

Kinetics & Mechanism of Decomposition of Hydrogen Peroxide Catalysed by Cu^{2+} & $\text{Cu}(\text{NH}_3)_4^{2+}$ Adsorbed on Alumina

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The decomposition of H_2O_2 at 30°C, catalysed by Cu^{2+} and $\text{Cu}(\text{NH}_3)_4^{2+}$ ions adsorbed on alumina, exhibits first order kinetics with respect to $[\text{H}_2\text{O}_2]$. 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 . A probable mechanism for the decomposition of H_2O_2 consistent with the kinetic data has been suggested.

Recently, it has been reported by Prasad and coworkers¹⁻⁴ 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. Such fast decomposition of H_2O_2 has practical applications as in fuel cells, rocket propellents, bleaching 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. This prompted us to undertake the title investigation.

Materials and Methods

Chromatographic grade alumina (Theodor Schuchardt) was washed repeatedly with boiling distilled water, dried, sieved (100-120 mesh) and finally activated at 150°C for 24 hr. The required amounts of activated alumina thus prepared were kept in contact with different solutions of copper sulphate (AR, BDH) for about 4 hr with constant stirring, filtered, washed repeatedly with distilled water and dried in air. The amount of unadsorbed Cu^{2+} in solution was determined using an atomic absorption spectrometer (Perkin-Elmer). Similarly $\text{Cu}(\text{NH}_3)_4^{2+}$ -adsorbed samples of alumina were prepared employing copper sulphate solutions containing excess of ammonia.

Hydrogen peroxide (30% wt/v, E Merck) was diluted by adding redistilled water. 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 Cu^{2+} or $\text{Cu}(\text{NH}_3)_4^{2+}$ -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 $\log(V_\infty - V_t)$ versus t (min) (Fig. 1), where V_t and V_∞ are the volumes of O_2 evolved 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 values of first order rate constant (k) calculated by measuring the slope of the first order linear plots decrease considerably with increase in $[\text{H}_2\text{O}_2]$ (Table 1). The decrease in k may possibly be due to decrease in pH of the solution as it has been noted that an increase in $[\text{H}_2\text{O}_2]$ from 1.12 to 11.20 volumes changes the pH of solution from 6.7 to 5.1. This is also quite evident from the fact that an increase in pH of solution from 6.0 to 8.05 increases the k value by 18.5 fold (at pH 6.0, 6.85, 7.20 and 8.05, $k \times 10^2$ (min^{-1}) values are 0.6, 1.4, 3.5 and 11.1 respectively under the conditions: amount of alumina = 1 g; amount of

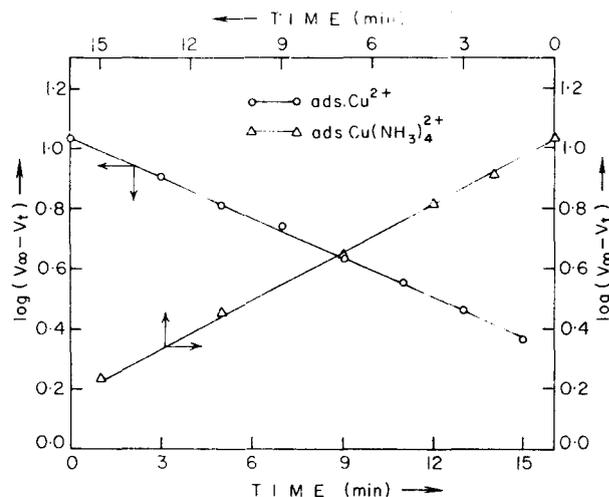


Fig. 1 — First order plot for the decomposition of hydrogen peroxide at 30°C ($[\text{H}_2\text{O}_2] = 1.12$ vol; amount of adsorbed ions = 0.16×10^{-2} g. g alumina)

Table 1—Effect of Varying [H₂O₂] on First Order Rate Constant

[Amount of alumina = 1 g; temp. 30°C]		
[H ₂ O ₂] (vol)	$k \times 10^2$ (min ⁻¹) on alumina	
	Cu ²⁺ -adsorbed*	Cu(NH ₃) ₄ ²⁺ -adsorbed*
0.56	—	12.9
1.12	10.2	11.5
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

*Amount adsorbed = 0.16×10^{-2} g/g alumina

 Table 2—Effect of Varying [H₂O₂] on First Order Rate Constant in Phosphate Buffer of pH 8.05

