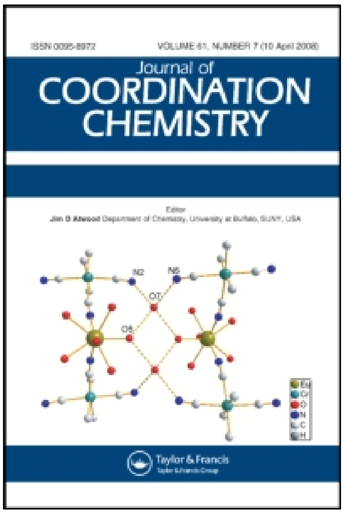

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KINETIC STUDY OF THE HYDROGEN PEROXIDE REACTION WITH THE 1-HYDROXYETHYLIDENE-1,1-DIPHOSPHONATOIRON(III) COMPLEX

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KINETIC STUDY OF THE HYDROGEN PEROXIDE REACTION WITH THE 1-HYDROXYETHYLIDENE-1,1-DIPHOSPHONATOIRON(III) COMPLEX

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The rate of reaction of [Fe(HEDP)] with H_2O_2 in 0.10 M KNO_3 solution was investigated at various temperatures. The observed rate law is given by the expression

$$-d[H_2O_2]/dt = \{(k_1 + k_2K_1[H^+]^{-1})/(1 + K_a^{-1}[H^+]^{-1})(1 + K_1[H^+]^{-1})\}\,[H_2O_2]_T[Fe(HEDP)]_T$$

where k_1 and k_2 are the rate constants in the presence of $[FeHL^-]$ and $[FeL^{2-}]$ complex species, respectively, and K_1 *is the ionisation constant of* $[FeHL^-]$*. The rate constants* k_1 *and* k_2 were determined at 30°C to be 0.024 ± 0.002 and 0.189 ± 0.005 $M^{-1}s^{-1}$, respectively. The corresponding activation enthalpies ($\Delta H_1^{\ddagger} = 73.8 \pm 10.5$ and $\Delta H_2^{\ddagger} = 58.9 \pm 0.8$ kJ mol^{-1}) and activation entropies ($\Delta S_1^{\ddagger} = -33 \pm 33$ and $\Delta S_2^{\ddagger} = -64 \pm 2$ J K^{-1} mol^{-1}) were calculated from a least-squares fit to Arrhenius plots. The results are compared with previously reported data for other complexes.

Keywords: Iron(III), phosphonate, peroxide, reaction, kinetics

INTRODUCTION

The kinetics of oxidation of hydrogen peroxide by the ethylenediaminetetraacetatoiron(III) complex in aqueous media showed that the general mechanism involves the rapid formation of an intermediate ternary complex[1] followed by the slow decomposition to products;[2] however, in the presence of the structurally related ethylenediaminetetrakis(methylenephosphonato)iron(III) complex, $[Fe(ENTMP)(H_2O)]^{5-}$, the reaction was found to be independent of peroxide concentration.[3] The difference in the course of reaction by both aminoacid complexes was attributed to differences in anionic potential surrounding the central ion and the stereochemistry of the phosphonate group which stabilises the coordinated water molecule – presumably through H-bonding with the free non-coordinating oxygens.

To assess the role played by each individual parameter on the reaction kinetics, we extended these measurements to other systems involving $[Fe(HEDP)]^-$ and $[Fe(NTMP)]^{3-}$ (HEDP is 1-hydroxyethylidene-1,1-diphosphonic acid and NTMP is nitrilotris(methylenephosphonic acid). Along the series $[Fe(ENTMP)]^{5-}$, $[Fe(NTMP]^{3-}$ and $[Fe(HEDP)]^-$, the number of coordinated phosphonates decreases from 4 to 2 and the net anionic charge drops from −5 to −1. While the

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coordinated water molecule in $[Fe(ENTMP)(H_2O)]^{5-}$ is caged by the surrounding phosphonate groups thus rendering its exchange with the HO_2^- nucleophile (or H_2O_2 molecule) rather difficult, in the case of $[Fe(HEDP)(H_2O)_3]^-$ at least one of the bound water molecules is remote from the phosphonate environment.

In this paper, we present the results obtained for Fe(HEDP)–H_2O_2 system.

