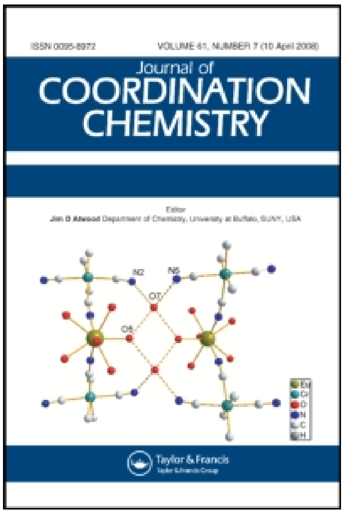

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# THE DECOMPOSITION KINETICS OF HYDROGEN PEROXIDE CATALYSED BY ETHYLENEDIAMINE-TETRAKIS(METHYLENEPHOSPHONATO)IRON(III)

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# THE DECOMPOSITION KINETICS OF HYDROGEN PEROXIDE CATALYSED BY ETHYLENEDIAMINE-TETRAKIS(METHYLENEPHOSPHONATO)IRON(III)

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The catalysed decomposition of hydrogen peroxide in the presence of ethylenediaminetetrakis(methylenephosphonato)iron(III) was studied at various temperatures. The observed rate law is given by

$$-d[H_2O_2]/dt = \frac{k_1K}{([H^+] + K)}[Fe(ENTMP)] .$$

where K is the acid-dissociation constant of the aquo complex. A mechanism involving the aquation of the ternary hydroxo complex as the rate-determining step is suggested. The values of $k_1$ and pK were determined at 35°C to be $0.62 \times 10^{-2}$ and 10.09 repectively. Activation enthalpy and activation entropy for the aquation reaction were determined from Arrhenius plots and found to be $\Delta H^\ddagger = 74.57$ kJ mol$^{-1}$ and $\Delta S^\ddagger = 202$ J K$^{-1}$ mol$^{-1}$. The results are compared with previously reported data on catalysis by the structurally related [Fe(EDTA)] species.

**Keywords:** Peroxide; kinetics, phosphonates, iron, complexes.

## INTRODUCTION

In earlier investigations, the disproportionation reaction of hydrogen peroxide in the presence of EDTA complexes of iron(III)[1], chromium(III)[2] and cerium(IV)[3] was studied. The kinetic expression deduced has a first-order dependency on both the polyaminocarboxylato complex and hydrogen peroxide. Spectrophotometric detection of the colored intermediates was possible in the cases of the iron(III) and cerium(IV) complexes. These intermediates are believed to be formed by either a peroxide-water (or hydroxide) exchange[4,5] or by substituting the peroxide molecule (or ion) for one of the coordinated carboxylate groups.[1B]

The experiments reported here were carried out with the objective of comparing the kinetics of peroxide disproportionation in the presence of the structurally related ethylenediamintetrakis(methylenephosphonato)iron(III) and ethylenediaminetetra-acetatoiron(III) complex ions. Both species retain the octahedral configuration in solution with the amino acid acting as a quinquidentate ligand and the remaining site is occupied by a coordinated water molecule.[6] However, they differ in their overall anionic charges as a result of substituting the negatively charged carboxylate groups by the doubly charged organophosphonate arms. This is expected to influence appreciably their tendencies toward substitution with nucleophiles such as $HOO^-$ or its conjugate acid.

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## EXPERIMENTAL

Ethylenediaminetetra(methylenephosphonic acid), ENTMP, was obtained from Monsanto Chemical Co. and recrystallised as described.[7] Ferric nitrate, sodium nitrate, sodium hydroxide and hydrogen peroxide were B. D. H. Analar grade.

The reaction was carried out in an amber glass vessel thermostatted to the required temperature. The pH was controlled with glycine-sodium hydroxide buffer and monitored simultaneously with each kinetic run using a Radiometer M 62 pH-meter fitted with a combined glass-calomel electrode. The activity coefficient of the hydrogen ion was taken as 0.782.

The rate of decomposition of hydrogen peroxide was followed titrimetrically. At set time intervals, appropriate aliquots of the reaction mixture were quenched with acidified potassium iodide solution and analysed for the residual contents of peroxide. In all experiments, the ratio of ENTMP:Fe(III) was kept at 1.35. The excess ENTMP was found adequate to avoid hydrolysis of the Fe(III) cation at higher pH's. The ionic strength of the medium was adjusted to 0.10 M with sodium nitrate.

