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The Iron(III)–Ethylenediaminetetraacetic Acid–Peroxide System[1]

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The purple complex formed in alkaline solutions containing Fe(III), EDTA, and H_2O_2 has been shown by spectrophotometric, potentiometric, and magnetic measurements to have the stoichiometric composition $Fe^{III}(EDTA)O_2{}^{3-}$. The complex is a catalyst for the decomposition of H_2O_2. At pH ≥ 10.5 decomposition is cleanly to H_2O and O_2. The rate shows a maximum near pH 9, and in this region a variety of organic substrates (including EDTA and the complex itself) are oxidized as well, the overall rate of H_2O_2 decomposition varying greatly with the substrates present. Evidence for the evolution of singlet oxygen in these systems was negative. Some analogs of EDTA behave similarly as catalysts, nitrilotriacetic acid being particularly effective.

In 1956 Cheng and Lott[3] reported the formation of a purple color by the interaction of excess hydrogen peroxide with the Fe^{III}–EDTA (ethylenediaminetetraacetic acid) complex in alkaline solution and offered two possible explanations for the phenomenon: a peroxy complex of Fe^{III}EDTA or chelated iron in a higher oxidation state. Both hypotheses have had subsequent adherents. Ringbom and coworkers[4] have interpreted their spectral evidence as supporting a peroxy complex formed from Fe^{III}EDTA and HOO^-, and others[5,6] have reached similar conclusions. Recently the rate of color formation has been investigated by stop-flow methods and was reported to obey the expression

$$\text{rate} = k[\text{EDTAFe(OH)}_2{}^{3-}][H_2O_2] \qquad (1)$$

over the pH range 9.0–11.0.[7] On the other hand a complexed ferrate ion structure has also been proposed for the colored substance, also on the basis of spectral evidence.[8] To date the purple complex is only known in solution, and is, in fact, quite unstable. It catalyzes the decomposition of H_2O_2,[9,10] and the system has also been reported to initiate the emulsion polymerization of styrene.[10]

Because of our interest in metal-catalyzed redox systems involving peroxides we decided to investigate this system. The work led initially to a study of some other properties of ferric complexes in alkaline solution,[11,12] but we now report spectral, potentiometric, and magnetic susceptibility data which essentially confirm Ringbom's formulation.[4] In addition we have examined some properties of the decomposition of the complex, both in the presence and in the absence of organic substrates. These reactions turn out to be surprisingly complex, the system showing both catalase and peroxidase activity, decomposing H_2O_2 to oxygen and water and attacking organic substrates, the relative importance of the two paths depending upon pH.

Results

Spectrophotometric Studies.—On the basis of X-ray crystal structure determinations, Hoard has concluded that in weakly acid solutions the ferric EDTA complex is heptacoordinate and binds 1 equiv of water: $Fe(EDTA)H_2O^-$.[13,14] At higher pH's it behaves as a weak acid,[15,16] presumably changing to $Fe(EDTA)OH^{2-}$, and also undergoes dimerization (olation)[16] to form an oxo-bridged structure, $Fe(EDTA)OFe(EDTA)^{4-}$.[11,12] Thus at least two equilibria are involved with equilibrium constants at 13°

$$Fe(EDTA)H_2O^- \rightleftharpoons Fe(EDTA)OH^{2-} + H^+ \qquad K_2 = 1.6 \times 10^{-8}\ {}^{16} \qquad (2)$$

$$2Fe(EDTA)OH^{2-} \rightleftharpoons Fe_2(EDTA)_2O^{4-} + H_2O \qquad K_3 = 4 \times 10^{2}\ {}^{17} \qquad (3)$$

and at the pH's with which we are concerned the complex is almost entirely in the hydroxy and dimeric forms. Addition of hydrogen peroxide leads to the formation of a new purple complex, for which we obtain λ_{max} 520 nm, ϵ 528 (compared with 547, 543, and 530 reported earlier), and for which we find the same stoichiometry reported by Ringbom. (Equation 1 is also the stoichiometric equivalent of eq 4.)

$$Fe(EDTA)OH^{2-} + HO_2{}^- \rightleftharpoons Fe(EDTA)O_2{}^{3-} + H_2O \qquad (4)$$

The equilibrium constant for (4) was calculated as described in the Experimental Part, both ignoring the dimerization (3) which was relatively unimportant in most systems and taking it into account. Results appear in Table I. The two calculations give com-

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[17] H. J. Schugar, A. T. Hubbard, F. C. Anson, and H. B. Gray, *J. Am. Chem. Soc.*, **91**, 71 (1969); Gustafson and Martell gave 890.[16]

TABLE I

SPECTROMETRIC FORMATION CONSTANTS FOR THE $Fe^{III}(EDTA)O_2$ COMPLEX AT 13°[a]

pH	$10^2[H_2O_2]_t$,[b] *M*	$10^3[Fe]_t$,[b] *M*	Log *K'*[c]	Log *K*[c]
8.2	4.0	2.0	4.20	4.47
8.5	34.8	2.0	4.39	4.48
8.5	4.0	2.0	4.24	4.47
8.5	0.39	2.0	4.01	4.29
8.5	4.0	10.0	4.03	4.52
8.5	4.0	6.0	3.97	4.39
9.0	4.0	2.0	4.24	4.41
9.0	1.0	6.0	4.05	4.44
9.5	4.0	2.0	4.23	4.32
9.5	0.39	2.0	4.11	4.31
10.0	4.0	2.0	4.18	4.22
10.5	4.0	2.0	4.23	4.23
11.0	4.0	2.0	4.07	4.05
11.5	4.0	2.0	4.02	3.99
		Av	4.14	4.33
		Av dev	0.10	0.13

