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Kinetics of Heterogeneous Decomposition of Hydrogen Peroxide

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Abstract. The kinetics of the decomposition of hydrogen peroxide was studied in aqueous medium in the temperature range 25–40°C in the presence of Wofatit KPS-resin in the form of Cu(II)-ammine complex ions. The rate constant was deduced at various degrees of resin cross-linkage and different concentrations of hydrogen peroxide. The order of the decomposition reaction varied from first order to half order, i.e., the order of the reaction decreased with increasing the concentration of H_2O_2. The decomposition process was found to be a catalytic reaction which was controlled by the chemical reaction of H_2O_2 molecules with the active species inside the resin particles. The mechanism of the reaction can be summarized by the equation $-\mathrm{d}[H_2O_2]/\mathrm{d}t = k_1 \sqrt{K_1}K_2[H_2O_2][Cu(NH_3)_4]^{2+}/[H^+]$ in which the subsequent reactions of the probable active complex are discussed.

Key words: H_2O_2 decomposition, Wofatit KPS-resin, Cu(II)-ammine complex ions.

1. Introduction

Many molecules, notably amine and ammonia, when brought into contact with an ion exchange resin in the metal ion form yield intensely coloured complexes [1,2]. The complex ions obtained in this way are strongly attached to the resin. It was found [3] that the transition metal-ammine complexes have an enzyme-like activity in the decomposition of hydrogen peroxide. The catalytic decomposition of hydrogen peroxide in the presence of copper salts and its complexes with imidazole [4], 2,2′-bipyridyl [5], ethylenediamine [6] and histamine [7,8] has been studied. It has been reported [4–8] that the decomposition of H_2O_2 by copper complexes may proceed through a combination of a molecular mechanism, in which a presumed intermediate species, $[Cu(ligand)_xHOO^-]^+$, reacts with HOO^- and a free-radical mechanism involving reversible oxidation-reduction of cupric-cuprous couple and the formation of free radicals, e.g., HO_2 and OH.

The catalytic decomposition of H_2O_2 has been extensively studied [9] in the presence of Cu(II)-ammine complex ions in aqueous media giving the brown coloured diamagnetic peroxocopper complex that decomposes by time with the evolution of oxygen. Such a complex product changes to a green coloured compound on standing for several hours and finally to a sky-blue colour after several days.

However, the decomposition reaction of H_2O_2 in the presence of resins in the form of transition metal-ammine complex ions has not so far been studied. The present work aims at the utilization of a resin in the form of Cu(II)-ammine complex ions as a catalyst in studying the kinetics of the heterogeneous decomposition reaction of hydrogen peroxide.

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2. Experimental

2.1. THE WOFATIT KPS-RESIN IN THE FORM OF Cu(II)-AMMINE COMPLEX IONS

Wofatit KPS (4, 12, 16% DVB) resin in the hydrogen ion form was used as a cation exchanger. It was produced as spherical-shaped beads of sulphonated styrene divinylbenzene copolymer in the hydrogen form by EKB Wolfen, in the German Democratic Republic. The average particle diameter of the resin beads was 0.06 mm. The resins were regenerated with 2N HCl, thoroughly washed and air-dried. Its moisture content was determined by drying a sample overnight at 110 °C under atmospheric pressure. The total weight capacity of the exchanger was determined statically with the aid of the batch method [10] and was found to decrease with increasing resin cross-linkage. The values were 4.74, 4.48 and 4.33 meq/g dry H^+-form at resin cross-linkage of 4,12 and 16% DVB, respectively. The resin was converted to the Cu^{2+}-form by equilibrating it statically with a solution of copper sulphate (1 M). The resin in the Cu^{2+} form was collected and washed with twice-distilled water until it was free from any excess of copper sulphate solution. Ammonium hydroxide solution (2 M) was added to the resin in the Cu^{2+} form which was converted to a resin in the form of stable Cu(II)-ammine complex ions. Finally, the resin was washed with twice-distilled water until it was free from any excess ammonium hydroxide.

2.2. THE HYDROGEN PEROXIDE SOLUTION

A 30% hydrogen peroxide solution (AR grade from Merk, Schuchardt, München, Germany) was used. Four different initial concentrations of hydrogen peroxide solution were chosen in the range of $(2.4–9.5) \times 10^{-2}$ M. Each of these concentration was obtained by mixing 2 ml of a freshly prepared stock solution of H_2O_2 with 18 ml twice-distilled water. The initial concentration of hydrogen peroxide was determined iodometrically using standard sodium thiosulphate solution [11].

