Kinetics & Mechanism of Decomposition of Hydrogen Peroxide Catalysed by Co$^{2+}$ Adsorbed on Alumina

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Decomposition of H$_2$O$_2$ at 30°C, catalysed by Co$^{2+}$ ions adsorbed on alumina shows first order dependence in [H$_2$O$_2$]. As the amount of surface adsorbed ions increases, the first order rate constant initially increases linearly, reaches a maximum and decreases thereafter. Further, the rate constant increases almost proportionally with increase in pH of the solution from 6.5 to 8.7. A probable mechanism has been suggested.

The kinetics of decomposition of H$_2$O$_2$ catalysed by Cu$^{2+}$ and Cu(NH$_3$)$_2$$^{2+}$ adsorbed on alumina were investigated by us earlier$^1$. The title investigation is an extension of our earlier work. The results presented in this note show trends similar to those reported earlier.

The Co$^{2+}$ adsorbed alumina samples were prepared by the procedure adopted for Cu$^{2+}$ adsorbed samples$^1$. After each adsorption experiment, Co$^{2+}$ remaining in solution was determined by EDTA titration using xylene orange as an indicator$^2$. The kinetics of decomposition was followed gasometrically, as described earlier and the first order rate constants were calculated as in the previous investigation$^1$.

As in the earlier study on Cu$^{2+}$ adsorbed alumina, decomposition of H$_2$O$_2$ in the presence of Co$^{2+}$ adsorbed on alumina shows nearly first order dependence in [H$_2$O$_2$] in any particular run. A gradual decrease in k values with increase in [H$_2$O$_2$] is observed. Thus under the conditions: amount of alumina = 0.5 g; amount of Co$^{2+}$ adsorbed = 3.15 mg; temp. = 30°C, the first order rate constants ($k \times 10^2$, min$^{-1}$) were 6.9, 5.5, 4.7, 4.0, 5.0 and 8.0 volumes respectively. The decrease in k values may be attributed to increase in oxygen pressure at higher volumes of H$_2$O$_2$. In conformity with earlier investigations$^5$. It has been observed$^1$ that as [H$_2$O$_2$] increases from 1.12 to 11.20 volume, the pH changes from 6.7 to 5.1. The influence of pH on the rate constant has also been studied. The k values determined at different initial [H$_2$O$_2$] in phosphate buffer (pH = 8.7) appear to be almost constant. For instance under the conditions: alumina taken = 0.5 g; Co$^{2+}$ adsorbed = 2.3 mg; and temp. = 30°C the first order rate constants ($k \times 10^2$, min$^{-1}$) were 2.1, 1.8, 1.8 and 1.7 at initial [H$_2$O$_2$] of 1.1, 2.2, 4.4 and 8.8 volumes, respectively. The value of k increases linearly with the increase in pH of the reaction medium, using phosphate buffer for adjusting the pH.

The effect of varying concentration of surface adsorbed ions on k has also been studied. The results show that as the concentration of adsorbed Co$^{2+}$ ions is varied from 0.6 to 3.15 mg on a fixed amount of alumina surface (0.5 g), the value of k initially increases almost linearly, reaches a maximum and decreases thereafter. Similar results have also been reported$^1$ for the decomposition of H$_2$O$_2$ catalysed by Cu$^{2+}$ and Cu(NH$_3$)$_2$$^{2+}$ adsorbed ions. Thus considerable decrease in k value at higher concentration of surface adsorbed Co$^{2+}$ ions may possibly be due to the formation of binuclear surface complexes of the type [$\cdot$Co(O$_2$)Co$^-$]$_2^+$/$\cdot$Co(O$_2$)Co$^-$]. The formation of such complexes during aerial oxidation of CoCl$_2$ solution in the presence of a variety of complexing ligands has already been reported in literature$^6$. These complexes might be more stable than the intermediate complex formed at lower concentrations of the catalyst. Thus, the amount of catalyst should be less than or equal to 2.3 mg/0.5 g alumina for effective decomposition of H$_2$O$_2$. Further, a positive intercept on Y-axis indicates some decomposition of H$_2$O$_2$ by alumina itself.

It is worth mentioning that when Co$^{2+}$ adsorbed alumina sample is added to a solution of H$_2$O$_2$, its initial pink colour changes to muddy and remains as such even after the complete decomposition of H$_2$O$_2$. After completion of the reaction, the catalyst was filtered off, repeatedly washed with distilled water, and dried at room temperature. A portion of the catalyst obtained when treated with conc. HCl gave an intense blue coloration indicating the presence of Co$^{3+}$/Co$^{2+}$ on the surface of alumina. Its magnetic susceptibility measurements showed the presence of paramagnetic species, such as Co$^{2+}$ even after using the catalyst for the decomposition of H$_2$O$_2$. IR spectrum indicated the presence of water/OH$^-$ and absence of peroxy group in the sample.
The above kinetic results suggest that the decomposition of H₂O₂ in the presence of the catalyst may proceed through steps (1-4) shown in Scheme 1.

Scheme 1 has been proposed by considering the various steps involved in the oxidation and reduction of H₂O₂. Oxidation of Co (II) to Co (III) with H₂O₂ in aqueous solution has already been reported.

Scheme 1 leads to rate law (5)
\[
\frac{d[H₂O₂]}{dt} = k₁C₃[H₂O₂] + k₂C₃[H₂O₂] - k₃C₃[H⁺] \quad \ldots (5)
\]
where C₁ = number of free Co²⁺ ions on the surface of alumina at any time t, C₂ = number of Co²⁺ ions on the surface of H₂O₂ at time t, and C₃ = number of Co²⁺ ions in the form of intermediate complex on the surface of alumina at time t. C₁, C₂, and C₃ are given by Eqs (6-8) respectively by applying the steady state treatment and assuming Cₚₖ = C₁ + C₂ + C₃.

Equations (5-8) lead to the rate law (9).
\[
\frac{d[H₂O₂]}{dt} \propto \frac{k₃k₄C₉[H₂O₂]Cₚₖ}{k₃k₄C₉[H₂O₂] + k₄k₅[H⁺] + k₆k₇[H₂O₂]} \quad (9)
\]

When [H₂O₂] is not sufficiently high, rate law (9) reduces to
\[
\frac{d[H₂O₂]}{dt} \propto \frac{k₃k₄C₉[H₂O₂]Cₚₖ}{k₃k₄C₉[H₂O₂] + k₄k₅[H⁺] + k₆k₇[H₂O₂]} \quad (10)
\]

According to Eq. (11) a plot of \( \frac{d[H₂O₂]}{dt} \) versus [H₂O₂] should be linear with a positive intercept. This is found to be so (Fig. 1), indicating the validity of the rate law (11) and hence of the proposed mechanism. The value of k₃ (i.e. rate of disproportionation of the adsorbed intermediate complex) has been found to be 345.1 volume min⁻¹ g⁻¹.

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References
4 Cotton F A & Wilkinson Geoffrey, Advanced inorganic chemistry, (Wiley-Eastern, New Delhi), 1970 pp (a) 868; (b) 873.