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The Kinetics of Decomposition of Hydrogen Peroxide in the Presence of Ethylenediaminetetraacetatoiron(III) Complex

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The rate of decomposition of hydrogen peroxide in the presence of ethylenediaminetetraacetatoiron(III) complex is investigated under variable conditions of hydrogen peroxide and iron-EDTA concentrations, pH, ionic strength and temperature. The following rate law holds:

$$Rate = k_4K_3[FeY(OH)^{2-}][H_2O_2] + + k_3K_1K_2\frac{[FeY(OH)^{2-}][OOH^-]}{[H^+]}$$

The rate constants and the related thermodynamic parameters are calculated. Substitution controlled mechanisms are suggested to account for the formation of the violet peroxy intermediate.

Introduction

Some of the enzymes which act specifically on hydrogen peroxide or its derivatives, namely the catalase and peroxidase contain ferriprotoporphyrin (haematin) prosthetic groups. These substances act as catalysts for the following reactions;

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (1)$$

$$ROOH + AH_2 \rightarrow H_2O + ROH + A \qquad (2)$$

It is not clear yet whether the role of catalase in the organism is to decompose H_2O_2 (reaction 1) or to catalyse a peroxidation reaction (reaction 2). Several substrates can be oxidised *in vitro* by catalase and H_2O_2 [1–4].

Because of the great difficulties in choosing either mechanism, several models were reviewed by Sigel [5] to describe the catalytic chemistry of catalase and peroxidase. Preliminary investigations of the iron–EDTA–H_2O_2 system [6] turned out to be surprisingly complex, and showed both catalase and peroxidase activities, in that it decomposes H_2O_2 and attacks organic substrates and the relative importance of the two paths is pH dependent.

Due to the similarities between catalase and the iron-EDTA complex and because of the interest in the subject matter, a thorough understanding of the relatively simple system, iron–EDTA–H_2O_2, might give a clue as to the mechanism of H_2O_2 decomposition by catalase and a corresponding deep insight into its chemistry.

Experimental

Ethylenediaminetetraacetatoiron(III) complex, [FeY], was prepared by dissolving 0.1 mol of ferric ammonium sulphate in concentrated solution of Na_2H_2EDTA (0.1 mol). Ammonium hydroxide solution was then added drop-wise with constant stirring to bring the pH of the mixture between 8 and 9 and the resulting solution was heated for 10 minutes at 80–90 °C. The deep red solution obtained was then filtered to get rid of the unreacted iron and the mother liquor was treated with a sufficient amount of dimethylformamide so as to maintain a final molar ratio of 1:1 of DMF to water. The red solid was readily separated after vigorous stirring and scratching on the container walls. The complex was filtered, washed well with ethanol, dried at 110 °C over night and analysed for its iron contents.

Freshly prepared solutions of this reagent were obtained by dissolving an appropriate weight in doubly distilled water.

Procedure

In an amber glass flask, precalculated volumes of Na[FeY] complex and Na_2H_2EDTA were mixed together in such a ratio as to maintain the final molarity of EDTA contents equivalent to the normality of hydrogen peroxide. Sodium nitrate solution was then added in a sufficient amount to maintain

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the ionic strength of the medium constant at 0.1, unless otherwise specified. The pH of the resulting mixture was adjusted using ammonium hydroxide–ammonium chloride buffer and then was allowed to thermostate at the required temperature. At this stage, a precalculated volume of hydrogen peroxide was added to make up the final volume of the reacting mixture, 250 ml.

Addition of hydrogen peroxide was always accompanied by a change in colour from the typical orange colour of the iron-EDTA complex to an intense violet colour.

The kinetics of decomposition of H_2O_2 were followed iodometrically [7] by analysing 10 ml aliquots at suitable time intervals. The measurements were invariably followed up to 90% completion as was indicated by the amount of the residual hydrogen peroxide. A blank experiment was made for each run in order to account for the excess iodine liberated from the oxidation of iodide ions by the $[FeY^-]$ anion.

The optical density measurements were recorded using a thermostated Unicam SP 1800 spectrophotometer.

All reagents were analytical grade materials.

