Kinetics of ligand exchange reaction of Cu(OH)$_2$-poly(vinyl alcohol) complex with potassium cyanide

Chien-Lang Ku and Jyh-Horung Chen*
Department of Chemistry, National Chung-Hsing University, Taichung, Taiwan, R.O.C. 40227
and Lian-Pin Hwang
Department of Chemistry, National Taiwan University and Institute of Atomic and Molecular Science, Academia Sinica, Taipei, Taiwan, R.O.C.
(Received 20 August 1990; revised 11 October 1990; accepted 14 December 1990)

The kinetics of the ligand exchange reaction between the green complex of Cu(OH)$_2$ included in poly(vinyl alcohol) (PVA) and potassium cyanide (CN$^-$) was studied by a stopped-flow method at pH 11.6-12.60, at ionic strength $\mu = 0.1$ (KCl) and at 25 C. The Cu(OH)$_2$ is believed to be of type Cu$_n$(OH)$_{2n-2}$. Therefore the polynuclear complex of the Cu$_n$(OH)$_{2n-2}$ included in helical PVA chains can be expressed as PVA-Cu$_n$(OH)$_{2n-2}$. The rate law, written as:

$$r = \frac{d[PVA - Cu_n(OH)_{2n-2}]}{dt}$$

can be explained by four different reaction paths. In paths 1 and 2, the reactions are initiated by attack of H$^+$ on the polynuclear copper complex Cu$_n$(OH)$_{2n-2}$ included inside the PVA helical chains. In path 1, the intermediate, Cu$_n$(OH)$_{2n-3}$ is formed in the bulk water. However, in path 2, the intermediate, PVA Cu$_n$(OH)$_{2n-1}$(H$_2$O), is formed inside the PVA helix. In the highly alkaline region, paths 3 and 4 involve the ligand substitution reaction. In path 3, the Cu$_n$(OH)$_{2n-2}$ is believed to be released from PVA helical chain and combines with CN$^-$ in the exterior bulk water. In path 4, the rate-determining step is the bimolecular ligand exchange reaction between PVA-Cu$_n$(OH)$_{2n-2}$ and CN$^-$.

A possible mechanism for the substitution reaction is discussed.

(Keywords: kinetics; ligands; complexes)

INTRODUCTION

An aqueous solution of Cu$^{2+}$ ion and poly(vinyl alcohol) (PVA) shows a green complex at pH > 6. It has been believed to date that the complex has a chelate type structure$^{1,2}$. However, the experimental results of electron spin resonance and proton relaxation rate measurement cannot be explained by the chelate type structure of the green complex$^{3,4}$. In accordance with magnetic susceptibility measurement, Yokoi et al.$^{3,5}$ showed that the effective moment, $\mu_{eff}$, determined for aqueous PVA Cu$^{2+}$ solution was 1.33 $\mu_B$ at pH 7.0 or 1.47 $\mu_B$ at pH 9.0. The result indicates the formation of a polynuclear Cu$^{2+}$ complex with a strong antiferromagnetic interaction at pH > 6. This polynuclear complex Cu$_n$(OH)$_2$ is believed to be of the type [Cu$_n$(OH)$_{2n-2}$. Furthermore, the invariance of the proton spin-lattice relaxation rate of H$_2$O with increase of Cu$^{2+}$ ion concentration in aqueous PVA-Cu$^{2+}$ solution at pH 12.5 suggests that all the Cu$^{2+}$ ions, in the form of cupric hydroxide, are surrounded by helical PVA chains with their hydrophobic backbones facing towards the complex and the hydrophilic OH groups facing towards the bulk water$^{3,4}$. The polynuclear copper of Cu$_n$(OH)$_{2n-2}$ included in PVA chains can be expressed as PVA-Cu$_n$(OH)$_{2n-2}$. This inclusion type structure of PVA Cu$_n$(OH)$_{2n-2}$ complex is sometimes called a 'cluster model' (or clathrate type) structure$^{6}$. According to the cluster model, the PVA chain plays a role in the prevention of cupric hydroxide clusters from aggregations.

