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Kinetics and Mechanism of Decomposition of Hydrogen Peroxide Catalyzed by Co^{3+} and $[Co(NH_3)_4]^{3+}$ Adsorbed on Alumina

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The decomposition of H_2O_2 at 30° catalyzed by Co^{3+} ions, adsorbed on alumina, exhibits first order kinetics with respect to $[H_2O_2]$. As the amount of surface adsorbed ions increases, the value of first order rate constant initially increases linearly, reaches a maximum and decreases thereafter. It is found that pH greatly influences the decomposition of H_2O_2 consistent with the kinetic data.

Key words: Kinetics, Mechanism, Decomposition, Hydroigen peroxide.

INTRODUCTION

Recently, it has been reported that the decomposition of H_2O_2 in the presence of metal ions as homogeneous catalysts is slow but it is fast when these ions are used along with small amounts of alumina or beryllium oxide[1–4]. Such fast decomposition of H_2O_2 has practical applications in fuel cells, rocket propellants, bleaching[5], etc. where H_2O_2 is used as a source of oxygen. In view of this, H_2O_2 decomposition through heterogeneous catalysis is worth investigating but such studies are quite limited and have been made with a view to exploring the possibility of lowering the activation energy[6–10]. This prompted the author to undertake the title investigation.

EXPERIMENTAL

Chromatographic grade alumina (CDH) was washed repeatedly with boiling distilled water, dried, sieved (100–20000 mesh) and finally activated at 150°C for 24 h. The required amounts of activated alumina thus prepared were kept in contact with different solutions of cobalt chloride (AR, BDH) for about 4 h with constant stirring, filtered, washed repeatedly with distilled water and dried in air. The amount of unadsorbed Co^{3+} in solution was determined using an atomic absorption spectrometer (Perkin-Elmer). Similarly $[Co(NH_3)_4]^{3+}$ adsorbed samples of alumina were prepared employing cobalt chloride solution containing excess of ammonia. Hydrogen peroxide (30% w/v, E. Merck) was diluted by adding redistilled water free from carbon dioxide gas. Disodium hydrogen phosphate and potassium dihydrogen phosphate (both AR) were used for the preparation of the buffer solution. The kinetics of decomposition was followed by adding a definite amount of Co^{3+} or $[Co(NH_3)_4]^{3+}$ adsorbed alumina sample into a solution of hydrogen peroxide (10.0 mL) and measuring the volume of evolved oxygen by a gasometric technique.

RESULTS AND DISCUSSION

The plots of log $(V_\infty - V_t)$ *vs.* time (min) (Fig. 1), where V_t and V_∞ are volume at time t and at infinite time respectively, show that the decomposition of H_2O_2 in any particular run follows first order kinetics with both the catalysts. However, the slope of the first order linear plots decreases considerably with increase in volume of $[H_2O_2]$ (Table-1). The decrease in k may possibly be due to decrease in pH of the solution from 6.7 to 5.1. This is also quite evident from the fact that an increase in pH of solution from 7.0 to 8.05 increases the k value by 18.5 fold (at pH 6.0, 1.4, 7.20, 3.5 and 8.5). $K \times 10^2$ (min^{-1}) values are 0.6, 1.4, 3.5 and 11.1 respectively under the conditions: amounts of alumina = 1 g; absorbed $Co(NH_3)_4^{3-} = 0.16 \times 10^{-2}$ g/g alumina; $[H_2O_2] = 1.2$ vol. Table-2, which summarises the results of the variation of $[H_2O_2]$, thereby provides justification for the above explanation.