Results and Discussion

As early as 1956, Cheng and Lott [8] showed that the purple coloured species formed when excess hydrogen peroxide is added to an alkaline solution of iron(III)-EDTA is attributed to the formation of either a peroxy complex of iron(III)-EDTA or a chelated iron in a higher oxidation state. Later, Ringbom *et al.* [9] and others [10, 11] interpreted their results on the basis that the species formed is $[FeY(OOH)^{2-}]$ and the kinetics of its formation over the pH range 9–11 were studied using a stopped flow technique [12].

Preliminary spectrophotometric studies showed that the purple complex formed has a λ_{max} 50 nm and molar extinction coefficient $\epsilon = 528$ in excellent agreement with that previously reported [6] (*cf.* Fig. 1). The value of ϵ was calculated on the assumption that, in the presence of large excess of hydrogen peroxide, the concentration of the purple species is equivalent to the concentration of $[FeY^-]$ species.

Magnetic susceptibility measurements of the $[FeY^-]$ complex at different pH values showed that in weakly acidic solutions, the magnetic moment obtained is consistent with the presence of a high spin ferric iron species. The decrease in magnetic moment with increasing pH of the medium was attributed to the formation of the low spin dimer complex [13]. In the presence of H_2O_2 and at pH values >9.5, where the peroxy complex formation is almost complete, the magnetic moment measured [6] suggested the presence of only high spin ferric complex and excluded any possibility of dimer formation. In addition, it rules out the presence of iron in an oxidation state higher than 3.

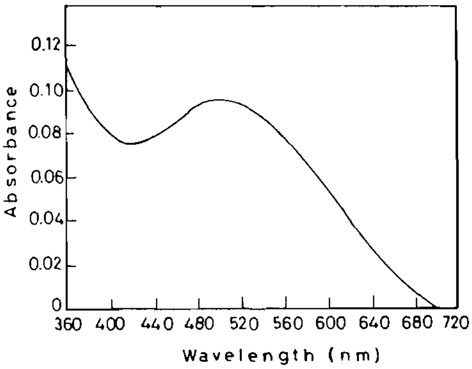

Fig. 1. Absorption spectra of $[FeY(OOH)^{2-}]$ complex at 25 °C.

All the observations outlined above are consistent with a formulation of the complex as $[Fe^{III}Y(O_2)^{3-}]$ or some stoichiometric equivalent such as $[Fe^{III}Y(OOH)(OH)^{3-}]$. This species is reported to have both catalase [6] and peroxidase [6, 10] activities, in that it decomposes H_2O_2 to O_2 and water and also attacks organic substrates.

Preliminary measurements of the rate of decomposition of H_2O_2 in the presence of $[FeY^-]$ complex and in the absence of uncomplexed EDTA are always accompanied by the formation of $Fe(OH)_3$ precipitate. This phenomenon is attributed to the catalytic oxidation of the complexed ligand by H_2O_2 molecules liberating ammonia and carbon dioxide. At this stage the rate of H_2O_2 decomposition increases sharply as a result of the heterogeneous catalysis played by the colloidal particles.

Walling *et al.* [6] were able to evaluate the relative magnitudes of both catalytic and peroxidatic reactions of H_2O_2 with EDTA (free and/or complexed) in the presence and absence of other competing organic substrates such as ethylene glycol. Over the pH range studied (*ca.* 7.75–10.5), the ratio of peroxydatic/catalytic [6] reactions was found to be a decreasing function of the pH of the reaction medium and the peroxidatic effect is completely inhibited at pH $\geqslant$ 10.5, *i.e.* the reaction proceeds only via the route of catalytic decomposition of hydrogen peroxide. It has been also shown [6] that in the presence of ethylene glycol, the latter is attacked in preference to EDTA, effectively protecting the complex from decomposition even when little excess of EDTA is present. Increasing the ratio [EDTA]/[Fe(III)] retards the peroxidatic effects. Oxidations of organic substrates other than ethylene glycol gave widely varying rate constants. Thus in the pre-

TABLE I. Observed Rate Constants for the Decomposition of Hydrogen Peroxide in the Presence of 0.2 mmol of Ethylenediaminetetraacetatoiron(III) Complex Ion at 25 °C.

