl radicals, provides *prima facie* evidence that such mechanisms are involved, although their details may prove to be quite complex, and that such paths may be quite a general feature of H_2O_2 decomposition catalyzed by transition metal complexes.

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