[Amount of alumina = 0.5 g; temp. 30°C]		
[H ₂ O ₂] (vol)	$k \times 10^2$ (min ⁻¹) on alumina	
	Cu ²⁺ -adsorbed*	Cu(NH ₃) ₄ ²⁺ -adsorbed†
1.12	20.3	12.8
2.24	18.2	13.2
4.48	15.9	11.5
8.96	16.8	12.1

*Amount adsorbed = 0.25×10^{-2} g

†Amount adsorbed = 0.18×10^{-2} g

adsorbed Cu(NH₃)₄²⁺ = 0.16×10^{-2} g/g alumina; [H₂O₂] = 1.12 vol.). Table 2, which summarises the results of the variation of [H₂O₂] at a constant pH of 8.05, shows that the values of k are nearly constant irrespective of [H₂O₂], thereby providing justification for the above explanation.

The results in Fig. 2A, where k values are plotted against the amount of adsorbed metal ions on alumina, show that as the amount of adsorbed Cu²⁺ ions are 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 Cu(NH₃)₄²⁺-adsorbed alumina exhibits an identical behaviour (Fig. 2B). Further, the values of k calculated for unit amount of adsorbed ions appear to be approximately constant at initial few concentrations of both the catalysts, indicating thereby that the rate of decomposition is first order at lower amounts of catalysts.

At this stage it is worthwhile to mention some visual observations noted during the experiments. A greyish brown colour on the surface of adsorbed alumina sample was invariably seen in the reaction vessel for reactions with [H₂O₂] > 2.24 volumes and the concentration of surface adsorbed ions > 0.51×10^{-2} g/g alumina. The brown coloured product formed on

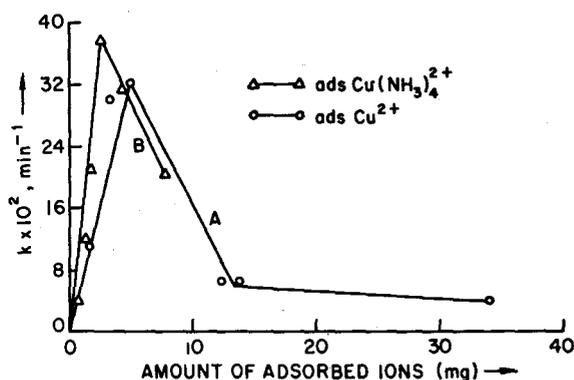
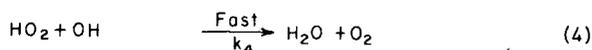
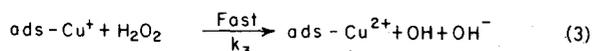
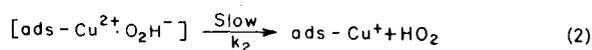
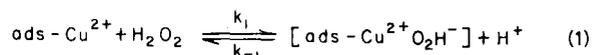


Fig. 2—Effect of amount of adsorbed ions on first order rate constant at 30°C ((A) and (B): [H₂O₂] = 2.24 vol; amount of alumina: (A) 1 g; and (B) 0.5 g)

the surface of catalyst persisted as long as any residual amount of H₂O₂ remained undecomposed. However, no visible colour change was found and initial blue surface of the adsorbed alumina remained as such during the experiment when either the amount of adsorbed ions was $\leq 0.51 \times 10^{-2}$ g/g alumina or [H₂O₂] < 2.24 volumes.

The formation of greyish brown colour on the surface of Cu²⁺-adsorbed alumina in the presence of H₂O₂ has also been reported by earlier workers². It was considered that enhanced decomposition of H₂O₂ was mainly due to the formation of the said greyish brown surface adsorbed complex.

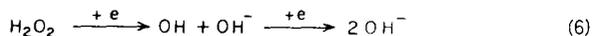
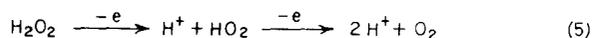
On the basis of our experimental results, we believe that surface adsorbed, ion-catalysed decomposition of H₂O₂ follows two reaction paths. When [H₂O₂] ≥ 2.24 volumes and the amount of adsorbed ions > 0.51×10^{-2} g/g alumina, the decomposition proceeds via the formation of a brown surface intermediate as already suggested. On the other hand, when [H₂O₂] < 2.24 volumes and the amount of adsorbed ions $\leq 0.51 \times 10^{-2}$ g/g alumina, 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 Cu²⁺ or Cu(NH₃)₄²⁺ ions adsorbed on alumina should be 0.51×10^{-2} g/g



Scheme 1

alumina or less in order to bring out the decomposition of H_2O_2 more effectively. Under this condition the decomposition of H_2O_2 in the presence of both the catalysts may proceed through steps (1-4) shown in Scheme 1.