10^{-9} $[H^+]^{-1}$ (M^{-1})	10^3 $[H_2O_2]$ (N)	10^5 k_{obs} (s^{-1})
4.85	8	20.66
	7	21.11
	6	21.11
	5	19.40
2.43	8	12.85
	7	12.47
	6	13.30
	5	12.10
0.77	8	10.94
	7	11.04
	6	10.46
	5	10.65
0.23	8	3.42
	7	3.74
	6	3.63
	5	3.45

sence of glycine or ethylenediamine, the peroxidatic reaction proceeds very slowly at rates less than 10^{-3} mmol/min (compared to 0.03 mmol/min in the case of ethylene glycol) taking almost 24 hr to give complete reaction. At the same time, these substances acted as efficient inhibitors for the decomposition of EDTA complex.

Because of the structural similarities between EDTA, ethylenediamine and glycine, it can be reasonably assumed that the rate of peroxidatic reaction of EDTA is of the same order of magnitude as that reported for ethylenediamine and glycine and the contribution of this reaction to the overall process is of minor importance, particularly in the pH range considered in the present investigation (*ca.* 8.5–10).

Addition of excess EDTA is also used to minimize the concentration of the free iron content below the solubility of ferric hydroxide, *i.e.*

$$[\mathrm{Fe}] = \frac{[\mathrm{FeY^-}]}{K^{\mathrm{Fe}}_{\mathrm{FeY}}\cdot[\mathrm{Y^{4-}}]} < \frac{K_{so}}{[\mathrm{OH}]^3} \qquad (3)$$

where $K^{\mathrm{Fe}}_{\mathrm{FeY}}$ and K_{so} are the stability constants of iron-EDTA complex and the solubility product of ferric hydroxide respectively. Substituting for these values [14] in equation (3), it is evident that, at pH 9.8, the ratio $[H_2Y^{2-}]/[FeY^-]$ must be >6 in order to avoid completely heterogeneous catalytic decomposition of H_2O_2.

The results obtained at 25 °C, and listed in Table I, indicate that the rate of decomposition of hydrogen

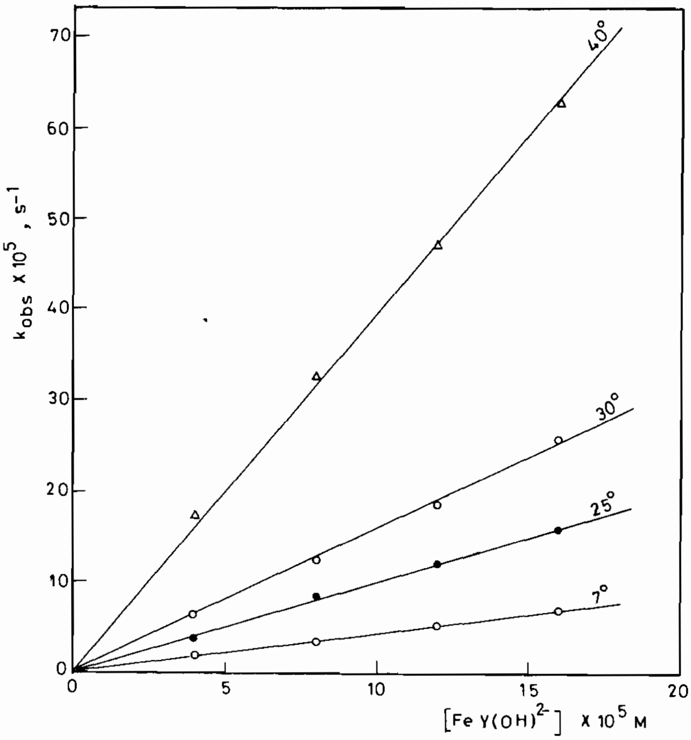

Fig. 2. Variation of the first order rate constant, k_{obs}, with $[FeY^-]$ at various temperatures. pH = 9.8; $[H_2O_2] = 4 \times 10^{-3}$ N; and I = 0.1.