[a] All experiments in the presence of 0.24 *M* $NaClO_4$, 8% *t*-butyl alcohol, and fivefold excess EDTA. [b] Total concentrations. [c] *K* and *K'* were calculated with and without taking dimerization into account.

parable overall consistency, but the second does show a smaller scatter at low pH and high iron concentration where dimerization becomes appreciable. Both sets also indicate an apparent decrease in *K*'s at higher pH's, perhaps due to further transformations of the Fe(EDTA)OH complex (the complex is reported to ionize further at high pH[15] and is also somewhat unstable). If we take dimerization into account but neglect data at pH >10.5, we obtain $K = 2.4 \times 10^4$ with an average deviation of 12%. This is slightly higher than previous values $[(3.9\text{–}9.8) \times 10^3]$[4,5,7] obtained at 25°.

Potentiometric Studies.—At pH's at which H_2O_2 is only slightly ionized, eq 4 predicts that addition of H_2O_2 to the ferric EDTA complex will lead to the liberation of acid. The prediction was investigated by mixing solutions of H_2O_2 and complex, adjusted to the same pH, and determining the amount of base required to restore the pH to its original value. The amount of base required may be expressed in terms of a pseudo-equilibrium constant (eq 5), where $[OH^-]$ represents the added base. A typical set of data in which H_2O_2

$$K'' = [OH^-]/([Fe] - [OH^-])([H_2O_1] - [OH^-]) \quad (5)$$

was added to a ferric EDTA solution, both at pH 10.5, and the amount of base required to readjust the pH determined appears in Table II. Consistency is good, and very poor fits were obtained using other stoichiometries.

TABLE II

EVALUATION OF EQ 5

H_2O_2[a]	*K''*	H_2O_2[a]	*K''*	H_2O_2[a]	*K''*
0.05	6.20	0.20	6.09	0.50	6.00
0.10	6.35	0.30	6.25	0.70	6.08

[a] Millimoles of H_2O_2 added to 0.10 mmol of ferric EDTA.

Magnetic Susceptibility Measurements.—The magnetic moment of the ferric EDTA complex has been reported as 6.07 BM at pH 6 (theoretical for high-spin iron, 5.92 BM) but decreases at higher pH due to formation of the low-spin dimer.[11]

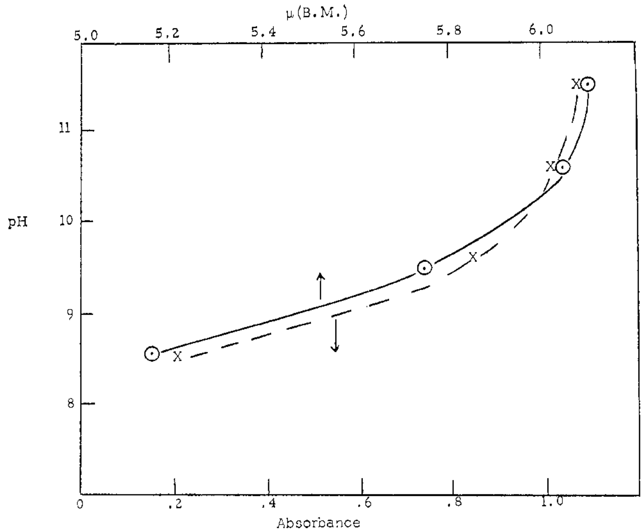

Figure 1.—Comparison of magnetic moment and absorbance of the $Fe(III)\text{–}EDTA\text{–}H_2O_2$ complex.

The magnetic behavior of the peroxy complex was investigated by the nmr method of Evans[18] and is shown in Table III. At pH 8.5 there is some drop in moment due to dimer formation, but values at pH 10.5 and 11.5, where peroxy complex formation is almost complete, give the moment of high-spin Fe(III). Plots of magnetic moment and absorbance at 520 nm *vs.* pH yield similar curves, Figure 1, and it is evident that the results are inconsistent with formulations involving other valence states of iron. All the observations which we have described are consistent with a formulation of the complex formed in $Fe(III)\text{–}EDTA\text{–}H_2O_2$ systems as $Fe^{III}(EDTA)O_2{}^{3-}$ or some stoichiometric equivalent such as $Fe^{III}(EDTA)\text{-}O_2HOH^{3-}$. The stoichiometry is inconsistent with a dimeric structure, and magnetic susceptibility measurements and our potentiometric measurements (plus the simple observation that the complex may be repeatedly decomposed and regenerated by lowering and raising pH) rule out any higher oxidation state of iron.[19] Of the possible stoichiometric equivalents, $Fe^{III}(EDTA)O_2{}^{3-}$ appears the most plausible on the basis of several arguments. It is analogous to a number

TABLE III

MAGNETIC PROPERTIES OF $Fe(EDTA)O_2{}^{3-}$ [a]

pH	Splitting, cps	$10^3\chi_m$, cgsu	*μ*, BM	Absorbance (520 nm)
6.0[b]	3.96	15.74	5.97	. . .
8.5	2.92	11.61	5.13	0.19
9.5	3.65	14.51	5.74	0.82
10.5	4.04	16.06	6.03	1.02
11.5	4.09	16.26	6.07	1.05

[a] Using 0.042 *M* H_2O_2, 0.002 *M* Fe, 0.01 *M* EDTA, and 8% *t*-butyl alcohol at 8°. [b] No H_2O_2.