EXPERIMENTAL

Reagents and Solutions

1-Hydroxyethylidene-1,1-diphosphonic acid (H_5L) was obtained from Monsanto Chemical Co., St. Louis, Mo and was purified by precipitation as the lead salt and the free ligand was then stripped off by passing H_2S gas through a suspension of the ligand salt in water. Lead sulphide and the unreacted lead phosphonate were filtered off and the aqueous solution of the free ligand was freeze dried (M. P. 103–105°C). The purity of the solid was checked by titrating the ligand solution with a standard solution of CO_2-free sodium hydroxide. Other reagents, iron(III) nitrate, potassium nitrate, sodium hydroxide and hydrogen peroxide, were B.D.H. AnalaR grade.

Measurements

The detail of the kinetic procedure is essentially the same as described before.[4] All the measurements were obtained at 0.10 M ionic strength using potassium nitrate as the background electrolyte. The pH of the reaction medium was controlled with ammonia, glycine or borax buffer[5] depending on the pH range and monitored simultaneously with each kinetic run using a Radiometer M62 pH-meter fitted with a combined glass-calomel electrode. The activity coefficient of the hydrogen ion at 0.10 M ionic strength was taken as 0.782.[6] In all measurements, the ratio of HEDP : Fe(III) was kept constant at 1.05 to ensure that iron was present only in the complexed form.

Spectral measurements were obtained at ambient temperature with a Perkin-Elmer spectrophotometer. All measurements were obtained using 1.00 cm path length quartz cuvettes.

RESULTS AND DISCUSSION

Potentiometric titration curves of HEDP with sodium hydroxide show the presence of two distinct inflections corresponding to the liberation of two and three protons respectively. The pK values associated with the step-wise equilibria

$$H_{n-1}L + H^+ \rightleftharpoons H_nL$$

were determined to be 10.98; 6.87, 2.54 and 1.7 for n = 2, 3, 4, and 5, respectively.[7]

Because of its stereochemistry, HEDP acts only as a tridentate ligand in its coordination with a single cation despite the presence of five donating atoms.[8] However, the presence of these extra sites promotes the formation of polynuclear complexes. Earlier potentiometric studies on the Fe(III)-HEDP system[9] indicated the presence of the FeL^{2-}, $Fe(HL)^-$, $Fel(HL)^{6-}$ and Fe_2L^+ species, depending on the medium pH and the molar ratio of metal to ligand. Under the present experimental conditions, the concentration of the polynuclear complexes is negligible ($0.2 < C_M < 1.0$ mM and $C_L : C_{Fe} = 1.05$). The estimates of the logarithmic values of the stability constants of the other three species are 21.60, 16.21 and 29.10 respectively.[9]

In alkaline media, the Fe(III)–HEDP mixture develops a strong band at 296 nm with $\varepsilon_{max} = 424\ M^{-1}\ cm^{-1}$. This is probably associated with the deprotonation of the coordinated hydroxy group in the $FeHL^-$ complex. Addition of H_2O_2 to this solution causes a slight shift in the absorption maxima (λ_{max} 293 nm; ε_{max} 640 M^{-1} cm^{-1}) and the appearance of an absorption shoulder at about 305–315 nm with $\varepsilon_{max} \simeq 500\ M^{-1}\ cm^{-1}$. Such changes in the spectral characteristics are ascribed to the formation of ternary peroxo complexes.

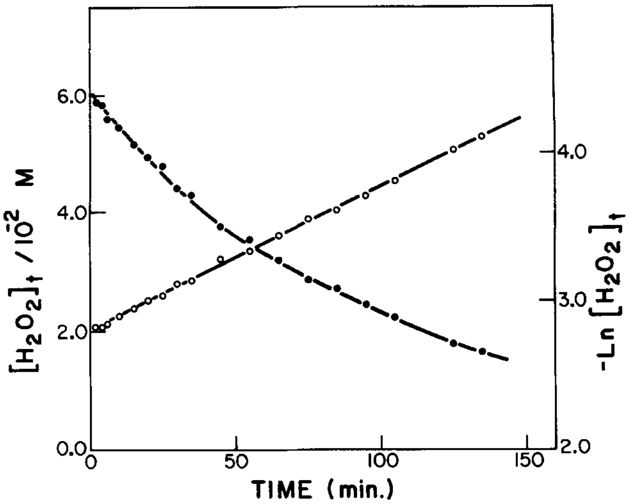


FIGURE 1 Plot of the residual peroxide concentration *vs.* time and the corresponding pseudo-first-order plot; $[H_2O_2] = 60.2$ mM; $[Fe(III)\text{–}HEDP]_T = 0.38$ mM; Temp. = 50°C; pH = 9.85.

