CATALYTIC BEHAVIOUR OF $[Cu(en)_2]^{2+}$ SORBED ON ZIRCONIUM MOLYBDATE IN THE DECOMPOSITION OF HYDROGEN PEROXIDE

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Summary

Zirconium molybdate has been used as a support on which $[Cu(en)_2]^{2+}$ has been sorbed. The catalytic activity has been studied via hydrogen peroxide decomposition at different temperatures, using different concentrations of hydrogen peroxide and different amounts of catalyst. A probable mechanism for the reaction is suggested on the basis of the kinetic data obtained.

Introduction

The heterogenization of homogeneous catalysts is an area of intense current interest [1, 2]. Complexes have been affixed to polymers [1, 3], formed in zeolite cavities [4, 5] and affixed to silica or alumina surfaces [6]. Recently, bulky complexes have been incorporated between the layers of a smectite clay (hectorite) by an ion-exchange process and these products have exhibited interesting catalytic behaviour [7, 8].

The ion-exchange method of catalyst immobilization is simple when compared to the procedures required for the attachment of complexes to polymers. The attractiveness of the method is further increased by providing temperature- and solvent-stable inorganic ion exchangers of known structure as supports. The ion-exchange properties of α -zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$, have been examined in detail [9-11], and it has been shown that in the hydrogen form this compound is an acidic catalyst [12, 13]. The synthesis and ion-exchange properties of crystalline zirconium molybdate [14] and amorphous zirconium molybdate [15, 16] were studied earlier. To date, no work has been undertaken to examine the catalytic properties of these compounds (zirconium molybdate).

Hydrogen peroxide participates in a variety of chemical reactions [17]. Transition metal ions such as Co^{II} , Ni^{II} and Cu^{II} , and their complexes [18 - 20] as well as many materials in the solid [21] and colloidal states [22], have been found to be active in the disproportionation of hydrogen peroxide. Recently, it has been reported that metal ions such as Cu^{II} , Co^{II} and Cr^{II} , and their complexes, when supported on alumina or silica exhibit catalase-like activity

in the decomposition of hydrogen peroxide [23 - 25]. In the present study, the hydrogen peroxide decomposition reaction was chosen as a model reaction. This paper deals with the kinetics of hydrogen peroxide decomposition catalysed by $[Cu(en)_2]^{2+}$ sorbed on to zirconium molybdate. The rate of the chemical reaction and the factors influencing the rate, such as the amount of catalyst, substrate concentration and temperature, are also discussed.

Experimental

Preparation of zirconium molybdate

Zirconium molybdate was prepared by the ammonium molybdate method as reported earlier [14]. Aqueous solutions of zirconyl oxychloride and ammonium molybdate were mixed until precipitation was complete. The resulting gel was digested for several hours at room temperature, washed with conductivity water to effect the removal of any excess chloride ions, filtered and dried at 100 °C. For kinetic studies, the gel was reduced to the desired particle size and graded by sieving. It was then converted to the hydrogen form by immersion in 1 mol dm⁻³ HCl solution, the acid being replaced intermittently. It was then washed several times with conductivity water, filtered and dried at 100 °C.

Sorption of $[Cu(en)_2]^{2+}$ on to zirconium molybdate

Ethylenediamine (0.01 mol) was added to a solution of copper(II) nitrate (0.01 mol) in ethanol. The solution was concentrated until precipitation of the solid commenced. The solid isolated was filtered, washed and dried. A known amount of this complex was dissolved in 25 ml of conductivity water to prepare a 0.05 mol dm⁻³ solution of the $[Cu(en)_2]^{2+}$ complex. The acid-treated ion exchanger (1 g) was placed in a glass conical flask fitted with a stopper and the solution of the complex ion prepared as above added. The exchanger was kept in contact with the complex ion solution for 24 h with intermittent shaking. It was finally filtered, washed with conductivity water to effect complete removal of the adhering complex and dried at 100 °C. All washings were collected along with the filtrate to determine the quantity of Cu^{II} ion remaining. The concentration of Cu^{II} ion present on the exchanger was calculated from the difference between the initial and final concentrations of the solution.