TABLE-1

EFFECT OF VARYING $[H_2O_2]$ ON FIRST ORDER RATE CONSTANT

$[H_2O_2]$	$k \times 10$ (min^{-1}) on alumina	
	Co^{3+} adsorbed	$Co(NH_3)_4^{3-}$ adsorbed
0.56	–	12.9
1.12	10.2	1.5
2.24	8.7	9.4
4.48	7.5	8.3
5.60	5.2	6.7
8.40	4.4	5.1
11.20	3.3	4.8

TABLE-2

EFFECT OF VARYING $[H_2O2]$ ON FIRST ORDER RATE CONSTANT IN PHOSPHATE BUFFER OF pH 8.05 (AMOUNT OF ALUMINA = 0.5 g TEMP. = 30°C)

$[H_2O_2]$	$k \times 10$ (min^{-1}) on alumina	
	Co^{3+} adsorbed	$Co(NH_3)_4^{3-}$ adsorbed
1.12	20.3	12.8
2.24	18.3	13.2
4.48	15.9	11.5
8.96	16.8	12.4

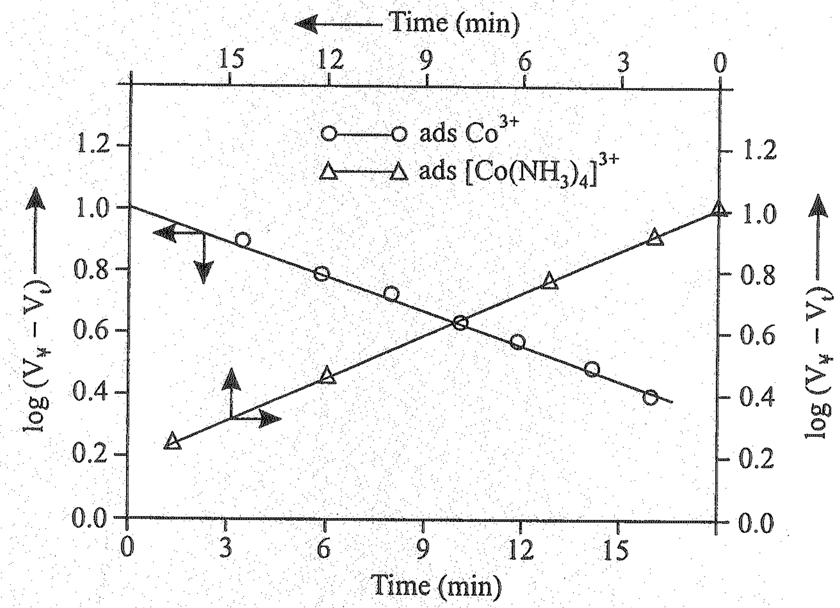

Fig. 1. First order plot for the decomposition of hydrogen peroxide at 30°C ($[H_2O_2]$ = 1.12 vol., amount of adsorbed ions = 0.16×10^{-2} g/g alumina)

The result in Fig. 2A, where k values are plotted against the amount of adsorbed metal ions on alumina, show that as the amount of adsorbed Co^{3+} ions is varied from 0.16×10^{-2} to 3.42×10^{-2} g/g alumina, the value of k initially increases linearly, attains a maximum and decreases thereafter. The sample of $Co(NH_3)_4^{3+}$ adsorbed alumina exhibits an identical behaviour. Further, the values of k are calculated for unit amounts of catalyst.

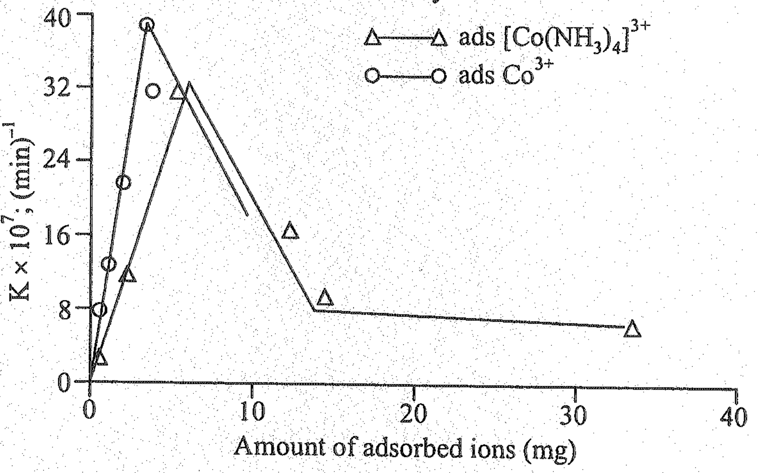

Fig. 2. Effect of amount of adsorbed ions on first order rate constant at 30°C (A) and (B) $[H_2O_2]$ – 2.24 vol. amount of alumina