TABLE II. Observed Rate Constants for the Decomposition of Hydrogen Peroxide in the Presence of 4 mmol of H_2O_2, I = 0.10 *M* ($NaNO_3$).

Temp. (°C)	10^{-9} $[H^+]^{-1}$ (M^{-1})	10^5 $[FeY^-]$ (*M*)	10^5 k_{obs} (s^{-1})
7	4.85	16	7.00
		12	5.40
		8	3.57
		4	2.03
25	4.85	16	16.00
		12	12.00
		8	8.72
		4	3.62
	2.43	16	9.90
		12	7.68
		8	5.98
		4	3.57
	0.23	16	2.90
		12	2.28
		8	1.75
		4	1.00
30	4.85	16	25.90
		12	18.50
		8	12.45
		4	6.30
	2.43	16	16.12
		12	12.12
		8	9.18
		4	3.63
	0.77	16	10.97
		12	8.27
		8	5.37
		4	2.45
	0.23	16	7.23
		12	5.25
		8	3.58
		4	2.27
40	4.85	16	62.87
		12	47.15
		8	33.03
		4	17.40
	0.77	16	33.40
		12	25.55
		8	17.63
		4	11.50

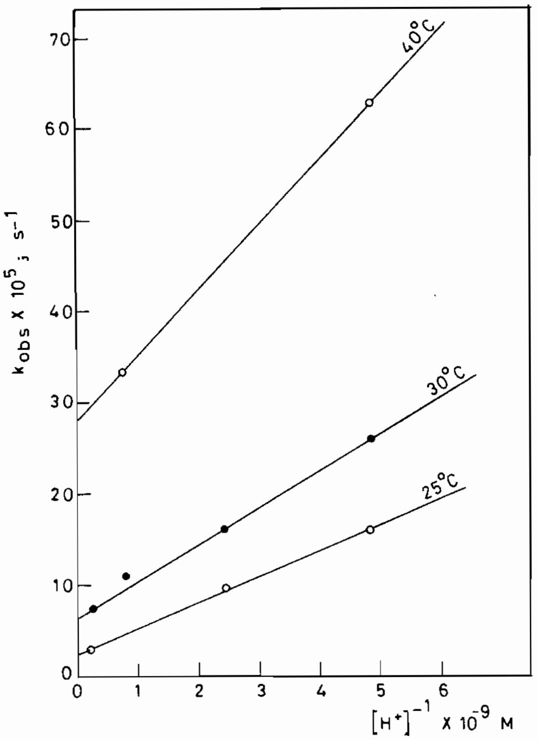

Fig. 3. Variation of the rate constant, k_{obs}, with $[H^+]^{-1}$ at the different temperatures studied. $[H_2O_2]$ = 4 × 10^{-3} *N*; $[FeY^-]$ = 16 × 10^{-5} *M* and I = 0.1.

peroxide is first order in $[H_2O_2]$. Plots of the logarithmic value of the residual concentration of H_2O_2 *vs.* time t, give a constant value for the observed rate constant, k_{obs}, irrespective of the initial concentration of H_2O_2 and at prefixed conditions of pH and $[FeY^-]$. It follows,

$$\text{Rate} = -d[H_2O_2]/dt = k_{obs}[H_2O_2] \quad (4)$$

Similarly, at prefixed experimental conditions of temperature, $[H_2O_2]$ and pH, the values of k_{obs} are found to increase linearly with increasing concentration of $[FeY^-]$ as shown in Fig. 2. This suggests that, at constant pH, the following rate equation holds:

$$\text{Rate} = -d[H_2O_2]/dt = k_{obs}[H_2O_2]$$

$$= k[FeY^-][H_2O_2] \quad (5)$$

Apparently, decreasing the pH from 9.8 to 8.5 suppresses appreciably the catalytic activity of $[FeY^-]$ complex. For example, at 25 °C and $[FeY^-]$ = 0.16 m*M*, the value of k_{obs} decreases from 1.6 to 0.29 × 10^{-4} s^{-1} in going from pH 9.8 to pH 8.5. Similar results are obtained at all other initial concentrations of the iron complex and at different temperatures studied (*cf.* Table II).