2.3. KINETIC MEASUREMENTS

A 100 ml conical flask containing a definite weight (0.01 g) of the air-dried resin in the form of Cu(II)-ammine complex ions together with 18 ml twice-distilled water was placed in a water-shaker thermostat for half an hour. Two milliliters of standard stock solution of H_2O_2 were added quickly to the conical flask and the time was recorded. After a measured time, the reaction was quenched by quickly sucking the reaction mixture through a G2 sintered glass. Five millilitres of the filtrate were withdrawn and the undecomposed hydrogen peroxide was determined iodometrically. The reaction was carried out in the temperature range 25–40 ± 0.1 °C. All reagents were of AR grade.

A brown-coloured compound was formed at the beginning of mixing the hydrogen peroxide with the resin in the form of Cu(II)-ammine complex ions. The amount of the brown compound increased with the progress of the reaction, i.e., with the increase of the rate of the decomposition of H_2O_2.

Before the addition of hydrogen peroxide, the pH of twice-distilled water in the presence of the resin was 7.4. After the addition of hydrogen peroxide, the pH decreased within the first minute of the reaction and reached a value of 7.2, then increased until it reached a value of 8.0 at the end of the reaction.

It was impossible to carry out the decomposition reaction in the presence of an acid, buffer or electrolyte solution. The resin in the form of Cu(II)-ammine complex ions was regenerated in the presence of these solutions. This is expected in the light of the metal ion bleed principle [12].

3. Results

The decomposition reaction of hydrogen peroxide in the presence of Cu(II)-ammine complex ions was carried out at 25, 30, 35 and 40°C. The initial peroxide concentration was kept constant at 9.5×10^{-2} M while the degree of resin cross-linkage was varied. In some experiments the degree of resin cross-linkage was kept constant (4% DVB) whereas the initial H_2O_2 concentration was changed in the range $(2.4–9.5) \times 10^{-2}$ M.

The true rate constant, k, and the order of the reaction, n, were determined by adjusting n to get an optimum linear plot of $[H_2O_2]^{(1-n)}$ vs time (Figure 1) according to the following

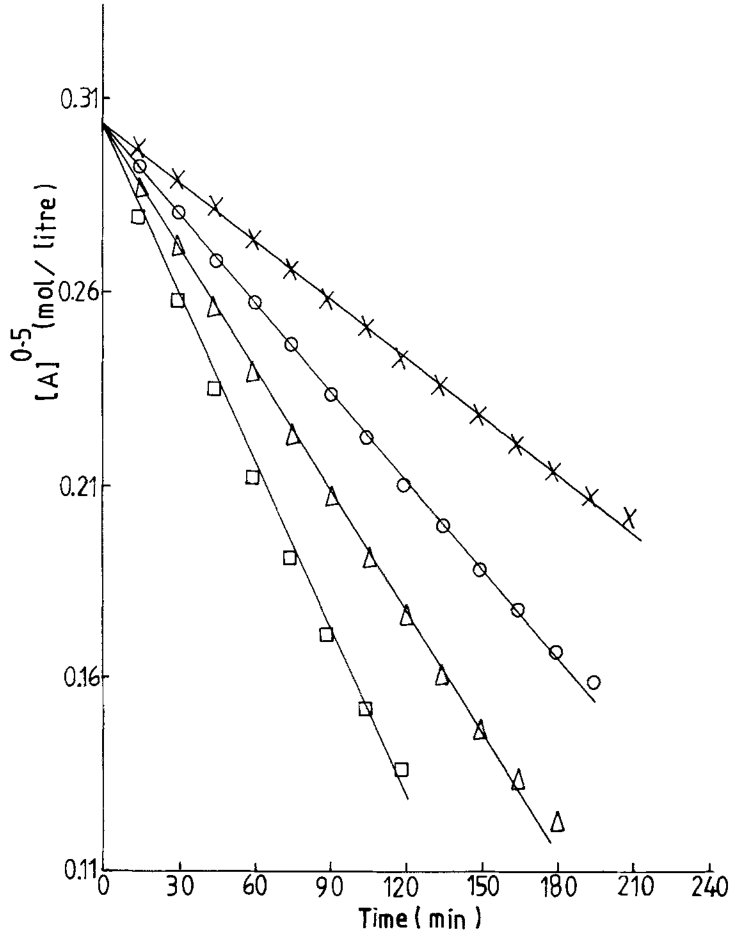

Fig. 1. Illustration of the $[H_2O_2]^{0.5}$-time curves for the decomposition of $H_2O_2(9.5 \times 10^{-2}$ M) in the presence of 0.01 g air-dried resin of Wofatit KPS-resin (16% DVB) in the form of Cu(II)-ammine complex ions (X : 25, ○: 30, △: 35 and □: 40°C).