The kinetics of the peroxide decomposition were studied over the pH range 8.3–11.0, ionic strength 0.10 M and temperatures 30, 40 and 50°C over a range of H_2O_2 and complex concentrations. Pseudo-first-order conditions were maintained in all runs by using a large excess of hydrogen peroxide over the ferric complex. Fig. 1 presents an example of the plots obtained for the residual peroxide concentration as a function of time and the corresponding first-order plots. The latter were found to be linear for at least three half-lives or more with a residual $[H_2O_2]_t/[Fe(III)HEDP]_T$ ratio $\geqslant 16$. The pseudo-first-order rate constants obtained from the slopes of these plots using a linear least-squares program are listed in Table I. At prefixed conditions of pH, temperture, $[H_2O_2]$ and ionic strength, the observed rate constants are directly proportional to the total iron contents. Accordingly, the rate of peroxide decomposition is given by

$$\text{Rate} = k_{obs}[H_2O_2][Fe(III)HEDP]_T \qquad (1)$$

where $[Fe(III)HEDP]_T$ is the total concentration of iron in all possible forms corrected for the presence of the catalytically inactive $FeL(HL)^{6-}$ and FeL_2^{7-} complexes ($\leqslant$ 5%). The lack of activity of the latter species is attributed to the absence of "free-labile" sites in the coordination sphere of the metal ion.[10-12]

TABLE I
Observed rate constants for the reaction of hydrogen peroxide with [Fe(III)–HEDP]; $[H_2O_2]_i = 60.2$ mM; $I = 0.10$ M (KNO_3).

$[Fe(III)\text{–}HEDP]_{cor}{}^a$ (mM)	Temp. (°C)	pH	$k_{obs}/10^{-5}$ (s^{-1})
0.38	30	8.30	1.1 ± 0.3
0.38	30	8.80	1.6 ± 0.5
0.38	30	9.41	3.0 ± 0.8
0.38	30	9.90	4.5 ± 0.6
0.38	30	10.29	5.3 ± 0.8
0.38	30	11.00	6.3 ± 0.9
0.38	40	8.30	2.3 ± 0.7
0.38	40	9.18	4.5 ± 0.9
0.38	40	9.48	6.0 ± 0.3
0.38	40	9.80	8.3 ± 0.6
0.38	40	9.95	9.4 ± 0.6
0.19	40	9.95	5.0 ± 0.5
0.57	40	9.93	15.2 ± 0.4
0.76	40	9.91	19.7 ± 1.2
0.95	40	9.95	25.4 ± 1.2
0.38	40	10.22	11.0 ± 0.5
0.38	40	11.00	13.4 ± 0.6
0.38	50	8.30	6.4 ± 0.4
0.38	50	8.83	7.9 ± 1.1
0.38	50	9.32	10.0 ± 0.6
0.38	50	9.85	15.9 ± 0.5
0.38	50	10.62	24.4 ± 1.2
0.38	50	11.03	26.2 ± 0.4

[a] Corrected for the presence of $FeL(HL)^{6-}$ and FeL_2^{7-} species.

The dependence of the observed rate constants on the medium pH is presented in Fig. 2. These results are consistent with the rate law

$$-d[H_2O_2]/dt = \{(k_1 + k_2K_1[H^+]^{-1})/(1 + K_a^{-1}[H^+]^{-1})(1 + K_1[H^+]^{-1})\}[H_2O_2]_T[Fe(HEDP)]_T \qquad (2)$$

where k_1 and k_2 are the rate constants in the presence of $[FeHL]^-$ and $[FeL^{2-}]$ complex species respectively, K_a is the protonation constant of H_2O_2 ($pK_a = 11.75$[13]) and K_1 is the ionisation constant for the reaction

$$FeHL^- \rightleftharpoons FeL^{2-} + H^+ \qquad (3)$$

The term $(1 + K_a^{-1}[H^+]^{-1})$ accounts for the undissociated fraction of hydrogen peroxide and is approximately unity within this pH range. The specific rate constants as well as the ionisation constant for reaction (*3*) were calculated at different temperatures by fitting the equation

$$k_{obs} = (k_1 + k_2K_1[H^+]^{-1})/(1 + K_a^{-1}[H^+]^{-1})(1 + K_1[H^+]^{-1}) \qquad (4)$$