Kinetic studies

A weighed quantity of the catalyst was shaken with 10 ml (4 vol) of hydrogen peroxide in the thermostat at 25 °C. The desired concentration of hydrogen peroxide was obtained by successive dilution from the stock solution. The volume of oxygen evolved was measured at various time intervals and also after complete decomposition of hydrogen peroxide using a gas burette [26]. Experiments were carried out at different temperatures within the range 25 - 40 °C. The influence of various quantities of the catalyst used $(0.025 \cdot 0.075 \text{ g})$ was studied at 30 °C. The effect of varying the concentration of hydrogen peroxide was also studied at 30 °C.

Chemical and instrumental analyses

Zirconium was determined gravimetrically as zirconium oxide, molybdenum was determined gravimetrically as molybdenum oxide using the α -benzoin oxime method while Cu^{II} was estimated iodometrically. The IR spectra of various samples were obtained on a Shimadzu IR-408 spectrometer using the KBr disc technique.

Reflectance spectra of samples using barium sulphate as a reference were recorded on a Shimadzu PR-1 instrument.

Results and discussion

Chemical analyses indicate that the Zr:Mo ratio in zirconium molybdate is 1:2. Other workers have provided analytical data in agreement with this result [13, 14]. Inorganic cation exchangers prepared by combining Group IV oxides with more acidic Group V and Group VI oxides have the general formula $M(HXO_4)_2 \cdot H_2O$, where M = Zr and X = P, Mo or W. The H⁺ ions of the OH groups contained within such solids are exchangeable.

The IR spectrum of Cu^{II} ethylenediamine sorbed on to zirconium molybdate exhibits broad bands in the ranges ~3300 cm⁻¹ and ~1600 cm⁻¹. This may be attributed to merging of the —OH and —NH stretching and —OH and —NH bending modes, respectively.

The reflectance spectra of $[Cu(en)_2]^{2+}$ ($\lambda_{max} = 590 \text{ nm}$) and Cu^{II} ethylenediamine sorbed on to zirconium molybdate ($\lambda_{max} = 570 \text{ nm}$) exhibit a broad band. The shift in the λ_{max} positions from 590 nm to 570 nm may be due to a slight distortion in the geometry around the Cu centre due to the sorption of $[Cu(en)_2]^{2+}$ on to zirconium molybdate.

Kinetic studies

In the present investigation, the kinetic analysis is based on the initial rate data, since the reaction rate approached equilibrium values after extended time intervals.

The order of reaction with respect to hydrogen peroxide was determiend from the slope of the linear plots of log(initial rate of O_2 production) versus log[H₂O₂] (Fig. 1) using the same amount of the catalyst in each case and a fixed temperature (30 °C). The order of reaction with respect to the catalyst was obtained from the slope of the plot of log(initial rate of O_2 production) versus log[catalyst] (Fig. 2), keeping the H₂O₂ concentration constant and employing a fixed temperature (30 °C). The values of the reaction orders for the catalyst are given in Tables 1 and 2.

On the basis of the average order of the reaction with respect to catalyst and hydrogen peroxide, a power law expression for the catalytic decomposition process can be written as:

$$r = d[O_2]/dt = K_r[cat]^m[H_2O_2]^n$$
⁽¹⁾



Fig. 1. Plot of $\log(d[O_2]/dt)$ versus $\log[H_2O_2]$.



Fig. 2. Plot of $\log(d[O_2]/dt)$ versus $\log[\text{catalyst}]$.

where r is the rate of reaction and K_r the reaction rate constant. According to eqn. (1), a plot of $d[O_2]/dt$ versus $[cat]^m[H_2O_2]^n$ should be linear and pass through the origin. Such a plot is depicted in Fig. 3 indicating good agreement between the rate data and the power law expression. From the data listed in Table 1, it is also clear that the reaction is first order with respect to hydrogen peroxide.

Although the apparent reaction rate constant K_r in eqn. (1) includes some other constants, it can be taken as a direct measure of the catalytic activity

TABLE 1

Concentration of $H_2O_2(vol)$	Specific reaction rate, $10^4 K (\min^{-1})$	Order of reaction with respect to $[H_2O_2]$
5.00	2.5	
7.50	2.4	0.86
10.00	2.4	

Catalytic activity of $[Cu(en)_2]^{2+}$ -sorbed ion exchanger at different hydrogen peroxide concentrations at 30 °C^a

^aQuantity of catalyst, 0.05 g; volume of hydrogen peroxide, 10 ml (4 vol).