equation [13]:

$$[A]^{1-n} = [A_0]^{1-n} - (1 - n)\,kwt \tag{1}$$

where $n \neq 1$, $[A_0]$ is the initial concentration of H_2O_2, w is the weight of dry resin in g, and $[A]$ is the concentration at time t. It is clear from Table I that the rate constant was not only temperature dependent but it also changed as a function of resin cross-linkage.

It is recommended that the order of the reaction is determined by more than one method. The determination of the order as a function of concentration was performed by applying Equation (1). This method gave the value of the order, n, equal to 0.5 at a constant H_2O_2 concentration of 9.5×10^{-2} M at different degrees of resin cross-linkage.

On the other hand, the order of the reaction was determined as a function of time, n'. The ratio of the time required for 75% reaction to that for 50% reaction is diagnostic of the reaction order. The values of $t_{3/4}/t_{1/2}$ were in the range 2.1–1.9. These values correspond to a first-order reaction with respect to H_2O_2. It was found that n' increased with decreasing the initial concentration of H_2O_2 (Table I).

It is useful to provide a quantitative treatment of the decomposition of H_2O_2 in terms of the values of the activation parameters. The activation energy, E, was computed from Arrhenius plots (Figure 2) using the IBM PC (2.1) disk operating system. It is clear that the values of E (Table I) were in the range of chemical reactions [14], i.e., between 41.8 and 83.7 KJ/mol. The change of free energy of activation, ΔG^*, was deduced from Eyring's equation [14]. The change of enthalpy of activation, ΔH^* was evaluated from the relation [14]

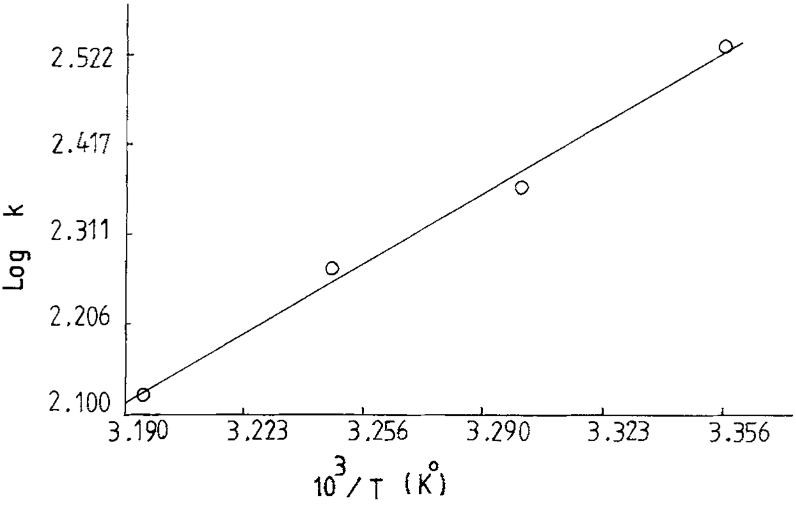

Fig. 2. Illustration of an Arrhenius plot for the decomposition of H_2O_2(9.5×10^{-2} M) in the presence of the resin Wofatit KPS (12% DVB) in the form of Cu(II)-ammine complex ions.

$$\Delta H^* = E - RT \tag{2}$$

The change of the entropy of activation, ΔS^*, was calculated according to the relationship [14].

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{3}$$

Table I. The rate constant (per g-dry resin) and the activation parameters for the decomposition reaction of H_2O_2 in the presence of Wofatit KPS-resin (0.01 g air-dried resin) in the form of Cu(II)-ammine complex ions

Type of resin	Water content %	$[H_2O_2] \times 10^2$ M	$k \times 10^2 (M^{1-n} sec^{-1})$				n	E (KJ/mol)	ΔG^* (KJ/mol)	ΔH^* (KJ/mol)	ΔS^* (J/mol-deg)
			25°C	30°C	35°C	40°C					
16% DVB	18.65	9.5	0.213	0.315	0.429	0.585	0.5	51.8 ± .09	89.18	49.35	− 130.37
12% DVB	22.71	9.5	0.300	0.436	0.541	0.758	0.5	46.4 ± .04	88.44	43.90	− 145.79
4% DVB	33.93	9.5	0.303	0.477	0.757	1.121	0.5	69.72 ± 3.8	85.32	67.18	− 61.35
		7.2	0.619	0.838	1.602	2.426	0.65				
		4.8	0.934	1.547	2.270	3.531	0.7				
		2.4	2.406	3.716	5.688	8.609	0.8				