At fixed concentration of the iron-EDTA complex, the values of k_{obs} are found to increase linearly with decreasing $[H^+]$ (see Fig. 3), and the following relationship holds,

$$k_{obs} = k_1' + k_2'[H^+]^{-1} \quad (6)$$

Substituting equations (5) and (6) into (4), it can be easily shown that,

$$\text{Rate} = -d[H_2O_2]/dt = k_{obs}[H_2O_2]$$

TABLE III. Summary of the Values of the Acid-dependent and Independent Rate Constants at the Various Temperatures Studied.

Temp. (K)	k_1 (M^{-1} s^{-1})	10^{10} k_2 (s^{-1})	10^2 k_3 (s^{-1})
298	0.21	1.75	2.37
303	0.46	2.33	3.13
313	2.03	4.18	5.65

$$\text{Rate} = k_1[FeY^-][H_2O_2] + k_2[FeY^-][H_2O_2][H^+]^{-1} \quad (7)$$

where

$$k_1 = k'_1/[FeY^-] \quad (8)$$

and

$$k_2 = k'_2/[FeY^-] \quad (9)$$

Values of the calculated acid-dependent (k_2) and acid-independent (k_1) rate constants at the various temperatures are summarised in Table III. Plots of log k_1 (or log k_2) *vs.* 1/T give the expected Arrhenius plots as shown in Fig. 4A (or 4B).

Equation (7) states that the empirical forms of the activated complexes for the parallel paths are [$FeY\cdot OOH^{2-}$] and $FeY\cdot H_2O_2^-$]. Schwarzenbach and Heller [15] have investigated the hydroxyl complexes of iron-EDTA species and have shown that in alkaline media two complexes with one and with two hydroxyl groups coexist. The relationship between these forms is given by the equation,

$$[FeY(OH)^{2-}]/[FeY(OH)_2^{3-}] = 10^{9.5}[H^+] \quad (10)$$

According to this expression the complex with one hydroxyl group predominates at pH values below 9.5 while the complex with two hydroxyl groups predominates at pH values above 9.5. One might expect that the coloured hydrogen peroxide intermediate is formed by the substitution of a perhydroxyl group for a hydroxyl group according to sequence (11) and/or (12),

$$[FeY(OH)^{2-}] + OOH^- \rightleftharpoons [FeY(OOH)^{2-}] + OH^- \quad (11)$$

$$[FeY(OH)_2^{3-}] + OOH^- \rightleftharpoons [FeY(OH)(OOH)^{3-}] + OH^- \quad (12)$$

However, measurement of the stability constants reported for this system [9], showed that the apparent formation constant, K′,

$$K' = \frac{[FeY\cdot H_2O_2^-]}{[FeY^-][H_2O_2]} \quad (13)$$

is pH-dependent whereas that calculated by substituting for [H_2O_2] by [OOH^-] in equation (13) using the acid dissociation constant for hydrogen peroxide gives a new value K which is independent of pH, where

$$K = \frac{[FeY\cdot H_2O_2^-]}{[FeY^-][OOH^-]} \quad (14)$$

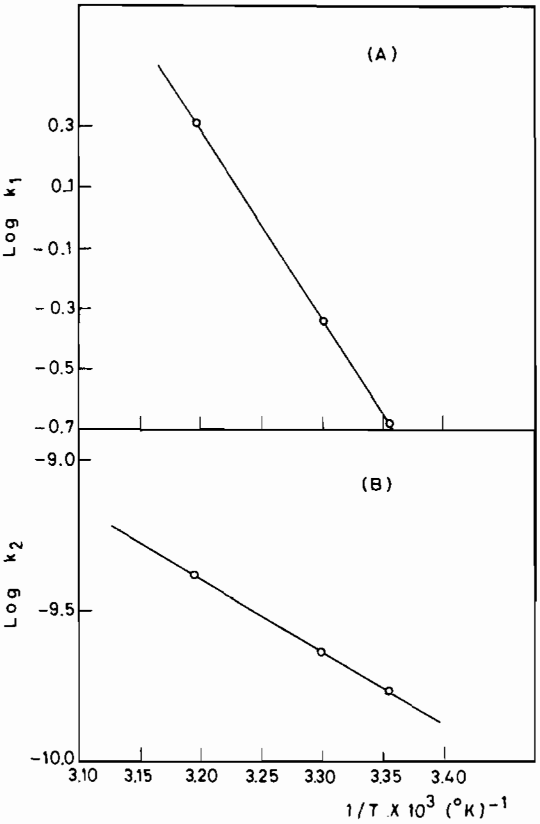

Fig. 4. Arrhenius plots for the acid-independent (A) and dependent (B) rate constants, I = 0.1.