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(18) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(19) If, for example Fe(III) were oxidized to ferrate, 5 equiv of protons would be liberated compared with 1 equiv observed.

of other known species $Fe(EDTA)X^{2-}$; similar colored species are formed from a number of other ferric chelates at high pH (*vide infra*), but we detect no colored complex from $Fe(EDTA)OH^{2-}$ and either hypochlorite or *t*-butyl hydroperoxide. In fact such systems are stable at room temperature and give no evidence of reaction. Accordingly a second ionizable hydrogen appears to be involved in complex formation. Finally, the optical absorption observed is not simply a bathochromic shift of the EDTA complex absorption, but a new peak and presumably a charge-transfer band, plausibly associated with the electron-transfer process

$$\mathrm{Fe^{III}(EDTA)O_2{}^{2-} \rightleftharpoons Fe^{II}(EDTA)O_2\cdot{}^{-}} \qquad (6)$$

facilitated by the stability of the superoxide anion. Thus in contrast *hydroperoxy* complexes of hydrated ferric ion simply show a bathochromic shift of usual ferric ion absorption.[20] If this interpretation is correct, the driving force for complex formation can be rationalized as involving the replacement of OH^- by more nucleophilic OOH^-. The resulting complex should be more acidic than H_2O_2, it loses a proton to the alkaline medium, and the resulting $O_2{}^{2-}$ ion is even more strongly bound to iron.

Catalytic Properties of the Fe(III)-EDTA-H_2O_2 System.—In alkaline solution Fe^{III}-EDTA complexes catalyze the decomposition of hydrogen peroxide and its oxidation of a variety of organic substrates including free and complexed EDTA. The phenomena involved show complicated pH and concentration dependence and at this point we can give little more than a descriptive summary of our findings with some brief comments about possible reaction paths.

The rate of H_2O_2 decomposition is very slow below pH 8, rises to a flat maximum at pH 9–10, and then declines. At pH 10.5 and above decomposition is cleanly to O_2 and water; organic substrates are not attacked and have no effect on rate, which, however, decreases slightly with increasing ionic strength. Oxygen evolution is close to zero order over most of the reaction and apparently first order in iron, which exists almost entirely as a peroxy complex under these conditions, Table IV. At lower pH's in the region of maximum decomposition rate, H_2O_2 both decomposes to O_2 and attacks EDTA, oxidizing it to CO_2 and ammonia. Since this reaction liberates acid, it is conveniently followed by measuring the amount of sodium hydroxide which must be added to maintain constant pH. Because the reaction destroys the complex, systems not containing excess EDTA soon turn from violet to yellow and then precipitate ferric hydroxide.[21] At this point the rate of H_2O_2 decomposition drops sharply.

TABLE IV

EFFECT OF IRON CONCENTRATION ON H_2O_2 DECOMPOSITION AT pH 10.5[a]

10^4[Fe], *M*	d[O_2]/d*t*, mmol/min	10^4[Fe], *M*	d[O_2]/d*t*, mmol/min
2	0.006	6	0.024
4	0.013	8	0.029

[a] [H_2O_2] = 0.040 *M*, 2 mmol total; [EDTA] = 0.0020 *M*; temperature 30°.

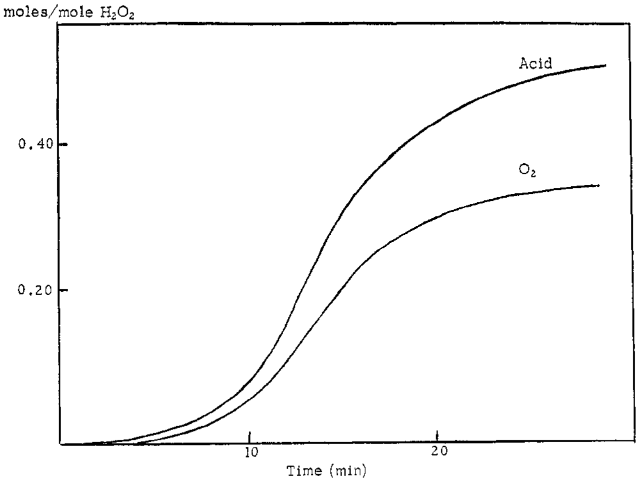

Figure 2.—Formation of acids and O_2 in glycol oxidation: H_2O_2, 0.04 *M;* Fe, 0.0004 *M;* EDTA, 0.002 *M;* glycol, 0.68 *M;* pH 9; temperature 30°.

In this pH range other substrates compete with EDTA for oxidation by hydrogen peroxide and have large effects on the overall rate of decomposition which can be either accelerated or retarded. Since the effect of ethylene glycol was particularly large, it was studied in relative detail.