4. Discussion

The rate constant, which is only temperature dependent, decreases with increasing the degree of resin cross-linkage. This is because the rate constant is a function of the intraparticle diffusion coefficient of the reactant. The latter decreases with increasing the degree of resin cross-linkage (Table I).

The order as a function of time ($n' = 1.0$) was greater than that as a function of concentration ($n = 0.5$). This is a sign of the formation of an intermediate which has an inhibiting effect on the rate of the reaction [15]. The order of the reaction decreases with increasing the initial concentration of H_2O_2. This supports the step-wise mechanism [13, 14].

The formation of the brown compound (peroxo-copper complex) on the resin gave the possibility of isolating the peroxo-copper complex from the reaction medium. Consequently it was possible to carry out an experiment starting with the resin containing the peroxo-copper complex. Figure 3 shows the decomposition-time curves for two reactions having the same origin. The first reaction was carried out in the presence of the resin in the form of the Cu(II)-ammine complex ions.

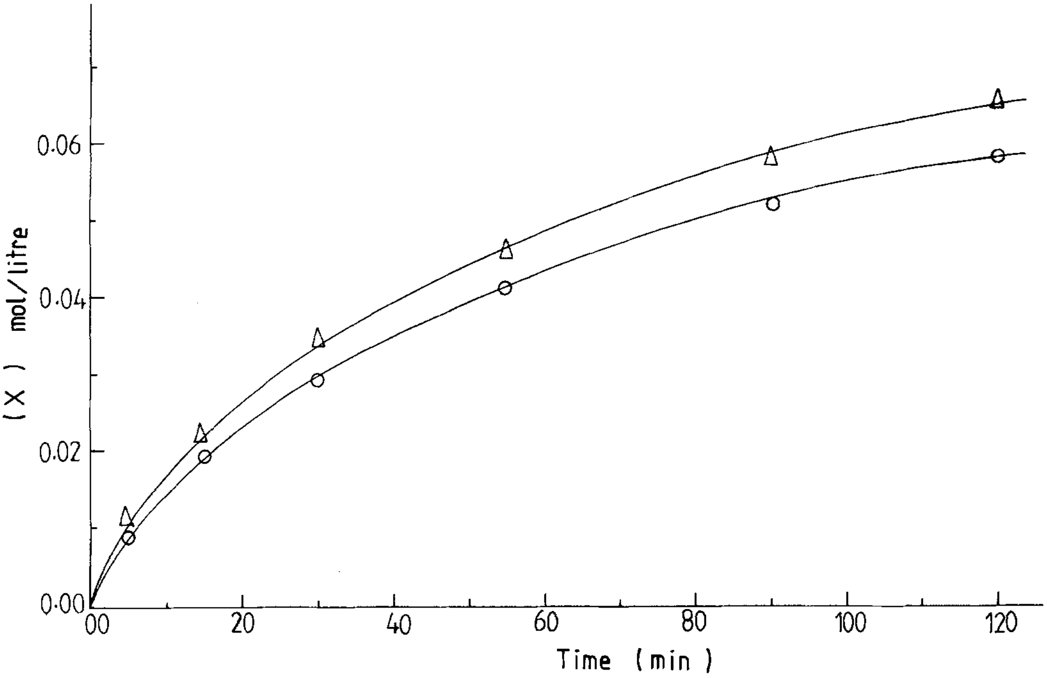

Fig. 3. Illustration of the reaction decomposition-time curves for the decomposition of H_2O_2(9.5×10^{-2} M) in the presence of 0.01 g air-dried Wofatit KPS resin (12% DVB) in the form of ○: Cu(II)-ammine complex ions and △: peroxo-copper complex (brown compound) at 30°C.

After this reaction was finished, the resin was collected, washed and was used in the second reaction in the form of the peroxo-copper complex (brown compound). Under the same working conditions, the rate constant with the peroxo-copper complex was greater than that with the Cu(II)-ammine complex ions. The order of the reaction as a function of concentration was equal to 0.5 in both cases. This experiment on the one hand threw light on the role of the peroxo-copper complex (brown compound) in catalyzing the decomposition reaction of H_2O_2. This means that the brown compound contains an active species. On the other hand, it emphasized the presence of an induction period at the beginning of the reaction due to the formation of the active species when the resin is used in the form of the Cu(II)-ammine complex ions.