In conclusion, if sequence (11) or (12) held, the value of K′ should behave as a pH-independent constant, which is not the case. It seems therefore more likely that a hydroxyl group is replaced by a peroxide group [9], O_2^{2-}, according to equations (15) and/or (16),

$$[FeY(OH)^{2-}] + OOH^- \rightleftharpoons [FeY(O_2)^{3-}] + H_2O \quad (15)$$

or

$$[FeY(OH)_2^{3-}] + OOH^- \rightleftharpoons [FeY(OH)(O_2)^{4-}] + H_2O \quad (16)$$

The peroxy species then dissociates slowly to give [FeY^{2-}] and $O_2^{\cdot -}$. The peroxyl ion radical reacts rapidly with H_2O_2 to liberate oxygen gas, hydroxyl ion and hydroxyl radical. One possible route is the propagation of the H_2O_2 decomposition through a sequence very similar to that suggested by Barb *et al.* [16] for the Fe^{3+}ion-catalysed decomposition of H_2O_2. It has been also suggested by the same authors [16] and recently by Walling *et al.* [17] that suitable substrates can act as effective traps for the hydroxyl radical. This is consistent with the results obtained in this study. To summarise, the following scheme is proposed to account for the different steps involved in the acid-dependent route;

Scheme 1:

$$H_2O_2 \xrightleftharpoons{K_1} OOH^- + H^+ \qquad (17)$$

$$[FeY(OH)^{2-}] + OOH^- \xrightleftharpoons{K_2} [FeY(O_2)^{3-}] + H_2O \qquad (18)$$

$$[FeY(O_2)^{3-}] \xrightarrow{k_3} [FeY^{2-}] + O_2^{\cdot -} \qquad (19)$$

$$O_2^{\cdot -} + H_2O_2 \xrightarrow{\text{fast}} O_2 + OH^- + OH^{\cdot} \qquad (20)$$

$$OH^{\cdot} + H_2O_2 \xrightarrow{\text{fast}} H_2O + OOH^{\cdot} \qquad (21)$$

$$OOH^{\cdot} + [FeY^{2-}] \xrightarrow{\text{fast}} HOO^- + [FeY^-] \qquad (22)$$

$$[FeY^-] + OH^- \rightleftharpoons [FeY(OH)^{2-}] \qquad (23)$$

and the rate determining step (RDS) is given by equation (19). Accordingly,

$$(-d[H_2O_2]/dt)_{\text{acid-dep.}}$$

$$= k_3[FeY(O_2)^{3-}]$$

$$= k_3K_2[FeY(OH)^{2-}][OOH^-]$$

$$= k_3K_1K_2\frac{[FeY(OH)^{2-}][H_2O_2]}{[H^+]} \qquad (24)$$

Analogously, Scheme 2 is suggested to account for the acid-independent route,

Scheme 2:

$$[FeY(OH)^{2-}] + H_2O_2 \xrightleftharpoons{K_3} [FeY(OH)(H_2O_2)^{2-}] \qquad (25)$$

$$[FeY(OH)(H_2O_2)^{2-}] \xrightarrow{k_4} [FeY^{2-}] + H_2O + OOH^{\cdot} \qquad (26)$$

$$OOH^{\cdot} + [FeY(OH)^{2-}] \xrightarrow{\text{fast}} [FeY^{2-}] + H_2O + O_2 \qquad (27)$$

$$2[FeY^{2-}] + H_2O_2 \xrightarrow{\text{fast}} 2[FeY(OH)^-] \qquad (28)$$

and the rate of H_2O_2 decomposition according to this route is given by:

$$(-d[H_2O_2]/dt)_{\text{acid-indep.}} = k_4[FeY(OH)(H_2O_2)^{2-}]$$

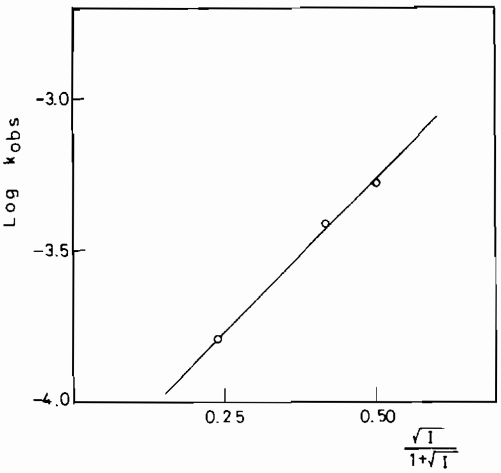

Fig. 5. Effect of ionic strength on the rate of decomposition of hydrogen peroxide in the presence of $[FeY^-]$ complex.

$$= k_4K_3[FeY(OH)^{2-}][H_2O_2] \qquad (29)$$

The overall rate of decomposition is obtained by combining equations (24) and (29) to give:

$$\text{Rate} = -d[H_2O_2]/dt$$

$$= k_4K_3[FeY(OH)^{2-}][H_2O_2] + k_3K_1K_2\frac{[FeY(OH)^{2-}][OOH^-]}{[H^+]} \qquad (30)$$

Comparison of eqns. (7) and (3) shows that,

$$k_2 = k_3K_1K_2 \qquad (31)$$

$$k_1 = k_4K_3 \qquad (32)$$

Given that [9], $K_1 = 10^{-11.75}$ and $K_2 = 10^{3.62}$, values of k_3 are found to be 2.37, 3.13 and 5.65 $\times 10^{-2}$ s^{-1} at 25, 30 and 40 ℃ respectively.

The effect of ionic strength, I, on the rate of reaction is studied at three different values, namely those at $I = 0.1$, 0.5 and 1.0. In all measurements, the concentration of $[FeY(OH)^{2-}]$ complex is fixed at 0.16 m*M*, the pH of the medium is adjusted to 9.8 and the temperature is kept at 25 ℃. Figure 5 illustrates the linear dependence of log k_{obs} on the ionic strength of the medium. It is obvious from these data that increasing the ionic strength catalyses the rate of decomposition of hydrogen peroxide. This effect is attributed to the ion-pair formation between $[FeY(OH)^{2-}]$ and sodium ions through the free acetate group. A measure of the slope of the linear relationship log k_{obs} *vs.* $\sqrt{I}/(1 + \sqrt{I})$ gives a value of 2.04 which is in good support of this view (the theoretical value for a 1:2 electrolyte is 2.02). Com-

TABLE IV. Activation Parameters for the Acid-dependent and Acid-independent Mechanisms for the Decomposition of Hydrogen Peroxide at 25 °C.

	$\Delta E^{\#}$ (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (e.u.)
RDS in the acid-dependent route	45.81	43.32	−124
Overall parameters for the acid-independent route	128.86	126.32	−134

pensation of one of the two negative charges on the iron complex is expected, on the other hand, to favour its interaction with OOH^- ion.

Values of the energies of activation, $\Delta E^{\#}$, and entropies of activation, $\Delta S^{\#}$, for the overall acid-independent pathway and that calculated for the RDS of the acid-dependent mechanism are shown in Table IV. It is generally known that [18], positive entropy values are normally associated with reactions accompanied by topological changes whereas negative values can be ascribed to rate determining substitution processes with retention of configuration. Evidence for these conclusions is gained from the studies reported on the substitution reactions of cobalt(III) complex species [19–23]. The large negative entropy for the acid-dependent mechanism is attributed to the severe restriction of solvent molecules around a transition state of higher charge (a value of −42 e.u. is expected per one unit of (Z_AZ_B), where Z_A and Z_B are the charges of reactants A and B respectively) in addition to a substitution of water molecule for the $O_2^{\bullet -}$ ion with retention of configuration (sequence 19).

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