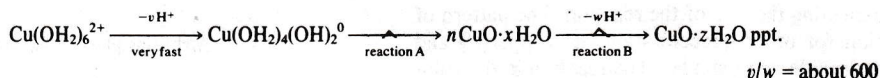# A KINETIC STUDY ON THE PRECIPITATION REACTION OF HYDROUS COPPER(II) OXIDE

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Abstract—A kinetic study on the precipitation of hydrous copper(II) oxide has been made. The reaction proceeds through two rate-determining states, A is homogeneous and B is heterogeneous:

$$Cu(OH_2)_6^{2+} \xrightarrow[\text{very fast}]{-vH^+} Cu(OH_2)_4(OH)_2^0 \xrightarrow[\text{reaction A}]{} nCuO \cdot xH_2O \xrightarrow[\text{reaction B}]{-wH^+} CuO \cdot zH_2O \text{ ppt.}$$

$$v/w = \text{about 600}$$

Two reaction times, τ_A and τ_B, defined for the A and B reactions, were found to be functions of the initial concentration of copper(II) ion and hydroxide ion.

$$1/\tau_A = k_A[Cu^{2+}]_0[OH^-]_0 \tag{1}$$

$$1/\tau_B = k_B[OH^-]_0 \tag{2}$$

where $k_A = 1.6 \times 10^3$ mole$^{-2} \cdot$ sec^{-1} and $k_B = 1.6$ mole$^{-1} \cdot$ sec^{-1} at 50°C.
Equation (2) holds under the conditions $[Cu^{2+}]_0 = 1.0 \times 10^{-3}$ mole $\cdot$ l^{-1}. The activation energies, $E_A = 4.6$ Kcal $\cdot$ mole^{-1} and $E_B = 18.3$ Kcal $\cdot$ mole^{-1}, were obtained. The reaction times, τ_A and τ_B, were affected by anions and by the dielectric constant of the solvent. The reaction times in the presence of anions could be expressed as follows.

$$1/\tau_A = (k_A + k_{Ax}[X^-]^{n_{Ax}})[Cu^{2+}]_0[OH^-]_0$$
$$1/\tau_B = (k_B + k_{Bx}[X^-]^{n_{Bx}})[Cu^{2+}]_0 \tag{3}$$

where $n_{Ax} = 2.5$, $k_{Ax} = 5.0 \times 10^8$ mole$^{-3} \cdot$ sec^{-1}, $n_{Bx} = 0.89$ and $k_{Bx} = 4.0 \times 10^2$ mole$^{-2} \cdot$ sec^{-1} for chloride ion, and $n_{Ax} = 2.8$, $k_{Ax} = 5.4 \times 10^6$ mole$^{-3} \cdot$ sec^{-1}, $n_{Bx} = 0.91$ and $k_{Bx} = 8.3 \times 10$ mole$^{-2} \cdot$ sec^{-1} for nitrate ion, at 50°C.

INTRODUCTION

Aquated metal ions precipitate as hydrous metal oxides in alkaline solutions. These reactions have been widely used to separate the metal ions from aqueous solutions in laboratory analysis. Many reports concern the equilibria of the precipitation reactions, but kinetic investigation have not been performed. The precipitation rates are extremely different from one metal ion to another. If the rate could be controlled, new analytical or industrial uses might develop.

The present work is a kinetic study of precipitation of an aquated metal ion. The copper(II) ion has been chosen and the reaction rate investigated in aqueous solution in the absence and presence of other electrolytes and in mixtures of water and organic solvents. An aquated metal ion dissociates protons during the formation of the hydrous metal oxide, so the rate was measured potentiometrically as a function of time.

EXPERIMENTAL

Reagents. Copper(II) perchlorate solutions, 1 M and 0.1 M: Cu(ClO₄)₂·6H₂O of analytical grade was dissolved in pure water, filtered through a glass filter and diluted to the desired concentration, and standardized iodometrically. Other reagents were of analytical grade.

Procedure. The required volume of the copper(II) solution was taken in a 150 ml cylindrical glass vessel and diluted to 100 ml with pure water. A rubber stopper, which was fitted with a double electrode, Horiba 6026-05T, and a glass stirrer with a small propeller driven by a d.c. motor, a glass tube with a cap

through which the alkaline solution will be added, and another tube for nitrogen gas, was inserted into the reaction vessel. The vessel was thermostatted in a water bath within ±0.2°C and allowed to stand for at least 30 min under nitrogen. The required volume of sodium hydroxide solution was added from a glass syringe within 0.5 sec. The pH of the solution was recorded as a function of time by means of a Horiba Recording Auto Titrator Type RAT-11.