At this stage it is worth while to mention some visual observations noted during the experiment. A greyish brown colour on the surface of adsorbed alumina sample was invariably seen in the reaction vessel for reaction with $[H_2O_2] > 2.24$ volumes and the concentration of surface of adsorbed ion $> 0.51 \times 10^{-2}$ g/g alumina. The pink coloured product formed on the surface of catalyst persisted as long as any residual amount of H_2O_2 remained undecomposed. However, no visible colour change was found and the initial blue surface of the adsorbed alumina remained as such during the experiment when either the amount of adsorbed ions was $\geq 0.51 \times 10^{2}$ g/g alumina or $[H_2O^2] > 2.24$ volume$^{s.}$

The formation of greyish pinkish colour on the surface of Co^{3+} absorbed alumina in the presence of H_2O_2 ,it was considered that the enhanced decomposition of H_2O_2 was mainly due to the formation of the said pinkish brown surface adsorbed complex.

On the basis of our experimental results, we believe that surface adosorbed, ion-catalysed decomposition of $[H_2O_2]$ follows two reaction paths. When $[H_2O_2] \geq 2.24$ volumes and the amount of absorbed ion $> 0.51 \times 10^{-2}$ g/galumina, the decomposition does not seem to proceed in the above manner. Further, the rate of decomposition is considerably decreased as brown surface is formed. This is also evident from Fig. 2 which exhibits a clear break in the curve, indicating change of mechanism. Therefore, the amount of $Co(NH_3)_4^{3+}$ ions adsorbed on alumina should be 0.51×10^{-2} g/g alumina or less in order to bring out the decomposition of H_2O_2 more effectively. Under this condition the catalysts may proceed through steps (1)–(4) shown in **Scheme-1**.

$$\text{ads-}Co^{3+} + H_2O \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [\text{ads-}Co^{3+}HO^{2-}] + H^+ \qquad (1)$$

$$\text{ads-}Co^{3+} + H_2O \underset{K_{-2}}{\overset{\text{Slow}}{\rightleftharpoons}} [\text{ads-}Co^{3+}HO^{2-}] + H^+ \qquad (2)$$

$$\text{ads-}Co^{3+} + H_2O_2 \underset{K_{-3}}{\overset{\text{Fast}}{\rightleftharpoons}} [\text{ads-}Co^{3+}OH] + OH^- \qquad (3)$$

$$HO_2 + OH \underset{K_{-4}}{\overset{\text{Fast}}{\rightleftharpoons}} H_2O + O_2 \qquad (4)$$

Scheme-1

The mechanism in **Scheme-1** has been proposed utilizing the oxidation and reduction of hydrogen peroxide by steps (5) and (6) respectively as reported elsewhere[5, 6]. The formation of free radicals OH and HO_2 as intermediate in the homogeneously metal ions catalysed decomposition of H_2O_2 has also been mentioned by several workers.

$$H_2O_2 \xrightarrow{-e} H^+ + HO_2 \xrightarrow{-3e^{\bullet}} 2H^+ + O_2 \qquad (5)$$

$$H_2O_2 \xrightarrow{-e} OH^+ + OH \xrightarrow{-3e^{\bullet}} 2OH \qquad (6)$$

The formation of free radicals. OH^- and HO_2 as the intermediates homogeneously metal ions catalysed decomposition of H_2O_2 has also been mentioned by several workers[11–15].

Based on **Scheme-1**, the rate law for the decomposition of H_2O_2 is given by Eqn. (7)

$$-d[H_2O_2]/dt = KC_1[H_2O_2] - K_4C_2[H^-]K_3C_3[H_2O_2] \qquad (7)$$

where C_1 = number of free $Co^{3+}/Co(NH_3)_4^{3+}$ ions on the surface of alumina at any time t_2, C_2=number of $Co^{3+}/Co(NH_3)_4^{3+}$ ions in the form of intermediate complex on the surface of alumina at time t, and C_3 = number of $Co^{3+}/Co(NH_3)_4^{3+}$ ions in the form of intermediate complex on the surface of alumina at time t.