TABLE V

EFFECT OF pH ON THE Fe-EDTA-H_2O_2-ETHYLENE GLYCOL REACTION[a]

pH	[Products], mol/mol of H_2O_2		Max. rate, mmol/min	
	Acids	O_2	Acids	O_2
7.75	0.40	0.05	0.024	0.002
8.0	0.38	0.06	0.037	0.004
8.5	0.35	0.10	0.071	0.012
9.0	0.27	0.19	0.054	0.030
9.5	0.17	0.32	0.027	0.052
10.0	0.09	0.39	0.011	0.046
10.5	0	0.48	0	0.015

[a] [H_2O_2] = 0.040 *M*, 2 mmol total; [Fe] = 0.0004 *M;* [glycol] = 0.068 *M;* [EDTA] = 0.0020 *M;* temperature 30°.

Oxidation of Ethylene Glycol.—After a short induction period, H_2O_2 decomposition is markedly accelerated in the presence of ethylene glycol. Both O_2 and acid are liberated, and the glycol is attacked in preference to EDTA,[22] effectively protecting the complex from decomposition even when little excess EDTA is present. Both rate and product distribution are pH dependent, Table V, but material balances calculated from the product data given indicate that nearly 0.50 equiv of acid is produced per molecule of H_2O_2 reacting with the glycol at all pH's. In any given experiment both oxygen and acid liberations follow sigmoid curves, and some typical plots appear in Figure 2. Rates reported in Table V and elsewhere are maximum values

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[20] M. G. Evans, R. George, and N. Uri, *Trans. Faraday Soc.*, **45**, 230 (1949).

[21] This phenomeonon was described by Kachanova and Purmal,[6] who however did not recognize its significance.

[22] The stoichiometry (moles of acid liberated/mole of H_2O_2 consumed) may vary from zero to unity for different oxidations. However for oxidation of glycol to glycolate, oxalate, or bicarbonate it is 0.5, 0.5, and 0.4, respectively (see below).

calculated from the linear portions of the curves. These maxima show a complex dependence on concentration of reactants. Excess EDTA retards the reaction, Table VI, further evidence that oxidations of EDTA and glycol are competitive, and, at constant EDTA, rates are approximately first order in iron and second order in H_2O_2, Table VII. Rate dependence on glycol concentration is given in Table VIII and shows that the rate rises with concentration up to approximately 0.25 *M* and then levels off. These experiments were carried out without excess EDTA and again illustrate the competitive nature of the oxidation since the amount of acid produced per millimole of H_2O_2 present before the reaction stops due to destruction of the complex drops at low glycol concentrations. The temperature dependence of the reaction at 25–40° was also examined briefly, and Figure 3 shows results at pH 9, with and without glycol, and at pH 10.5. Activation enthalpies and entropies are indicated in Figure 3 but are almost certainly composite quantities involving several rate constants.

Table VI

Effect of the [EDTA]/[Fe] Ratio on Glycol Oxidation[a]

[EDTA]/[Fe]	Acids formed	Max. rate
5	0.30	0.056
3	0.30	0.060
2	0.32	0.088
1	0.35	0.242
0.5	0.23[b]	0.112
0	<0.01[b]	<0.001

[a] Same conditions and units as Table V; pH 9. [b] Incomplete decomposition of H_2O_2.

Table VII

Effect of H_2O_2 and Fe Concentrations on Glycol Oxidation[a]

		Rate		
[H_2O_2]	[Fe]	Acids	O_2	Total
0.04	0.0008	0.094	0.097	0.191
0.04	0.0004	0.045	0.034	0.079
0.06	0.0004	0.084	0.083	0.167
0.02	0.0004	0.013	0.012	0.025

[a] Same conditions and units as Table V except as indicated; pH 9.

Table VIII

Effect of Glycol Concentration on Glycol Oxidation[a]

[Glycol]/[H_2O_2]	Acid formed[b]	Rate
36	0.32	...
1.70	0.27	0.054
0.50	0.24	0.050
0.25	0.24	0.050
0.10	0.15	0.036
0.05	0.06	0.008
0.025	0.05	0.007

[a] Same conditions and units as Table V except as indicated; pH 9. [b] Before drop in rate accompanying destruction of complex.

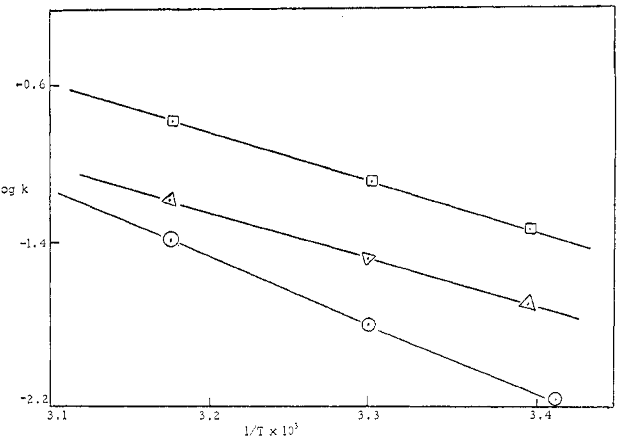

Figure 3.—Temperature dependence of Fe–EDTA–H_2O_2 reactions: ○, Fe–EDTA–H_2O_2–glycol, pH 10.5, $\Delta H^{\ddagger} = 16.5$ kcal, $S^{\ddagger} = -3.2$ eu; □, Fe–EDTA–H_2O_2–glycol, pH 9, $\Delta H^{\ddagger} = 12.0$ kcal, $S^{\ddagger} = -1.3$ eu; △, H_2O_2–EDTA–H_2O_2, pH 9; $\Delta H^{\ddagger} = 10.2$ kcal, $S^{\ddagger} = -3.5$ eu.