The mechanism in Scheme 1 has been proposed utilising 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 the intermediates homogeneously metal ion catalysed decomposition of H_2O_2 has also been mentioned by several workers⁷⁻¹¹.

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

$$-\frac{d[H_2O_2]}{dt} = k_1 C_1 [H_2O_2] - k_{-1} C_2 [H^+] + k_3 C_3 [H_2O_2] \quad (7)$$

where C_1 = number of free $Cu^{2+}/Cu(NH_3)_4^{2+}$ ions on the surface of alumina at any time t ; C_2 = number of $Cu^{2+}/Cu(NH_3)_4^{2+}$ ions in the form of intermediate complex on the surface of alumina at time t ; and C_3 = number of $Cu^{2+}/Cu(NH_3)_4^{2+}$ ions in the form of intermediate $Cu^+/Cu(NH_3)_4^+$ on the surface of alumina at time t .

Considering the steady state condition and the total concentration of Cu^{2+} or $Cu(NH_3)_4^{2+}$ adsorbed on alumina at any time t as: $C_{total} = C_1 + C_2 + C_3$, one obtains the relations (8-10)

$$C_1 = \frac{k_3(k_2 + k_{-1}[H^+])C_{total}}{k_1 k_2 + k_3(k_2 + k_{-1}[H^+] + k_1[H_2O_2])} \quad (8)$$

$$C_2 = \frac{k_1 C_1 [H_2O_2]}{k_2 + k_{-1}[H^+]} \quad (9)$$

$$C_3 = \frac{k_1 k_2 C_1}{k_3(k_2 + k_{-1}[H^+])} \quad (10)$$

Equations (7-10) lead to the rate law (11)

$$-\frac{d[H_2O_2]}{dt} = \frac{2k_1 k_2 k_3 C_{total} [H_2O_2]}{k_1 k_2 + k_3(k_2 + k_{-1}[H^+] + k_1[H_2O_2])} \quad (11)$$

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

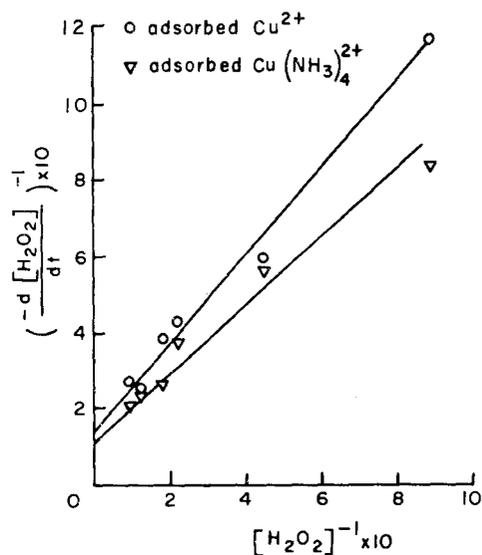


Fig. 3 -Plot of $\left(-\frac{d[H_2O_2]}{dt}\right)^{-1}$ versus $[H_2O_2]^{-1}$ (amount of adsorbed ions = 0.16×10^{-2} g/g alumina; $[H_2O_2] = 1.12$ vol)

$$-\frac{d[H_2O_2]}{dt} = \frac{2k_1 k_2 k_3 C_{total} [H_2O_2]}{k_1 k_2 + k_3(k_2 + k_{-1}[H^+])} \quad (12)$$

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 Eq. (13)

$$\left(-\frac{d[H_2O_2]}{dt}\right)^{-1} = \frac{1}{2C_{total}} \left(\frac{1}{k_3} + \frac{k_2 + k_{-1}[H^+]}{k_1 k_2} \right) \frac{1}{[H_2O_2]} + \frac{1}{2k_2 C_{total}} \quad (13)$$

According to Eq. (13) a plot of $(-d[H_2O_2]/dt)^{-1}$ 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 (13) 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 $Cu(NH_3)_4^{2+}$ adsorbed and Cu^{2+} adsorbed ions, respectively. These values of k_2 indicate that the rate of disproportionation of H_2O_2 with $Cu(NH_3)_4^{2+}$ adsorbed ions is higher than that with Cu^{2+} adsorbed ions, which is also evident from Table I.

Acknowledgement

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