The agreement between the calculated variation of k_{obs} with pH (solid curves) and the experimental values is shown in Fig. 2. Table II lists all the calculated constants together with the activation parameters obtained from Arrhenius plots. The error limits quoted for the enthalpies and entropies of activation were obtained at 90% confidence limits following standard procedures.[14]

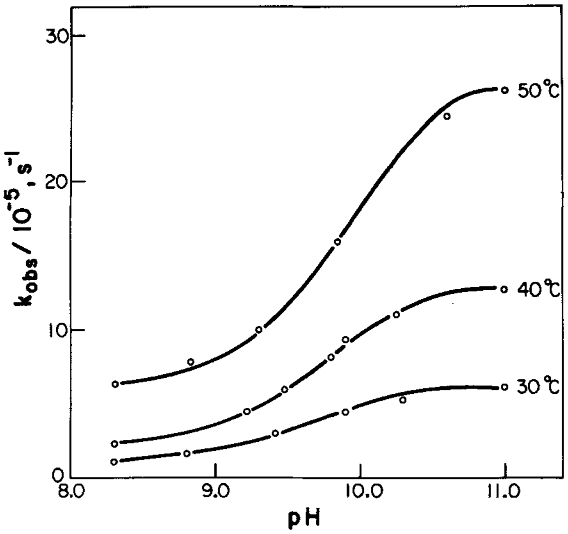


FIGURE 2 The variation of k_{obs} with pH for the reaction of H_2O_2 with [Fe(III)-HEDP]. Solid lines represent the calculated values of k_{obs} from the fitted rate constants at different pH values whereas experimental data are represented by the open circles.

TABLE II

Rate constants and activation parameters for the decomposition hydrogen peroxide catalysed by [Fe(III)–HEDP]; I = 0.10 M(KNO_3).

Temp. (°C)	$k_1/10^{-2}$ ($M^{-1}s^{-1}$)	$k_2/10^{-1}$ ($M^{-1}s^{-1}$)	pK_1
30	2.37 ± 0.17	1.89 ± 0.05	9.67 ± 0.05
40	5.26 ± 0.48	4.16 ± 0.20	9.75 ± 0.02
50	15.53 ± 0.92	8.55 ± 0.40	9.95 ± 0.04

$\Delta H_1^{\ddagger} = 73.8 \pm 10.5\ \mathrm{kJ\ mol^{-1}}$; $\Delta H_2^{\ddagger} = 58.9 \pm 0.8\ \mathrm{kJ\ mol^{-1}}$

$\Delta S_1^{\ddagger} = -33 \pm 33\ \mathrm{J\ K^{-1}}$; $\Delta S_2^{\ddagger} = -64 \pm 2\ \mathrm{J\ K^{-1}\ mol^{-1}}$

A sequence of changes consistent with the kinetic results for the acid-dependent and acid-independent processes is depicted in the following scheme

$$Fe(HL)^- + H_2O_2 \underset{k_r}{\overset{k_f}{\leftrightarrows}} Fe(HL)(H_2O_2)^- \xrightarrow{k} I_H \qquad \text{(slow)} \qquad (5)$$

and

$$FeL^{2-} + H_2O_2 \underset{k_r}{\overset{k_f'}{\leftrightarrows}} FeL(H_2O_2)^{2-} \xrightarrow{k'} I \qquad \text{(slow)} \qquad (6)$$

and the reaction proceeds to completion, presumably *via* a fast series of free radical reactions involving $HO_2^{\cdot}$, $O_2^{-}\cdot$ and/or $HO\cdot$.

TABLE III
Activation parameters for the disproportionation of hydrogen peroxide in the presence of different chelates; T = 303 K; I = 0.10 M (KNO_3).

Reaction	k $M^{-1}s^{-1}$	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}	Ref.
1. $Fe(HL)^{-} + H_2O_2$[a]	0.024	73.8	−33	p.w.[b]
2. $FeL^{2-} + H_2O_2$	0.189	58.9	−64	p.w.
3. $Fe(EDTA)(OH)^{2-} + H_2O_2$	0.46	126.3	−134	[2]
4. $Fe(EDTA)(OH)^{2-} + HOO^{-}$	130.5	42.7	−63	[2]
5. $Cr(EDTA)(H_2O)^{-} + H_2O_2$	0.018	58.9	−85	[15]
6. $Cr(EDTA)(OH)^{2-} + H_2O_2$	0.174	66.5	−40	[15]
7. $Ce(EDTA)(OH)^{-} + H_2O_2$	0.076	51.3	−97	[16]
8. $Ce(EDTA)(OH)_2^{2-} + H_2O_2$	0.229	41.8	−119	[16]
9. $Mn(ENTMP)(OH)^{6-} + H_2O_2$	33.0	17.0	−165	[4]
10. $Mn(ENTMP)(H_2O)^{5-} + H_2O_2$	2.2	83.0	+37	[4]

[a] L^{5-} = the anion of HEDP; [b] p.w. = present work.