The products of glycol oxidation are complex and were not examined in detail, although 10–20% CO_2 was shown to be produced. However, since rapid oxidation of an intermediate could account for the sigmoid curves observed (which show increased induction periods with increasing glycol concentration), oxidations of several possible oxidation products were examined, Table IX. Glyoxal and glyoxalic acid react rapidly with alkaline hydrogen peroxide, even in the absence of iron, and glycolic acid reacts at a rate similar to that of glycol itself, while oxalate is relatively stable and might be expected to accumulate in the system.

Table IX

Reactivities of Glycol Oxidation Products[a]

Compound[b]	Acid formed	Rate
$HOCH_2CH_2OH$	0.30	0.028
OCHCHO	1.91[c]	>0.150[c]
$HOCH_2COOH$	0.28	0.030
OCHCOOH	0.59[c]	>0.150[c]
HOOCCOOH	0.15	0.004
HCHO	0.89	0.011
HCOOH	0.05	0.001

[a] Conditions and units as in Table V except total H_2O_2 is 1 mmol and as otherwise indicated; pH 9. [b] Concentrations 0.040–0.068 *M*. [c] Same rate and yield in absence of FeEDTA.

Oxidation of Other Substrates.—Oxidations of a number of other materials were scanned at pH 9 by following rates and yields of acid formation, Table X. A number of polyhydroxy compounds showed significant acid formation, but widely varying rates, the cyclohexanediols being particularly slow. Fructose was examined in more detail and showed a pH dependence on acid and oxygen formation similar to that of glycol, although it yielded 0.14 mmol of acid even at pH 10.5. Controls indicated no oxidation in the absence of iron.[23] In addition to the compounds in Table X, a number of simple molecules—methyl, ethyl, isopropyl, *n*-propyl, *t*-butyl, and allyl alcohols, *n*-propylamine, acetonitrile, and acetic acid—were all found to yield acidic products (up to 0.25 mmol/mmol of

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(23) Oxidation of glyconic acids with ferric acetate and H_2O_2 (Ruff degradation) is an old reaction in carbohydrate chemistry: O. Ruff, *Ber.*, **31**, 1573 (1898).

TABLE X

OXIDATIONS BY Fe–EDTA–H_2O_2[a]

Compound	Acid formed	Rate
Ethylene glycol	0.30	0.028
Propylene glycol	0.26	0.007
cis-1,2-Cyclohexanediol	0.20[b]	0.0007
trans-1,2-Cyclohexanediol	0.22[b]	0.0005
Glycerol	0.28	0.030
Mannitol	0.25	0.003
Sorbitol	0.27	0.003
Salicylate	0.03[b]	<0.001
Fructose	0.50	0.015
Sucrose	0.58	0.005
Glucose	0.50	0.007
Galactose	0.49	0.011
Dimethoxymethane	0.56	0.001
Ethanolamine	0.24[b]	0.005
Glycine	0.04[b]	0.001
Ethylenediamine	0.11	0.002

[a] Same units and conditions as Table V but total H_2O_2 is 1 mmol; pH 9. [b] H_2O_2 decomposition incomplete.

H_2O_2) but at rates of less than 0.001 mmol/min, taking some 24 hr to give complete reaction. At the same time they acted as efficient inhibitors of the decomposition of the EDTA complex and, as noted earlier, for this reason *t*-butyl alcohol was added to stabilize systems for spectral and other measurements.

Alcohols also retard the oxidation of glycol, an equal quantity of isopropyl alcohol reducing the rate of acid formation by two-thirds. Phenol, di-*t*-butyl-*p*-cresol, galvinoxyl, and iodide also retard the oxidation of other substrates.

Finally, acrylonitrile was investigated as a substrate to see if it would undergo polymerization as reported for styrene.[14] Under usual conditions no polymer was detected, but small quantities precipitated from systems in which the H_2O_2:Fe ratio was reduced from usual values of 100 to near unity. At higher ratios both oxygen and acids were produced, but at a relatively slow rate. Since the high H_2O_2 experiments evolve considerable oxygen, which retards acrylonitrile polymerization and leads to relatively low molecular weight peroxidic products,[24] this may explain our failure to observe polymer under these conditions.

Other Chelating Agents.—We have examined a number of other chelating agents briefly. Not surprisingly, close structural analogs of EDTA, CDTA (cyclohexylenediaminetetraacetic acid) and HEDTA (N-hydroxyethylethylenediaminetriacetic acid), form similar complexes, Table XI, which undergo decomposition at pH 9 and catalyze the oxidation of ethylene glycol at rates quite similar to the EDTA complex. A number of other ligands gave no color change on addition of H_2O_2 but showed varying abilities to catalyze H_2O_2 decomposition and induce oxidation of ethylene glycol, Table XII. Pyrophosphate and tetra-β-hydroxyethylethylenediamine complexes show little catalytic properties, while triethylenetetramine complexes, systems previously investigated by Wang,[25] catalyze only H_2O_2 decomposition to O_2 and water, with little attack on either ligand or added glycol and thus seem to differ qualitatively from EDTA complexes. Nitrilotriacetic acid appears particularly interesting since it is a better catalyst for substrate oxidation than EDTA, gives high rates even at pH 7, and is more resistant to self-oxidation.