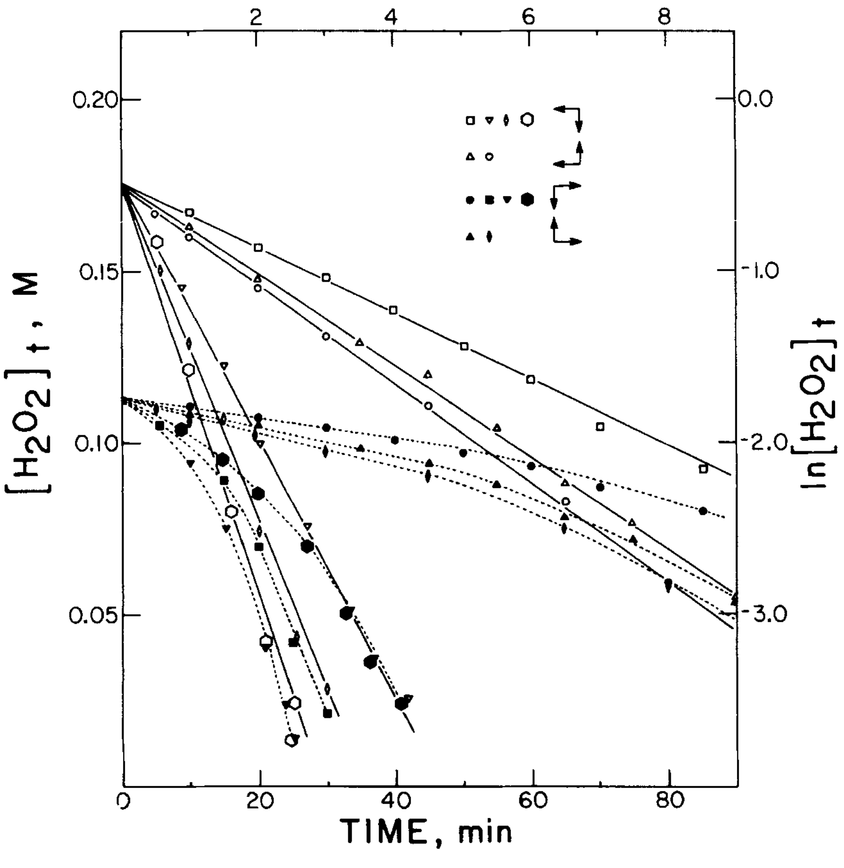


FIGURE 1 Pseudo-first-order plots (solid symbols-dotted lines) and zero-order plots (open symbols-solid lines) for the decomposition of hydrogen peroxide (0.175 M) in the presence of 3.73 M[Fe(ENTMP)]. □, ●: at 35°C and pH 10.55; ▽, ●: at 45°C and pH 10.12; ◇, ■: at 45°C and pH 10.40; O, ▼: at 45°C and pH 10.60; △, ▲: at 50°C and pH 10.30; ○, ♦: at 50°C and pH 10.39.

## RESULTS AND DISCUSSION

When hydrogen peroxide was injected into the ferric-phosphonate solution, the decomposition propagated at a constant rate until almost complete consumption of the peroxide. Figure 1 presents sample plots of the residual peroxide concentration determined at variable conditions of pH, temperature and catalyst concentration as a function of time. Also included, for the sake of comparison, are the first-order plots for the same set of experiments. Obviously, the zero-order plots hold better. Changing the initial peroxide contents did not affect the observed zero-order rate constants nor the linearity of the plots. The absence of dependency of the reaction rate of the initial content of peroxide was also observed in the catalytic study using [Fe(EDTA)] when the ratio of $[H_2O_2]_i/[Fe(EDTA)]_i$ exceeded 80 and at pH 9.1.[18] This ratio decreased markedly with increasing the pH of the reaction medium.

The zero-order rate constants for the catalytic reaction under various experimental conditions are listed in Table I. At constant pH and temperature, the values of $k_{obs}$ were found to increase linearly with increasing [Fe(ENTMP)] concentration which suggests a first-order dependency on the catalyst concentration. The pH profiles for the reaction at different temperatures are shown in Figure 2. Plots of $(k_{obs})^{-1}$ *vs* $[H^+]$ gave straight lines with a non-zero intercept as shown in Figure 3. In general, such a situation arises when one of the reactants is in equilibrium with its conjugate base and the latter is the only reactive species.[8].