At pH > 6 the green solution shows three absorption bands at 260, 370 and 630 nm. It is widely accepted that the 630 nm band is due to the d-d transition and the 260 nm band is due to charge transfer$^7$. The absorption band at 370 nm may be due to the $p_{xy}(O) \rightarrow d_{x^2-y^2}(Cu)$ charge transfer transitions$^3$, where $p_{xy}(O)$ denotes the $p_x$ orbital on bridging OH group in Cu$_n$(OH)$_{2n-2}$. The decomposition of the PVA Cu$_n$(OH)$_{2n-2}$ complex by the cyanide anion can be detected by the disappearance of the absorption shoulder band at about 370 nm, indicating that the cyanide breaks the Cu-OH bond of Cu$_n$(OH)$_{2n-2}$ included in the PVA chain.

Studies of the kinetics and mechanisms of the exchange reactions of Cu$^{2+}$-PVA complexes with ethylene diamine tetra-acetic acid (EDTA) have been reported by Suzuki et al.$^8$. They presumed that the Cu$^{2+}$-PVA complex had a chelate type structure$^{1,2,8}$. In the present study...
paper, however, the cluster model structure for the green complex is adapted to the investigation of the ligand exchange kinetics between PVA-Cu, (OH) 2+2 complex and potassium cyanide in aqueous solution.

EXPERIMENTAL

Chemicals

Hydrolysed (98.9%) PVA with weight-average molecular weight $M_w = 27000$ and number-average molecular weight $M_n = 14000$ was purchased from Aldrich Chemical Company. The triad tacticity of PVA with mm 22%, mr 50% and rr 28% was derived from the methine carbon peak in $^{13}$C measurements on a Bruker AM-400 NMR spectrometer$. The concentration of PVA was expressed in terms of the monomer residues. All other reagents were of analytical grade and were used without further purification.

Cu$^{2+}$ ion solutions were prepared from a stock solution of CuCl$_2$·2H$_2$O. PVA-Cu$_x$(OH)$_{2n-2}$ complex solutions were prepared as follows. An aqueous solution of Cu$^{2+}$ ion was added to the PVA solution, and the pH of the mixed solution was adjusted to the desired pH value with KOH solution. The ionic strengths of the PVA Cu$_x$(OH)$_{2n-2}$ were maintained at 0.1 M with KCl. The complex solutions thus obtained were equilibrated at 25 °C for 1 day before each experiment.

Method

U.v.-visible spectra were measured on a Hitachi U3210 spectrophotometer. The reactions were carried out in a stopped-flow apparatus of Union GA 401 spectrophotometer. The pH measurements were carried out with a Suntex SP-5A pH meter. In most cases, the kinetic measurements were made as follows. One solution containing ~0.02 M PVA and ~4 × 10$^{-3}$ M Cu$^{2+}$ ion was brought to the starting pH. Ionic strength was maintained at 0.1 M with KCl. A second solution of KCN, with KCl added to bring the ionic strength to 0.1 M, was brought to the same pH. These solutions were mixed in the ratio 1:1 (v/v) in a 1 cm cell of the stopped-flow spectrophotometer. An optical density range of 0 to 1 at 370 nm was used for the absorption measurements. All rates were measured at 25.0 ± 1.0°C and were averaged over six runs.

RESULTS AND DISCUSSION

Kinetic results

When excess cyanide solution is added to a solution of the PVA Cu$_x$(OH)$_{2n-2}$, the green solution discolours. This suggests that the exchange of the hydroxy in the PVA Cu$_x$(OH)$_{2n-2}$ complex with cyanide anion occurs under these experimental conditions and the reaction goes nearly to completion so that the reverse reaction can be neglected in the kinetic study. The overall ligand substitution in the presence of H$^+$ may be described as:

$$\text{PVA-Cu}_x(\text{OH})_{2n-2} + 4\text{CN}^- \rightarrow \text{PVA} + \text{Cu}^2(\text{CN})_{2}^{4-}$$
$$+ \frac{1}{2}\text{(CN)}_2 + \text{Cu}_{n-1}(\text{OH})_{2n-4} + 2\text{H}_2\text{O} \quad (1)$$

and in the highly alkaline region, it may be depicted as:

$$\text{PVA-Cu}_x(\text{OH})_{2n-2} + 4\text{CN}^- \rightarrow \text{PVA} + \text{Cu}^2(\text{CN})_{2}^{4-} + \frac{1}{2}\text{(CN)}_2 + \text{OH}^- + \text{Cu}_{n-1}(\text{OH})_{2n-3} \quad (2)$$