TABLE XI

COMPARISON OF Fe(III)–LIGAND–H_2O_2 SYSTEMS

Ligand	% complex, pH 9.5[a]	λ_{max}, nm	ϵ[b]
EDTA	78	520	528
CDTA	22	524	495
HEDTA	48	500	425

[a] $[H_2O_2] = 0.04\ M$; $[Fe] = 0.002\ M$; $[\text{ligand}] = 0.010\ M$; 8% *t*-butyl alcohol; temperature 13°. [b] At pH 10.5–11, assuming complete complex formation.

TABLE XII

CATALYTIC PROPERTIES OF ADDITIONAL FERRIC COMPLEXES

Ligand	O_2 evolution	Glycol oxidn
Triethylenetetramine	Very fast (pH 7–10)	None
Tetra-β-hydroxyethylethylenediamine	Very slow	Little
Ethylenediamine-diacetic acid	Similar to EDTA	Similar to EDTA
Nitrilotriacetic acid	Very fast (pH 9) Slow (pH 5)	Very fast (pH 7–9)
Pyrophosphate	Very slow	Not determined

Attempts to Detect Singlet Oxygen.—Some of the schemes proposed for the catalytic decomposition of H_2O_2 by metal complexes (*vide infra*) suggest that oxygen might be evolved in a singlet state. We have investigated this possibility using tetramethylethylene (TME) as a trap since it gives 60–70% yields of 2,3-dimethyl-3-hydroperoxy-1-butene with singlet O_2 evolved in the H_2O_2–NaOCl reaction.[26] Decomposition of H_2O_2 in aqueous methanol proceeds in the presence of TME to yield oxygen and acidic products as usual, but, in addition, small amounts of peroxidic materials were formed and identified as 2,3-dimethyl-3-hydroperoxy-1-butene and 2,3-dimethyl-2-hydroperoxybutane. Quantitative results appear in Table XIII. Since, in contrast to known singlet oxygen reactions, both saturated and unsaturated hydroperoxides are formed and since yields rise as actual oxygen formation decreases, significant singlet oxygen production seems ruled out, and the small yield of hydroperoxide formed is probably associated with the acid-forming reaction rather than oxygen evolution. The experiments described were carried out at relatively high iron concentrations since hydrogen peroxide decompositions in aqueous methanol are strongly retarded as previously noted, and slowed still further by TME. Rather similar results were found with several other Fe(III)–H_2O_2 systems, and attempts to trap singlet O_2 with 2,5-dimethylfuran, tetraphenylcyclopentadienone, and 1,3-cyclohexadiene were also unsuccessful.

Mechanism of the H_2O_2–Fe(III) Reaction.—The reaction of ferric ion and its complexes with H_2O_2 has been investigated extensively, but at present the inter-

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(24) F. R. Mayo, A. A. Miller, and G. A. Russell, *J. Am. Chem. Soc.*, **80**, 2500 (1958).

(25) J. H. Wang, *ibid.*, **77**, 4715 (1955).

(26) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

TABLE XIII

PRODUCTS IN THE H_2O_2–Fe–EDTA–TME SYSTEM[a]

pH	Oxygen[b]	Acids[b]	$CH_2{=}C$-$(CH_3)C(CH_3)_2$-OOH[c]	$(CH_3)_2CHC$-$(CH_3)_2OOH$[c]
8.0	7	77	5	12
9.0	40	52	5	8
10.0	86	15	4	2
11.0	100	0	1	0

[a] Conditions: H_2O_2, 45 mmol; TME, 12 mmol; Fe, 0.5 mmol; EDTA, 1. 5 mmol; volume 69–85 cm^3; temperature 14–18°. Results are the average of duplicate runs in good agreement. [b] Per cent based on H_2O_2. [c] Per cent based on TME.

pretations seem to exceed the number of systems studied, and the data reported here do little to clarify the situation. Even the reaction of simple hydrated ferric ion has had two mutually contradictory interpretations: a Fe(III)–Fe(II) redox chain originally proposed by Harber and Weiss and modified by Barb, Baxendale, George, and Hargrave[27] and a nonchain scheme involving a series of complexes and an Fe(V) species developed by Kremer and Stein.[28] In spite of their fundamental differences, the two schemes are surprisingly hard to distinguish. The spectroscopically demonstrated presence of ferric–peroxy complexes in no way rules out a radical chain, and both interpretations predict simple bimolecular kinetics at high H_2O_2:Fe ratios where the reaction has been most studied, with deviations under other conditions. The nearest approach to a critical experiment has been the reported measurement[27] of a steady-state concentration of Fe(II) in the system adequate to account for the decomposition rate *via* the well-characterized reaction

$$\mathrm{Fe(II)} + H_2O_2 \longrightarrow \mathrm{Fe^{III}OH} + \cdot OH \qquad (7)$$

The presence of organic substrates complicates matters further since they both undergo oxidation[29] and alter the rate of H_2O_2 decomposition,[30] but this can be accommodated qualitatively by either scheme.[31] Turning to complexed Fe(III), most investigators have preferred nonchain schemes involving various transformations of intermediate complexes, consistent with their experimental results,[32] which, however, are too varied to discuss here.