It is clear that the value of E (Table 1) with 4% DVB is greater than that with 12 and 16% DVB. This is attributed to the effect of intraparticle diffusion. The latter is much more pronounced with 12 and 16% DVB. This means that intraparticle diffusion can affect the rate of the reaction but it can never be the sole rate-determining step [12]. Any value of E in Table I is smaller than the reported values in the case of the decomposition of H_2O_2 in homogeneous solution [9]. The change in the enthalpy of activation, ΔH^*, (Table I) was smaller than the value of E with the quantity RT (Equation (2)).

The change in the free energy of activation, ΔG^*, (Table I) was in the range 85.3–89.2 KJ/mol. This value is in good agreement with that found in the heterogeneous decomposition of organic peroxides on the benzidine/montmorillonite intercalate [16].

Table I shows that the entropy of activation (ΔS^*) with 4% DVB is greater than that with 12 and 16% DVB. This means that the probability of forming the activated complex was affected by the degree of resin cross-linkage.

There are three possible mechanisms for the reactions: (i) the Cu(II)-ammine complex ion goes into solution where it meets the H_2O_2 molecules causing a homogeneous decomposition reaction, (ii) the Cu(II)-ammine complex ion reacts with H_2O_2 in a thin layer at the surface of the resin particles, and (iii) the reaction occurs throughout the catalyst particle.

The first mechanism is discarded due to the high stability of the Cu(II)-ammine complex ions attached to the resin and no significant release of the complex ions in the medium. If mechanism (ii) is correct, then one would expect that intraparticle diffusion is much slower than the chemical reaction. Intraparticle diffusion can affect the rate of the reaction but it can never be the sole-rate determining step. Accordingly, the reaction has to occur only in a thin layer at the surface of the resin particle because the reactant molecules would react before they have time to penetrate into the interior of the catalyst particle. In this case, the rate of the reaction would be controlled by either film diffusion or chemical reaction at the catalyst surface, whichever of these two processes is the slower one. But since the values of the activation energies obtained in the present investigation are in the range of chemical reaction, i.e., between 41.8 and 83.7 KJ/mol, one has also to dispense with the idea of having the reaction occurring in a thin layer at the surface of the resin particles. Moreover, with film diffusion control, the apparent activation energy is that of liquid phase diffusion, i.e., 8.4 to 20.9 KJ/mol. Mechanism (iii) is therefore the most likely mechanism to occur, i.e., the reaction throughout the catalyst particles. In this case the reactant molecules must diffuse into the reaction zone (i.e., in the pore liquid of the resin) and products must diffuse out.

It is noteworthy to mention that the reaction mechanism in homogeneous and/or heterogeneous catalysis using a resin is essentially the same as catalysis of a liquid phase reaction by ion-exchange resins. It is not, therefore, a true case of heterogeneous catalysis, but may be described more adequately as homogeneous catalysis in the pore liquid [12]. Since the peroxide anion, HOO^- exists [4] in the pH range used in the present work, it is possible to illustrate the mechanism of the reaction as follows:

$$2H_2O_2 \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} 2HOO^- + 2H^+ \tag{4}$$

$$[Cu(NH_3)_4]^{2+} + HOO^- \underset{\text{fast}}{\overset{K_2}{\rightleftharpoons}} [Cu(NH_3)_4OOH]^+ \tag{5}$$

$$[Cu(NH_3)_4OOH]^+ \xrightarrow[\text{slow}]{k_1} \text{Intermediate product (active species)}$$

$$\xrightarrow[\text{fast}]{+HOO^-} [Cu(NH_3)_4]^{2+} + O_2 + 2OH^- \tag{6}$$

$$2H^+ + 2OH^- \underset{\text{fast}}{\overset{\text{very}}{\rightleftharpoons}} 2H_2O \tag{7}$$