TABLE I

Observed rate constants for the decomposition of hydrogen peroxide in the presence of [Fe(ENTMP)]. $[H_2O_2]_T = 0.175$ M; I = 0.10 M ($KNO_3$)

| Temp. °C | pH | [Fe(ENTMP)] mM | $k_{obs}/10^{-5}$ ($M\ s^{-1}$) |
|---|---|---|---|
| 25 | 10.60 | 3.730 | 0.14 |
| | 10.80 | 3.730 | 0.21 |
| 35 | 9.88 | 3.730 | 0.73 |
| | 9.88 | 3.730 | 0.76 |
| | 10.10 | 3.730 | 1.03 |
| | 10.29 | 3.730 | 1.30 |
| | 10.55 | 3.730 | 1.58 |
| | 10.91 | 3.730 | 1.94 |
| 40 | 9.88 | 3.730 | 1.70 |
| | 10.08 | 3.730 | 2.15 |
| | 10.25 | 3.730 | 2.57 |
| | 10.58 | 3.730 | 3.13 |
| | 10.90 | 3.730 | 3.54 |
| 45 | 9.88 | 2.610 | 3.50 |
| | 9.86 | 3.730 | 4.90 |
| | 9.84 | 4.850 | 6.32 |
| | 9.87 | 5.970 | 7.85 |
| | 10.12 | 3.730 | 6.61 |
| | 10.40 | 3.730 | 8.85 |
| | 10.60 | 3.730 | 10.20 |
| | 10.75 | 3.730 | 10.99 |
| 50 | 9.88 | 3.730 | 11.72 |
| | 10.10 | 3.730 | 15.72 |
| | 10.30 | 3.730 | 21.65 |
| | 10.39 | 3.730 | 23.78 |
| | 10.56 | 3.730 | 27.80 |
| | 10.75 | 3.730 | 31.28 |

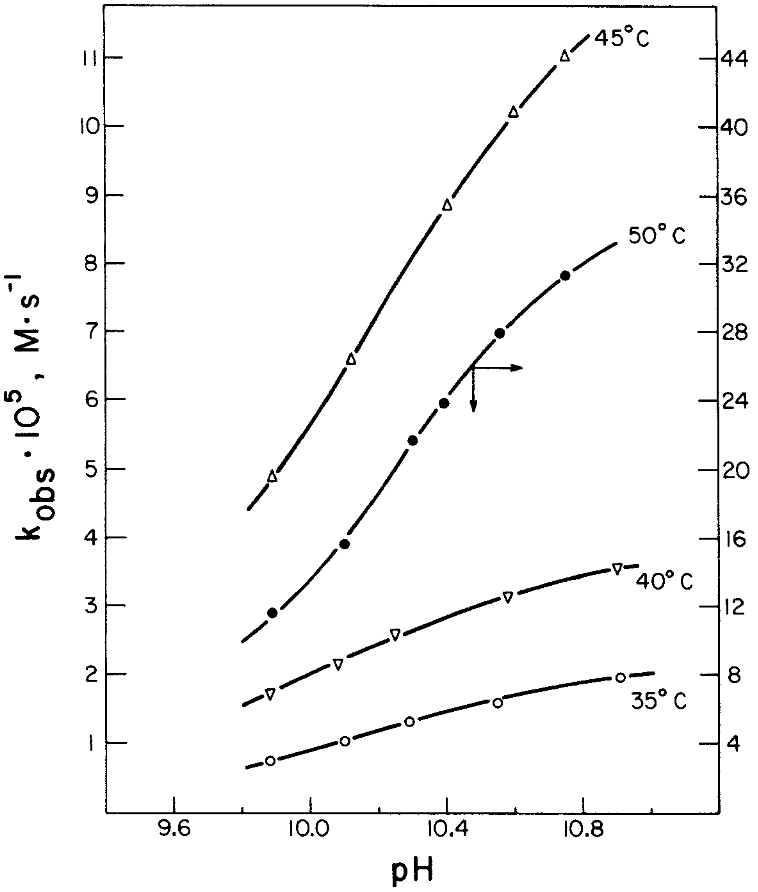


FIGURE 2 pH profiles for the disproportionation reaction at various temperatures; ([Fe(ENTMP)] = 3.73 mM).