The usual sleeve type calomel electrode was not used because the potassium chloride diffusing from it affected the reaction rate. Instead a double glass electrode, which hardly introduces any potassium chloride was used to measure pH of the solution.

At the room temperature, the reaction rate was very slow. So, the measurements were performed at 50°C except for the measurements of the activation energy.

Response time of glass electrode. To check the response time of the glass electrode, a 0.5 ml of 0.1 M sodium hydroxide and a 0.5 ml of 0.1 M sulfuric acid were added separately to a 100 ml of pure water and the time required to reach the equilibrium pH value was measured. It took about 80 sec for the alkaline solution and about 40 sec for the acidic solution. Under the present experimental condition, this dead time due to the electrode response did not affect our measurements.

RESULTS AND DISCUSSION

pH *Change as a function of time*

pH change as function of time is shown in Fig. 1 when a 0.5×10^{-3} M sodium hydroxide was added to a 1.0×10^{-3} M copper(II) perchlorate solution at 50°C. Until approx. 20 min has passed after the sodium hydroxide had been added, pH of the solution remains almost

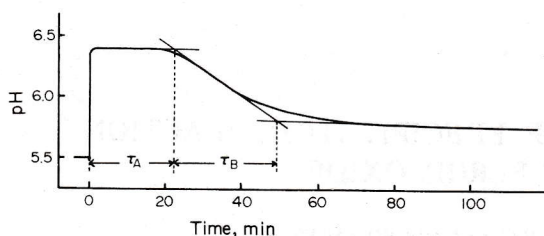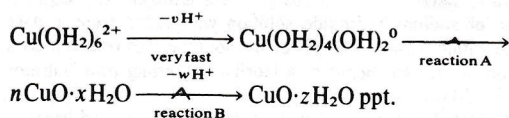Fig. 1. pH change as a function of time. Cu(II): 1.0×10^{-3} M,
NaOH: 0.5×10^{-3} M. Temp.: 50°C.

Fig. 3. Arrhenius plots of k_A and k_B.

constant. Then the pH begins to decrease as the pre-
cipitation of white copper(II) hydroxide takes place. The
pH reaches an equilibrium value after about 80 min has
passed, indicating the end of the reaction. The pattern of
the reaction for other concentrations of copper(II) and
sodium hydroxide were similar. The reaction in the solu-
tion is homogeneous in reaction A in which no change in
pH is observable and heterogeneous in reaction B in
which the pH decreases and the copper(II) hydroxide
precipitates.

The protons dissociated in reaction B, however, con-
sidering the change in pH, only amount to about 1/600 of
the moles of sodium hydroxide added. So, most of the
hydroxide ion reacts with the protons dissociated from
the aquated Cu^{2+} ion immediately after the sodium
hydroxide was added. The concentration of the Cu^{2+} ion,
measured by means of copper sensitive electrode,
however, was constant during the reaction. Considering
the copper electrode potential after and before the
sodium hydroxide had been added, Cu^{2+} ions cor-
responding to half the moles of sodium hydroxide added
reacted on adding the alkali. The conductivity did not
change in reaction A, and slightly increased in reaction
B. This increase may be due to the increase in hydrogen
ion concentration. The following reactions probably
occur[1], and the rate determining stages in the reactions
A and B may be as indicated below.

$$Cu(OH_2)_6^{2+} \xrightarrow[\text{very fast}]{-v H^+} Cu(OH_2)_4(OH)_2^0 \xrightarrow{\quad} \text{reaction A}$$

$$n CuO \cdot x H_2O \xrightarrow[\text{reaction B}]{-w H^+} CuO \cdot z H_2O \text{ ppt.}$$

where v/w = about 600.
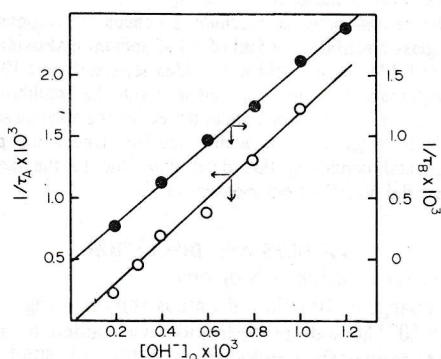

Fig. 2. Plots of $1/\tau_A$ and $1/\tau_B$ vs initial hydroxide ion, $[OH^-]_0$.
Cu(II): 1.0×10^{-3} M, Temp.: 50°C.