Considering the steady state condition and the total concentration of Co^{3+} or $Co^{3+}/Co(NH_3)_4^{3+}$ adsorbed on alumina at any time as: $C_{total} = C_1 + C_2 + C_3$, we obtained the relations (8)–(10):

$$C_1 = \frac{K_3(K_2 + K_{-1})[H^+]C_{total}}{K_1K_2^{+}K_3(K_2 + K_{-1}[H] + K_1[H_2O_2])} \tag{8}$$

$$C_2 = \frac{K_1C_1[H_2O_2]}{K_2+K_{-1}[H^+]} \tag{9}$$

$$C_3 = \frac{K_1K_2[Cu]}{K_3(K_2 + K_{-1}[H^+])} \tag{10}$$

Eqns. (7)–(10) lead to the rate law (11),

$$\frac{d[H_2O_2]}{d^1K_1} = \frac{2K_1K_2K_{total}[H_2O_2]}{K_2 + K_3(K_{2+} + K_{-1}[H^+] + K_1[H_2O_2])} \tag{11}$$

When $[H_2O_2]$ is not sufficiently high, the rate law (11) reduces to

$$\left(-\frac{d[H_2O_2]}{dt}\right) = \frac{2K_1K_2K_3C_{total}H_2O_2}{K_1K_2 + K_3(K_2 + K_{-1}[H^+])} \tag{12}$$

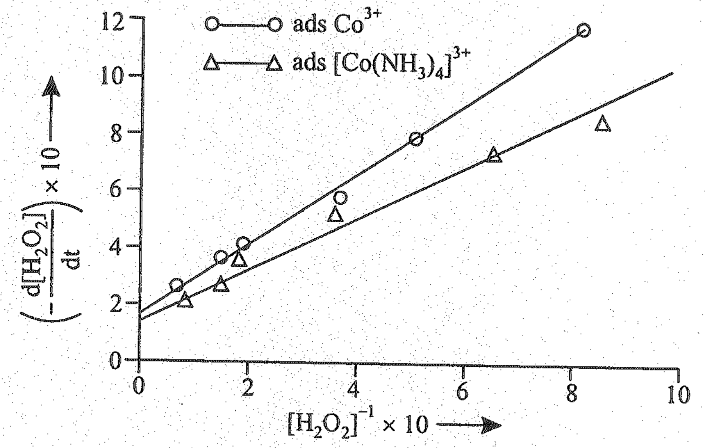

Fig. 3. Plot of $\left(\frac{-d[H_2O_2]}{dt}\right)$ *vs.* $[H_2O_2]$ (amount of adsorbed ions = 0.6 × 10^{-2} g/g alumina $[H_2O_2]$ = 1.12 vol.

This derived rate law (12) is in accord with our experimental findings. The validity of rate law (11) can further be examined by writing in the form of Eqn. (13).

$$\left(-\frac{d[H_2O_2]}{dt}\right)^{-1} = \frac{1}{2C_{total}}\left(\frac{1}{k_3} + \frac{K_2 + K_{-1}[H^4]}{K_1K_2}\right)\frac{1}{[H_2O_2]} + \frac{1}{2K_2C_{total}}$$

According to Eqn. (13) a plot of $(-d[H_2O_2]/dt)$ against $[H_2O_2]^{-1}$ should be linear with a positive intercept; this is found to be so, as seen from the plot in Fig. 3, indicating the validity of the rate law and hence of the proposed mechanism. The values of K_2 (*i.e.*, rate of disproportionation of the adsorbed intermediate complex) have been found to be 2841 and 2232 volume min^{-1} g^{-1} with $Co(NH_3)_4^{3+}$ adsorbed respectively. These values of K_2 indicate that the rate of disproportionation of H_2O_2 with $Co(NH_3)_4^{3+}$ adsorbed is higher than that with Co^{3+} adsorbed ions, which is also evident from Table-1.

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