Based on these results, the following rate law is formulated,

$$-d[H_2O_2]/dt = k_{obs}[Fe(ENTMP)(OH)]^{-6}$$

$$= \frac{k_1 K}{([H^+] + K)} [Fe(ENTMP)]_T \qquad (1)$$

where K is the ionisation constant for the reaction,

$$[Fe(ENTMP)(H_2O)]^{-5} \xrightleftharpoons{K} [Fe(ENTMP)(OH)]^{-6} + H^+ \qquad (2)$$

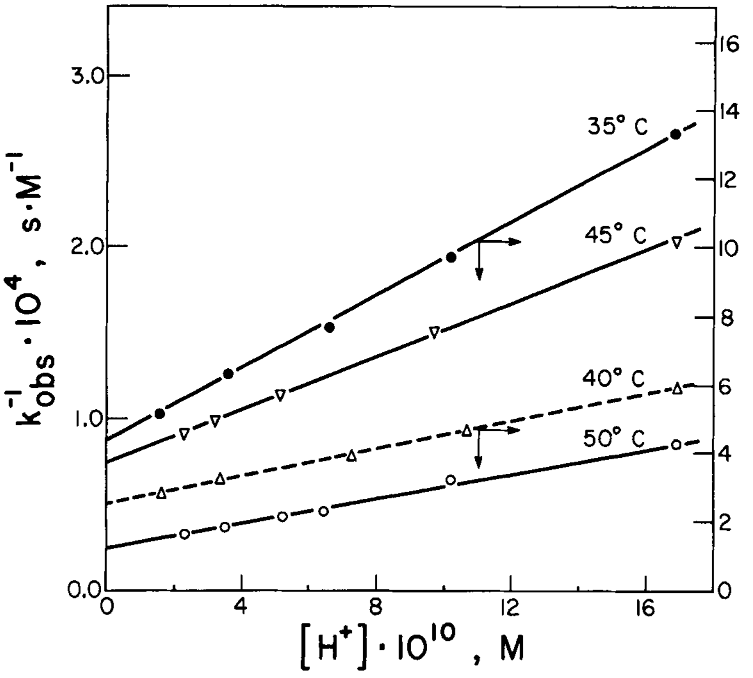


FIGURE 3 The inverse dependency of the rate constants, $k_{obs}$, on the concentration of the hydrogen ion at various temperatures.

and $k_1$ is the rate constant for the disproportionation reaction. The values of $k_1$ and K at various temperatures were calculated from the intercepts and slopes of the linear relationships shown in Figure 3 and are listed in Table II. Also included in Table II are the entropy and enthalpy of activation calculated from Arrhenius plots.

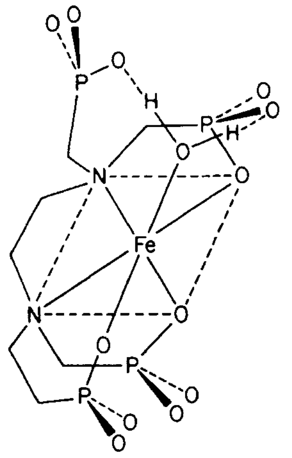
Earlier complexation studies of the reaction of ENTMP with ferric ion revealed the presence of both $[FeHY]^{-4}$ and $[FeH_2Y]^{-3}$ species in addition to the normal complex $[FeY]^{-5}$ (Y represents ENTMP anion). The corresponding pK values were determined from potentiometric measurements as 7.14 and 6.32[9] respectively. Under the present experimental conditions, (pH $\geqslant$ 9.8), the concentration of these protonated complexes is negligible.

TABLE II
Rate constants and activation parameters for the decomposition of hydrogen peroxide catalysed by $[Fe(ENTMP)(OH)]^{-6}$

| Temp. °C | $k_1/10^{-2}$ M. $s^{-1}$ | pK |
|---|---|---|
| 35 | 0.62 | 10.09 |
| 40 | 1.73 | 9.90 |
| 45 | 3.65 | 10.03 |
| 50 | 11.59 | 10.21 |

$\Delta H^{\ddagger}_{35} = 74.5$ kJ mol$^{-1}$, $\Delta S^{\ddagger}_{35} = 202$ J K$^{-1}$ mol$^{-1}$