From this mechanism the following rate equation could be deduced:

$$\frac{dx}{dt} = -\frac{d[H_2O_2]}{dt} = k_1[Cu(NH_3)_4OOH]^+ \tag{8}$$

but from Equation (5)

$$[Cu(NH_3)_4OOH^+] = K_2[Cu(NH_3)_4^{2+}][HOO^-]$$

and from Equation (4)

$$[HOO^-] = \sqrt{K_1}\,\frac{[H_2O_2]}{[H^+]}$$

thus,

$$\frac{dx}{dt} = -\frac{d[H_2O_2]}{dt} = k_1\sqrt{K_1}K_2\,\frac{[Cu(NH_3)_4^{2+}][H_2O_2]}{[H^+]} \tag{9}$$

where k_1 is the rate constant of the rate determining step (Equation (6)); K_1 and K_2 are the equilibrium constants of Equations (4) and (5), respectively. From Equation (9), it is clear that the rate of the reaction is proportional to $[H^+]^{-1}$, $[H_2O_2]$ and $[Cu(NH_3)_4^{2+}]$. Although the effect of pH on the rate of the reaction could not be studied in the present investigation, it is obvious that the rate of the reaction decreases with increasing the hydrogen ion concentration. This is also attributed to the fact that the Cu(II)-ammine complex ion is unstable in acidic medium.

The intermediate product (active species) in Equation (6) may contain the free radical ($HO_2^{\cdot}$). In this case the active species may have the formula [4], $[Cu^{(I)}(NH_3)_xHO_2^{\cdot}]^+$, i.e., it contains a univalent cuprous ion. x is introduced in the last formula as the cuprous ions have a tendency to be coordinated linearly with saturated nitrogen ligands. This means that the decomposition of H_2O_2 by copper complexes involves a redox reaction Cu(II) $\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$ Cu(I). The latter appears to favour the catalytic decomposition of H_2O_2 [4].

One can explain the kinetic data Equation (8) can be obtained by assuming the following sequence of reactions:

$$2H_2O_2 \overset{K_1}{\rightleftharpoons} 2H^+ + 2HOO^- \tag{4}$$

$$[Cu(NH_3)_4]^{2+} + HOO^- \overset{K_2}{\rightleftharpoons} [Cu(NH_3)_4OOH]^+ \tag{5}$$

$$[Cu(NH_3)_4OOH]^+ \xrightarrow{k_1} [Cu^I(NH_3)_x(HO_2^{\cdot})]^+ \tag{10}$$

$$[\mathrm{Cu^I(NH_3)}_x\mathrm{(HO_2^{\cdot})}]^+ + \mathrm{HOO^-} \xrightarrow{k_2} [\mathrm{Cu(NH_3)_4}]^{2+} + \mathrm{O_2} + 2\mathrm{OH^-} \tag{11}$$

$$2\mathrm{H^+} + 2\mathrm{OH^-} \rightleftharpoons 2\mathrm{H_2O} \tag{7}$$

This system incorporates both HO_2^- and radical processes.

Using the steady state approximation for the calculation of the concentration of the intermediate product, $[\mathrm{Cu^I(NH_3)}_x\mathrm{HO_2^{\cdot}}]^+$, we get:

$$\begin{aligned}&\mathrm{d}[\mathrm{Cu^I(NH_3)}_x\mathrm{(HO_2^{\cdot})}]^+/\mathrm{d}t\\&\quad = k_1[\mathrm{Cu(NH_3)_4OOH^+}] - k_2[\mathrm{Cu^I(NH_3)}_x\mathrm{(HO_2^{\cdot})^+}][\mathrm{HOO^-}] = 0\end{aligned} \tag{12}$$

Therefore,

$$[\mathrm{Cu^I(NH_3)}_x\mathrm{(HO_2^{\cdot})^+}] = \frac{k_1[\mathrm{Cu(NH_3)_4OOH^+}]}{k_2[\mathrm{HOO^-}]} \tag{13}$$

and

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = k_1[\mathrm{Cu(NH_3)_4OOH^+}], \tag{14}$$

which is the same as expression (8). This means that according to the steady-state approximation the rate of formation of O_2 is equal to the rate of the formation of the intermediate product (active species) and both are directly proportional to the concentration of the complex ion, $[\mathrm{Cu(NH_3)_4OOH}]^+$.

The brown compound (peroxo-copper complex) is formed in Equation (6). It is stable even after the experiment was completed. It was found to decompose with a change in its colour, giving a green colour on standing for several hours and a sky-blue compound on standing for several days. This change in colour was also observed in the homogeneous decomposition of H_2O_2 with Cu(II)-ammine complex ions [9]. The brown compound was regenerated to the H^+-form with 2N HCl and its total weight capacity was determined. This was found to be unchanged. This indicated that the resin was not degraded during the decomposition reaction of H_2O_2.

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