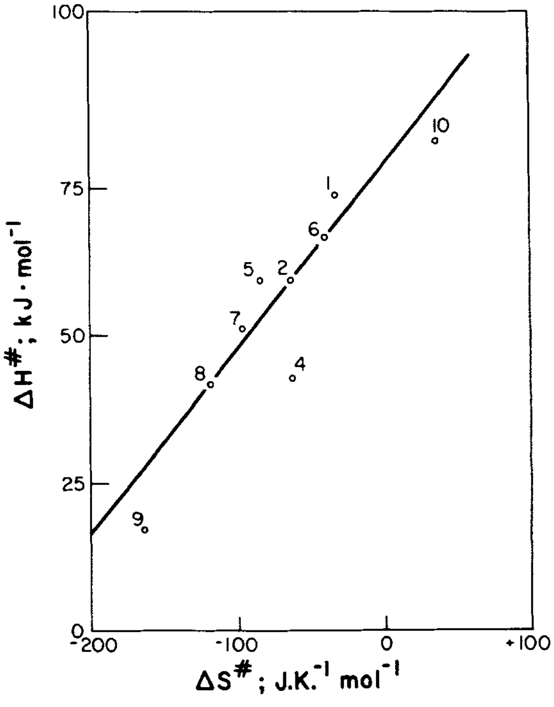
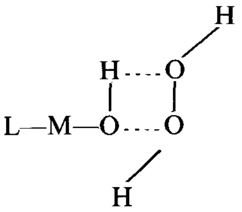


FIGURE 3 The isokinetic plot for the catalytic decomposition of H_2O_2 in the presence of different metal chelates. The numbers shown represent the reactions listed in Table III.

The specific rate constants k_1 and k_2 are basically composite parameters of $k_f k/k_r$ and $k_f' k'/k_r'$ respectively, where k(k') is the specific rate for the intramolecular electron transfer step and $k_f(k_f')$ and $k_r(k_r')$ are the rate constants for the formation and dissociation of the ternary complexes. The present data alone cannot discriminate between both processes as to which is the rate-determining step. However, comparison of the catalytic activity of Fe(III)–HEDP, EDTA complexes of Cr(III), Fe(III) and Ce(IV) and the ENTMP complex of Mn(II) (see Table III) shows that the values of k_1 and k_2 are invariably constant irrespective of the nature of the metal ion. If the intramolecular electron transfer is the rate controlling step one would expect a marked change in k values with the redox potential of the various complex species. Also, if the rate is controlled by peroxide molecule substitution for one of the bound carboxylate or phosphonate groups in their respective complexes the values of k_1 and k_2 would be sensitive to the nature of the metal–carboxylate (phosphonate) bond. However, the close resemblence of k values obtained for catalysis by the kinetically subtitution-inert Cr(III) complex, and other species with variable degrees of lability, rules out this possibility. By way of contrast, hydroxo-containing complexes are always catalytically more active than the corresponding aquo species. In Fig. 3, the values of activation enthalpies, $\Delta H^{\ddagger}$ for the series of reactions shown in Table III are plotted *versus* the activation entropies, $\Delta S^{\ddagger}$. Except for iron–EDTA system, the parallel changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ indicates that the disproportionation reaction proceeds *via* a common mechanism and a common rate-determining step.[17] The slope of this relationship is 314K as compared to the theoretical slope 303K predicted from the relationship

$$\Delta H^{\ddagger} = T\,\Delta S^{\ddagger} + \Delta G^{\ddagger} \qquad (7)$$

for compensation reactions dominated by changes in the solvation shell of the transition state. As suggested in an earlier paper,[15] the exchange could occur *via* an intermediate such as is shown below



This intermediate then eliminates water with proton rearrangement.

The deviation of $Fe(EDTA)(OH)^{2-}$ from the $\Delta H^{\ddagger}(\Delta S^{\ddagger})$ relationship supports the conclusions drawn from NMR relaxation time measurements,[18] in that the transient peroxo complexes are formed by substitution of the peroxide ion (or molecule) for one of the bound carboxylates.

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