TABLE 2

Influence of catalyst quantity on decomposition of hydrogen peroxide^a

Quantity of $[Cu(en)_2]^{2+}$ on surface (g)	Specific reaction rate, $10^4 K (min^{-1})$	Order of reaction with respect to [catalyst]
5.96×10^{-4} 1.19 × 10 ⁻³	1.20 2.40	0.65
1.78×10^{-3}	2.91	

^aReaction temperature $30 \pm 1^{\circ}$ C; volume of hydrogen peroxide 10 ml (4 vol).

for comparative purposes. Thus, it was found that the rate was independent of the initial concentration of hydrogen peroxide (Table 1), while an increase in the amount of catalyst increased the rate of reaction (Table 2) indicating that there is no dimerization of the metal complex in the heterogenized system over the concentration range studied. However, it was observed that the rate does not increase linearly with an increase in the amount of catalyst, since the rate of decomposition exhibits a fractional order with respect to the catalyst. An increase in the reaction temperature increases the rate of decomposition (Table 3).

The colour of the surface-adsorbed complex ion changed from blue to greenish yellow when it came into contact with hydrogen peroxide. This colour persisted for as long as any residual hydrogen peroxide remained in the system. After complete decomposition of the hydrogen peroxide, the catalyst regained its original blue colour. Similar results have been observed by Ram *et al.* [19, 23 - 25] during the decomposition of H_2O_2 using metal complexes supported on silica or alumina as catalysts. As reported earlier by other workers [18, 27, 28], this could be due to the formation of a peroxo species.

Based on the above observations, it is possible to derive a reaction mechanism and a rate equation for the system. It is known [18, 19] that H_2O_2 dissociates according to:

$$H_2O_2 \rightarrow HO_2^- + H^+$$

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(2)



Fig. 3. Plot of $d[O_2]/dt$ versus $[catalyst]^m [H_2O_2]^n$.

TABLE 3

Decomposition of hydrogen peroxide catalysed by $[Cu(en)_2]^{2+}$ -sorbed ion exchanger at different temperatures^a

Temperature (°C)	Specific reaction rate, $10^4 K$ (min^{-1})	Energy of activation ^b (kcal mol ⁻¹)	
25	1.56	en en la sont d'	
30	2.40	11.00	
35	3.00		
40	4.12		

"Quantity of catalyst, 0.05 g; volume of hydrogen peroxide, 10 ml (4 vol).

^bValues obtained from graph Fig. 4.



Fig. 4. Arrhenius plot of log k versus 1/T.

With metal complexes bound to supports, all the active sites do not participate in the reaction as demonstrated by the fractional order obtained with respect to catalyst concentration. Hence, we may write:

$$(\mathbf{ML}_n)_{\text{total}} = (\mathbf{ML}_n)_{\mathbf{a}} + (\mathbf{ML}_n)_{\mathbf{na}}$$
(3)

where M depicts the metal, L the ligand, n is an integer, and the subscripts a and na relate to accessible and non-accessible, respectively.

Thus, $(ML_n)_a$ may react with HO_2^- ions to form an intermediate complex:

$$(\mathrm{ML}_{n})_{\mathrm{a}} + \mathrm{HO}_{2}^{-} \underbrace{\stackrel{k_{1}}{\underset{k_{-1}}{\longrightarrow}}}_{\overset{k_{-1}}{\longrightarrow}} [(\mathrm{ML}_{n})_{\mathrm{a}} \mathrm{HO}_{2}^{-}]$$
(4)

A second molecule of H_2O_2 may then interact with the intermediate complex to form the products:

$$[(\mathrm{ML}_n)_{a}\mathrm{HO}_2^{-}] + \mathrm{H}_2\mathrm{O}_2 \xrightarrow{\kappa_2} (\mathrm{ML}_n)_{a} + \mathrm{O}_2 + \mathrm{H}_2\mathrm{O} + \mathrm{OH}^{-}$$
(5)

During the decomposition of hydrogen peroxide, a continuous increase in pH occurs confirming the liberation of OH^- ions as suggested by the above mechanism. Step (5) is slow and constitutes the rate-determining step. On the basis of the above mechanism the rate law may be written as:

$$Rate = d[O_2]/dt \propto [(ML_n)_a HO_2^{-}][H_2O_2]$$
(6)

$$Rate = d[O_2]/dt = k_2[(ML_n)_a HO_2^{-}][H_2O_2]$$
(7)

where k_2 is the rate constant.