Recent NMR relaxation studies[6] showed that the ferric-phosphonate complex is similar to $[Fe(EDTA)]^-$ in containing one water molecule in the first coordination sphere. The aquo-phosphonate complex may assume either the octahedral configuration with ENTMP acting as a pentadentate ligand leaving one of the phosphonate groups unbound or may form a heptacoordinate complex. Electronic spectral measurements were undecisive in distinguishing between both geometries, however the NMR data supports a structure with pentacoordinated ENTMP[6] akin to the EDTA complex.[10] Although both the polyaminophosphonate and the polyaminocarboxylate complexes retain the same configuration, their hydrolytic tendencies are widely different. In the case of trivalent meal complexes of EDTA, both the mono- and dihydroxo ternary complexes are formed with pK values of *ca* 7.5 and 9.4 respectively,[11] whereas the first hydrolysis constant for the $[Mn(ENTMP)(H_2O)]^{-5}$ complex is 10.13 as estimated from both kinetic and spectral measurements.[12] This difference is attributed in part to the cumulative negative charges surrounding the metal ion in the phosphonate species compared to its carboxylate analogue. In addition, the tetrahedral configuration of the phosphonate groups allows a simultaneous hydrogen bonding between the coordinated water molecule, the free phosphonate segment and/or the uncoordinated oxygen of one of the suitably disposed coordinated phosphonate groups as illustrated below.



These facts argues also for the unreactivity of the ternary aquo species toward substitution of the coordinated water molecule with $H_2O_2$ as is the case with $[Fe(EDTA)(H_2O)]^-$.[1]

Equation 1 however, predicts a single pathway for the decomposition of hydrogen peroxide which is first-order in $[Fe(Y)(OH)]^{-6}$ concentration. Accordingly, the slow step is probably that involving aquation of the ternary complex by a substituting water molecule for one of the coordinated phosphonate groups, as shown in (*3*).

$$[FeY(OH)]^{-6} + H_2O \xrightarrow{k_1} [FeY(OH)(H_2O)]^{-6} \text{ (slow)} \qquad (3)$$

This step is probably necessary to reduce the repulsion between the binegative phosphonate groups and the coordinated hydroxyl ion. An attempt to assess the role of solvolysis on the reaction rate was unsuccessful because of the limited solubility of the iron complex in solvents other than water. However, a marked enhancement of the catalytic rate was observed when mixed ethanol-water (*ca* 8–16% v/v) solvent was used. Also, the large positive activation entropy observed is consistent with a rate-limiting step associated with solvent reorganisation which is a consequence of the release of the binegative phosphonate group.

For the subsequent reactions, the following scheme is suggested;

$$[FeY(H_2O)(OH)]^{-6} + H_2O_2 \rightleftharpoons [FeY(H_2O)(OOH)]^{-6} + OH^- \qquad (4)$$

or alternatively,

$$[FeY(H_2O)(OH)]^{-6} + H_2O_2 \rightleftharpoons [FeY(H_2O_2)(OH)]^{-6} + H_2O \qquad (5)$$

the latter is more likely due to the strong labilising effect of the coordinated hydroxyl group. This is followed by the electron transfer steps (*6*)–(*10*).

$$[FeY(H_2O_2)(OH)]^{-6} \longrightarrow [FeY]^{-6} + H_2O + HO_2^{\bullet} \qquad (6)$$

$$HO_2^{\bullet} \longrightarrow O_2^{-\bullet} + H^+ \qquad (7)$$

$$[FeY(OH)]^{-6} + O_2^{-\bullet} \longrightarrow [FeY]^{-6} + O_2 + OH^- \qquad (8)$$

$$[FeY]^{-6} + H_2O_2 \longrightarrow [FeY(OH)]^{-6} + OH^{\bullet} \qquad (9)$$

$$[FeY]^{-6} + OH^{\bullet} \longrightarrow [FeY(OH)]^{-6} \qquad (10)$$

This mechanism differs from that proposed for catalysis by $[Fe(EDTA)(OH)]^{-2}$. In the latter case, the reaction proceeds through fast formation of ternary peroxo intermediates followed by the electron-transfer rate-determining step.[1]

To summarise, the enhancement of the reaction rate associated with the polyaminocarboxylate complex over the analogous polyphosphonate species is probably attributed to one or more of the following factors.

1 The lability of the [Fe(EDTA)] complex toward substitution by the hydroperoxyl ion† *versus* the strong H-bonding between coordinated water molecule and phosphonate groups in [Fe(ENTMP)] species probably renders substitution by other nucleophiles rather difficult.

2 The differences in hydrolytic tendencies of both species as a consequence of the differences in the negative charge potentials surrounding the central ion may be important.

3 The bulkiness of the tetrahedral phosphonate groups compared to the planar carboxylates may influence the reaction.

4 The relative polarisabilities of the P–O and C–O bonds[9] could play a role.

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†The rate of formation of $[Fe(EDTA)\text{-}(H_2O_2)]$ follows the kinetic expression Rate = $k[Fe(EDTA)(OH)][H_2O_2]$ with a k value of 250 $M^{-1}\ s^{-1}$ at 25°C.[13]

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