In interpreting our own results, the first (and unanswered) problem is to distinguish between chain and nonchain processes, noting that if free radicals ($HO\cdot$ and $HOO\cdot$ or $O_2\cdot^-$) are produced in H_2O_2–metal ion systems, chain processes become very likely. Initiation of styrene—and, less successfully, acrylonitrile—polymerization establishes that radicals can be produced in our systems, the rather indiscriminate nature of the oxidations observed resemble those brought about by hydroxyl radicals, and the elaborate kinetics showing both acceleration and retardation by added substrates are reminiscent of other complex radical chains. On the other hand, the available armorium of hypothetical complexes can certainly accommodate an equal variety of results. We plan to continue work on these interesting systems and can only note now that, since oxygen evolution and substrate attack run parallel in any one system, "catalase" and "peroxidase" activities probably here originate from some common intermediate.

Experimental Part

Reagents.—All solutions were prepared with deionized distilled water. Certified reagent $FeCl_3 \cdot 6H_2O$ and the disodium salt of EDTA were used directly in the preparation of stock Fe^{III}EDTA solutions. In most studies a 5:1 EDTA:Fe ratio was employed. preliminary work was carried out with no control of ionic strength, but most of the experiments reported here were carried out in solutions 0.24 *M* in $NaClO_4$, prepared by neutralizing 70% $HClO_4$ with NaOH. Hydrogen peroxide solutions were prepared by diluting 3 or 30% commercial H_2O_2 and analyzing by iodimetry.

Spectrophotometric measurements were made in thermostated cells in Cary 14 or Beckman DB instruments. We used essentially the same techniques as previous workers,[4,5,7] measuring absorbancy at 520 nm at 13° and varying pH against a reference containing all components except the ferric salt. Ionic strength was maintained at 0.24 *M* with $NaClO_4$ and *t*-butyl alcohol (8%) was incorporated as a decomposition inhibitor without alteration of the spectrum. The spectrum in a very large excess of H_2O_2 at pH 11.5 was taken as that of the completely formed peroxy complex (ϵ 528 cm^{-1} M^{-1}). Beer's law behavior was followed in the concentration range studied ([Fe] = (4–100) × 10^{-4} *M*).

The equilibrium constant *K'* was calculated from eq 4 and that for ionization of hydrogen peroxide

$$H_2O_2 \rightleftharpoons H^+ + HOO^- \qquad pK_a = 11.75 \qquad (8)$$

$$K' = \frac{[C](1 + 10^{11.75}[H^+])}{([Fe]_t - [C])([H_2O_2]_t - [C])} \qquad (9)$$

where [C] is the concentration of complex and $[Fe]_t$ and $[H_2O_2]_t$ are total concentrations of iron and peroxide, respectively. The constant *K* which takes into account dimerization of iron uses eq 3, 4, and 7; *i.e.*

$$K = \frac{4K_3[C](1 + 10^{11.75}[H^+])}{([H_2O_2]_t - [C])[(8K_3([Fe]_t - [C]) + 1)^{1/2} - 1]} \qquad (10)$$

Results are given in Table I. Equilibrium measurements at lower ionic strength give lower values of *K* as would be anticipated for a process of the charge type indicated.

Potentiometric measurements were carried out in a pH-stat by adding increments of H_2O_2 to FeEDTA solutions, previously adjusted to the same pH, and measuring the amount of 1.0 *N* NaOH required to restore the pH to its original value. Multiple experiments gave reasonable reproducibility, and at pH 10.5, 0.83–1.0 equiv of (base)·FeEDTA was required with 8–20-fold excesses of H_2O_2.

Magnetic susceptibility measurements were made by the nmr method of Evans.[18] Solutions containing 8% *t*-butyl alcohol were prepared as for spectral measurements and placed in nmr tubes along with thin-walled capillary tubes containing reference samples (all components but iron salt at the same pH). The separation of the methyl protons of the *t*-butyl alcohol in solution and reference was determined at 8° in a Varian A-60 nmr instrument at 50 cps and the difference in magnetic susceptibility was calculated. Negligible decomposition of H_2O_2 or the complex occurred during the measurement and the same solutions were used for the spectroscopic measurements.

Catalysis of H_2O_2 Decomposition.—Reactants were combined in the stirred thermostated (30°) titration vessel of a pH-stat, equipped with an airtight closure and connected to a gas buret.

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(27) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 591 (1951).

(28) M. L. Kremer and G. Stein, *ibid.*, **55**, 959 (1959); M. L. Kremer, *ibid.*, **58**, 702 (1962); **59**, 2535 (1963).

(29) M. L. Kremer, *Nature*, **184**, 720 (1959).

(30) J. M. Flicstein and M. L. Kremer, *J. Catalysis*, **8**, 145 (1967).

(31) Acetone retards the Fe(III)–H_2O_2 reaction, a result interpreted by Kremer as competitive complex formation.[30] However, it similarly inhibits the oxidation of alcohols by Fe(II)–H_2O_2 (Fenton's reagent), a clearly radical process: J. H. Merz and W. A. Waters, *J. Chem. Soc.*, S15 (1949).

(32) In part this preference seems to be because these systems have been studied as analogs of catalase and peroxydase, and it is difficult to envision enzymatic control of a free-radical chain process.

Decompositions were initiated by activating the pH-stat which delivered 1 *N* NaOH to bring the system to the desired pH. The reaction was followed both by the additional base added continually by the pH-stat to maintain pH and by O_2 evolution. Representative reactions were followed iodometrically by removing aliquots and determining total H_2O_2. Good agreement was obtained for rates of product formation and H_2O_2 consumption.