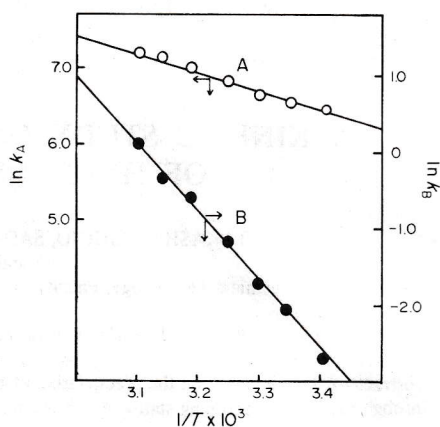### Rate equation and rate constant

To discuss the reaction rates, the reaction times, τ_A
and τ_B, are defined as indicated in Fig. 1. If the recipro-
cal of the reaction time $1/\tau_i$, i = A or B, where mth and
nth orders of the initial concentrations of copper(II) ion
and hydroxide ion, it would follow the following rate
equation.

$$1/\tau_i = k_i [Cu^{2+}]_0^{m_i} [OH^-]_0^{n_i} \qquad (1)$$

where i = A or B, k_i = rate constant, $[Cu^{2+}]_0$ and
$[OH^-]_0$ = respective initial concentrations of copper(II)
ion and hydroxide ion, and m_i and n_i = respective reac-
tion orders of copper(II) and hydroxide ions for the
reaction i.

To determine value of n_i, the reaction times, τ_A and τ_B,
were measured at different concentrations of hydroxide
ion for constant concentration of copper(II) ion at 50°C.
The results showed a linear relationship of both $1/\tau_A$ and
$1/\tau_B$ with the concentration of hydroxide ion as seen in
Fig. 2, indicating $m_A = 1$ and $m_B = 1$. $k_A [Cu^{2+}]_0^{m_A} = 1.7$
$mole^{-1} \cdot sec^{-1}$ and $k_B [Cu^{2+}]_0^{m_B} = 1.6$ $mole^{-1} \cdot sec^{-1}$ were
obtained from the slope. Then the reaction times, τ_A and
τ_B were measured at the different concentrations of
copper ion, and the result showed the linear relationship
of $k_A [Cu^{2+}]_0^{n_A}$ on the concentration of Cu^{2+} ion, indicat-
ing $n_A = 1$. $k_A = 1.6 \times 10^3$ $mole^{-2} \cdot sec^{-1}$ was obtained
from the slope. However, a similar relationship for
$k_B [Cu^{2+}]_0^{n_B}$ was not observed. Therefore, for the reac-
tion B, τ_B may be expressed by the following equation at
$[Cu^{2+}]_0 = 1.0 \times 10^{-3}$ M.

$$1/\tau_B = k_B [OH^-]_0 \qquad (2)$$

where $k_B = 1.6$ $mole^{-1} \cdot sec^{-1}$.

Activation energies of the reactions A and B

The reaction times, τ_A and τ_B, were measured for the
reaction between 1.0×10^{-3} M copper(II) ion and 0.5×10^{-3} M sodium hydroxide at temperatures between 20°C
and 50°C, and natural logarithms of k_A and k_B were
plotted vs the inverse of the absolute temperature.
Figure 3 shows the linear dependance and activation
energies $E_A = 4.6$ kcal $\cdot$ mole^{-1} and $E_B =$
18.3 kcal $\cdot$ mole^{-1} were obtained for reactions A and B
from the slopes.