Now from eqn. (3):

$$(\mathbf{ML}_n)_{\mathbf{a}} = (\mathbf{ML}_n)_{\text{total}} - (\mathbf{ML}_n)_{\mathbf{na}}$$
(8)

Applying the steady state principle to the formation of $[(ML_n)_aHO_2^-]$, we obtain:

$$k_{1}[(ML_{n})_{a}][HO_{2}^{-}] - k_{-1}[(ML_{n})_{a}HO_{2}^{-}] - k_{2}[(ML_{n})_{a}HO_{2}^{-}][H_{2}O_{2}] = 0$$
(9)

hence

$$[(ML_n)_a HO_2^{-}] = \frac{k_1[(ML_n)_a][HO_2^{-}]}{k_{-1} + k_2[H_2O_2]}$$
(10)

substituting this value in eqn. (7) gives:

$$\frac{\mathrm{d}[O_2]}{\mathrm{d}t} = \frac{k_2 k_1 [(\mathrm{ML}_n)_a] [\mathrm{HO}_2^{-}] [\mathrm{H}_2 O_2]}{k_{-1} + k_2 [\mathrm{H}_2 O_2]} \tag{11}$$

or

$$\frac{d[O_2]}{dt} = \frac{k_2 k_1 [(ML_n)_{\text{total}} - (ML_n)_{\text{na}}] [HO_2^-] [H_2O_2]}{k_{-1} + k_2 [H_2O_2]}$$
(12)

In the present investigation, the $[H_2O_2]$ value used is 10^3 -times more than $(ML_n)_{total}$; hence, $k_2[H_2O_2] \gg k_{-1}$. Under these circumstances, eqn. (12) reduces to:

$$\frac{d[O_2]}{dt} = k_1 [(ML_n)_{total} - [(ML_n)_{na}][HO_2^{-1}]$$
(13)

Now, from eqn. (2)

$$[\mathrm{HO}_{2}^{-}] = \frac{K[\mathrm{H}_{2}\mathrm{O}_{2}]}{[\mathrm{H}^{+}]}$$

where K is the equilibrium constant. Hence

$$\frac{d[O_2]}{dt} = \frac{Kk_1[(ML_n)_{total} - (ML_n)_{na}][H_2O_2]}{[H^+]}$$
(14)

or

$$\frac{\mathrm{d}[\mathrm{O}_2]}{\mathrm{d}t} = K_{\mathrm{r}}[(\mathrm{ML}_n)_{\mathrm{total}} - (\mathrm{ML}_n)_{\mathrm{na}}][\mathrm{H}_2\mathrm{O}_2]$$
(15)

where $K_r = Kk_1/[H^+]$ is a constant.

As explained earlier, the reaction is first order with respect to (i) the H_2O_2 concentration when the catalyst concentration is kept constant, and (ii) the catalyst concentration $(ML_n)_a$ when the hydrogen peroxide concentration is kept constant. This is in agreement with eqn. (15) above.

Conclusions

Investigations have been carried out to study the catalytic activity involved in hydrogen peroxide decomposition using $[Cu(en)_2]^{2+}$ sorbed on zirconium molybdate. Decomposition rates have been measured using gas volumetric techniques at four different temperatures (25, 30, 35 and 40 °C), three different concentrations of hydrogen peroxide and three different amounts of catalyst.

For the catalyst concerned, the decomposition of hydrogen peroxide was found to be first order. The specific reaction rate increases in direct proportion to the increase in the catalyst concentration and is independent of the concentration of hydrogen peroxide.

The value of energy of activation is $11.00 \text{ kcal mol}^{-1}$ suggesting that $[\operatorname{Cu}(\operatorname{en})_2]^{2+}$ sorbed on to zirconium molybdate is catalytically active. The activity of the complex ion $[\operatorname{Cu}(\operatorname{en})_2]^{2+}$ in the decomposition of hydrogen peroxide may be explained by the formation of a stable ternary complex between the Cu complex and an oxygen donor, *i.e.*, to the formation of an intermediate peroxo species. Since a metal complex bound to a support experiences restricted motion, reaction on such catalysts may be expected to be more rapid than on catalysts where the molecules are free [29].

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