Product identification was carried out on several oxidation reactions run on a larger scale, and figures below all refer to moles of product per mole of H_2O_2 consumed. With Fe^{III}EDTA + excess EDTA alone at pH 9, 0.14 mol of acid was produced. Acidification of a portion and sweeping through Ascarite showed it to be essentially all CO_2. A similar run at pH 7.5–8.5 in the presence of ethylene glycol gave 0.47 mol of acid but only 0.10 mol of CO_2. The remaining acid products (presumably glycolic or oxalic acids) were not identified. Nessler's test for ammonia was strongly positive in the first case but only weakly so in the second.

Alcohol oxidations at pH 8–10 gave small quantities of identifiable products. Isopropyl alcohol at pH 9 yielded 0.24 mol of acetone plus 0.15 mol of unidentified acids. Lesser quantities of each were formed at pH 10. Small amounts of the corresponding aldehydes were identified (by DNP derivatives and glpc retention time) from methyl, ethyl, and *n*-propyl alcohols, and the last also gave approximately 2% propionic acid.

Attempts to Detect Singlet Oxygen.—Decompositions were carried out in aqueous methanol buffered with ammonia (pH 8–11) in the presence of tetramethylethylene. The purple complex forms under these conditions and there is rapid evolution of oxygen. The organic layer was separated and was shown to contain small amounts of peroxidic material. For quantitative analysis, hydroperoxides were reduced with triethyl phosphite and the resulting alcohols were separated by glpc, collected, and identified by comparison with known materials. The same procedure applied to the H_2O_2–NaOCl reaction gave a 60–70% yield of 3-hydroxy-2,3-dimethyl-1-butene, derived from the corresponding peroxide.

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A Nuclear Magnetic Resonance Study of the β-*cis*-Ethylenediamine-N,N'-diacetatocobalt(III) Chelate System

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The complexes Na[Co(EDDA)(L)] (EDDA = ethylenediamine-N,N'-diacetate and L = oxalate and malonate) have been synthesized, and substantial yields of both the α-*cis* and β-*cis* (previously designated *trans* and *cis*, respectively) isomers have been isolated through a series of chromatographic steps and fractional crystallizations of the tetraphenylarsonium salts. Previously only trace quantities of isomers of similar complexes having this linear tetradentate in the β-*cis* configuration have been reported even though this configuration is often encountered for other linear tetradentates such as triethylenetetramine. A study of the pmr spectra of the β-*cis* isomers of the oxalate and malonate complexes together with a reinvestigation of the spectrum of β-*cis*-Co(EDDA)en^+ has shown the previously reported analysis of the pmr spectrum of the β-*cis* configuration to be incorrect. The new data obtained for this chelate system have been compared with pmr data previously reported for cobalt(III) complexes of the related ligands EDTA, ethylenediaminetriacetic acid (ED3A), and β-aminoethyliminodiacetic acid (AEIDA). This has permitted a systematic classification of the glycine ring methylene resonances (an AB spectrum) into four categories. This classification should prove useful in future stereochemical and kinetic studies of these and related chelates. Selective isotopic substitution of these methylene protons by deuterium proved to be invaluable in this study. The use of bond anisotropy arguments to assign stereochemistry has been reevaluated.

Introduction

Ethylenediamine-N,N'-diacetate (EDDA) and its N-substituted analogs show a high preference for the α-*cis*[3–6] configuration in complexes in which a diamine ligand is used in the remaining two positions.[4,5] It was postulated that the low yield of β-*cis*-Co(EDDA)en^+ obtained was due to greater nonbonding interactions between the amine protons of ethylenediamine with EDDA in this isomer.[4,6] To test this hypothesis a series of complexes has been prepared in which these steric interactions have been eliminated, Co(EDDA)L^- where L is oxalate (ox) or malonate (mal). Van Saun and Douglas[7] reported the isolation of the α-*cis* isomers of these complexes as well as the carbonate analog. However, in all cases less than 30% of the total yield based on moles of cobalt used was obtained. Thus it is possible that the β-*cis* isomers still remained in solution. Recently Garnett and Watts found that good yields of the β-*cis*-EDDA isomer could be obtained if the remaining two positions of the coordination sphere were occupied by carbonate, two chlorides, or two waters,[6] thus supporting the steric argument.

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(3) There has been no definite decision on how the various configurations of a tetradentate chelate should be designated. However it has been recently suggested[6] that the nomenclature introduced by A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965), for linear tetradentate ligands has wider application. Thus the designations employed by Legg, Cooke, and Douglas,[4,5] *trans* and *cis*, which refer to the relative positions of the terminal ligating atoms (the oxygens in the case of EDDA), become α-*cis* and β-*cis*, respectively. These designations are used in this report.

(4) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

(5) J. I. Legg, D. W. Cooke, and B. E. Douglas, *ibid.*, **6**, 700 (1967); J. I. Legg and B. E. Douglas, *ibid.*, **7**, 1452 (1968); J. I. Legg, *Chem. Commun.*, 675 (1967).

(6) P. J. Garnett, D. W. Watts, and J. I. Legg, *Inorg. Chem.*, **8**, 2534 (1969).

(7) C. W. Van Saun and B. E. Douglas, *ibid.*, **8**, 115 (1969).