Table 1. The mole fraction of organic solvent and dielectric constant at the minimum reaction rate, $1/\tau_A$, at 50°C

Solvent	Mole fraction at minimum of $1/\tau_A$	Dielectric constant ε
Acetone	0.07	57.3
Ethanol	0.10	56.8
Methanol	0.16	58.5
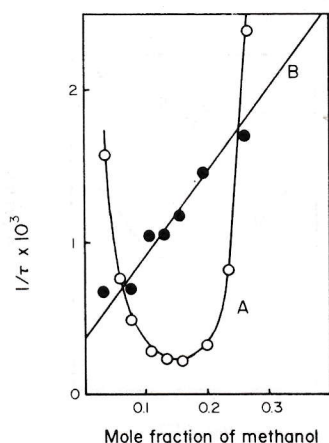
Fig. 4. Reaction rates, $1/\tau_A$ and $1/\tau_B$, in the mixture of water and methanol. Cu(II): 1.0×10^{-3} M, NaOH: 0.5×10^{-3} M.

Solvent effect on the reaction rate

The reaction rates in mixtures of methanol and water were measured at 50°C. The reaction rates $1/\tau_A$ and $1/\tau_B$ are plotted against the mole fraction of the methanol in Fig. 4. reaction A decreases with increase of the mole fraction up to 0.16, and then increases above 0.16. The rate of the reaction B increases with increase in mole fraction of methanol. Similar behavior was observed in mixtures with acetone or ethanol.

The mole fraction of the organic solvent at the minimum reaction rate of A are shown in Table 1 together with the dielectric constants of the solvent mixture[2]. The mole fractions vary, but the dielectric constants are almost constant. So, the rate of the reaction A may be affected mainly by the dielectric constant of the solvent, the rate decreasing with decrease in dielectric constant down to $\epsilon = 57$, further decrease in ϵ then dials to an increased rate.

The rate of reaction B increases with increase in mole fraction of the organic solvent. This may be due to the solubility of the copper(II) hydroxide.

Effect of electrolyte

To investigate the effect of salts on the reaction rate, it was measured with the presence of different concentrations of sodium chloride, sodium perchlorate and sodium sulfate. The pH as function of time in the presence of sodium chloride and sodium sulfate are shown in Figs. 5 and 6, respectively. The reaction rates of both A and B increase with increase in sodium chloride concentration as seen in Fig. 5. The rate of the increase for the B is larger than that for the A. The same behavior was observed with sodium nitrate. However,
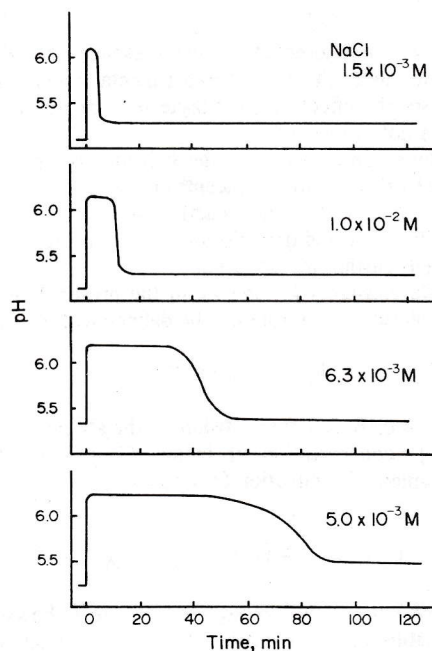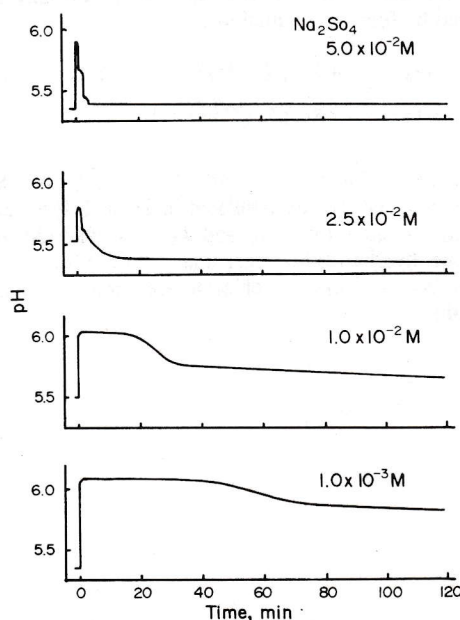

Fig. 5. pH changes as a function of time in the presence of sodium chloride. Cu(II): 1.0×10^{-3} M, NaOH: 0.5×10^{-3} M. Temp.: 50°C.

Fig. 6. pH changes as a function of time in the presence of sodium sulfate. Cu(II): 1.0×10^{-3} M, NaOH: 0.5×10^{-3} M.

Table 2. The reaction rates, $1/\tau_A$ and $1/\tau_B$, in the presence of anions at 50°C

Anion	A		B^+	
	n_{Ax}	k_{Ax}, $mol^{-3} \cdot sec^{-1}$	n_{Bx}	k_{Bx}, $mol^{-2} \cdot sec^{-1}$
Cl^-	2.5	5.0×10^8	0.89	4.0×10^2
NO_3^-	2.8	5.4×10^6	0.91	8.3×10

$+$ at $[Cu^{2+}]_o = 1.0 \times 10^{-3}$ M.

the rate was not affected by the presence of sodium perchlorate under the present experimental condition up to 1 M. So, the effect of electrolyte may be due to the anion and not to the cation.

In sodium sulfate solution, the behavior is similar to sodium chloride up to a concentration of 1.0×10^{-2} M. However, above this the reaction involved is quite different from the sodium chloride as seen in Fig. 5. This effect needs further investigation.

The rate constants k'_A and k'_B in the presence of the sodium chloride and nitrate can be defined as follows.

$$k'_i = k_i + k_{ix}[X^-]^{n_{ix}} \qquad (3)$$

where i = A or B, k_i = rate constant in the absence of the salt, $[X^-]$ = concentration of anion X^-, n_{ix} = reaction order of anion. The equation (3) leads to:

$$\log(k'_i - k_i) = \log k_{ix} + n_{ix} \log[X^-]. \qquad (4)$$

Log $(k'_i - k_i)$ are plotted vs log $[Cl^-]$. Figure 7 shows the linear relationship, and $n_{ACl} = 2.5$ and $n_{BCl} = 0.89$ were obtained from the slope and $k_{ACl} = 5.0 \times 10^8$ mole$^{-3} \cdot$ sec^{-1} and $k_{BCl} = 4.0 \times 10^6$ mole$^{-2} \cdot$ sec^{-1} were obtained from the intercept at $[Cl^-] = 1$. Plots for nitrate showed similar behavior. The reaction times τ_A and τ_B, in the presence of sodium chloride and nitrate may be expressed by following equations.

$$1/\tau_A = (k_A + k_{Ax}[X^-]^{n_{Ax}})[Cu^{2+}]_0[OH^-]_0 \qquad (5)$$

$$1/\tau_B = (k_B + k_{Bx}[X^-]^{n_{Bx}})[OH^-]_0 \qquad (6)$$

where eqn (6) is for the condition $[Cu^{2+}]_0 = 1.0 \times 10^{-3}$ M. n_{Ax}, n_{Bx}, k_{Ax} and k_{Bx} are tabulated in Table 2. It is very interesting to note that k_{Ax} and k_{Bx} for chloride are about one hundred-fold larger than those for nitrate, however, n_{Ax} and n_{Bx} for chloride are similar to those for nitrate.
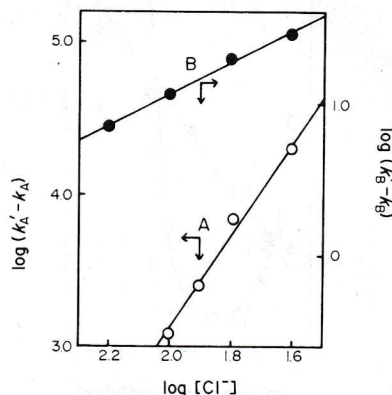

Fig. 7. Plot of $\log(k'_i - k_i)$, i = A or B, vs $\log[Cl^-]$. Cu(II): 1.0×10^{-3} M, NaOH: 0.5×10^{-3} M. Temp.: 50°C.

CONCLUSION

The precipitation of hydrous copper(II) oxide proceeds through two rate-determining stages, one of which is homogeneous and the other heterogeneous. However, the mechanism have not been established. The reaction rate was affected by the dielectric constant of the solvent and was accelerated by some anions. However, perchlorate ion did not affect the rate. This accelation mechanism seems to be complicated and will need further investigation.

This paper reports only the kinetic behavior of copper(II) hydroxide precipitation.

REFERENCES

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2. G. Åkerlöf, *J. Am. Chem. Soc.* **54**, 4125 (1932).