The reaction rates in mixing PVA-Cu$_x$(OH)$_{2n-2}$ complexes with a large excess of cyanide anions may be followed by monitoring the disappearance of absorption at 370 nm. The rates were too fast to be measured by conventional means and were therefore measured by the stopped-flow technique. Plots of ln(A$_n$ - A$_t$) as a function of reaction time, $t$, were obtained by using an extrapolated value (infinite value for the reaction) for A$_n$, A$_t$, and A$_0$. All plots obtained in these experiments showed, as expected, that the reaction in the presence of a large excess of cyanide anions was of pseudo-first order. Thus, the reaction of
PVA Cu\textsubscript{4+}CN\textsuperscript{-2} complex with a large excess of cyanide anion is expressed as:

$$r = \frac{d\left[\text{PVA Cu}_{4+}(\text{OH})_{\subscript{2n-2}}\right]}{dt}$$

$$= k_{\text{obs}}\left[\text{PVA Cu}_{4+}(\text{OH})_{\subscript{2n-2}}\right]$$

(3)

where $k_{\text{obs}}$ is the pseudo-first order rate constant.

The dependence of $k_{\text{obs}}$ on the initial concentration of cyanide anion was studied at a constant concentration of PVA Cu\textsubscript{4+}(OH)\textsuperscript{2+} and at pH 11.90. The plot of $k_{\text{obs}}$ against the initial concentration of cyanide anions for different PVA concentration is shown in Figure 3, from which it was found that $k_{\text{obs}}$ is proportional to [CN\textsuperscript{-}] with the slope $k_1$. If [CN\textsuperscript{-}] >> [Cu\textsuperscript{2+}], equation (3) can be rewritten as:

$$r = \frac{d\left[\text{PVA Cu}_{4+}(\text{OH})_{\subscript{2n-2}}\right]}{dt}$$

$$= k_1[\text{CN}][\text{PVA Cu}_{4+}(\text{OH})_{\subscript{2n-2}}]$$

(4)

With the help of data in Figure 3, it is shown in Figure 4 that within the experimental error, $k_1$ is inversely proportional to the concentration of PVA. The result may be expressed by:

$$k_1 = \frac{k_2}{[\text{PVA}]} + k_3$$

(5)

Substituting equation (5) into equation (4), the rate of ligand exchange reaction is expressed as:

$$r = k_2[\text{CN}][\text{PVA Cu}_{4+}(\text{OH})_{\subscript{2n-2}}]$$

$$+ k_3[\text{CN}][\text{PVA Cu}_{4+}(\text{OH})_{\subscript{2n-2}}]$$

(6)

Finally, the ligand exchange reactions were measured at 25°C with pH in the range 11.6-12.6. Figures 5 and 6 show plots of the $k_2$ and $k_3$ against the initial hydrogen ion concentration, respectively. From Figures 5 and 6,

**Figure 3** Plot of $k_{\text{obs}}$ versus cyanide anion concentration. [Cu\textsuperscript{2+}] = 5 x 10\textsuperscript{-4} M; [PVA] = 0.01 M (A), 0.02 M (D), 0.03 M (O), 0.04 M (x), 0.06 M (●); pH = 11.90; $\mu$ = 0.1 (KCl); 25°C

**Figure 4** Plot of $k_1$ versus reciprocal of PVA concentration for the ligand exchange reaction obtained from data given in Figure 3. [Cu\textsuperscript{2+}] = 5 x 10\textsuperscript{-4} M; pH = 11.90; $\mu$ = 0.1 (KCl); 25°C

**Figure 5** Plot of $k_2$ versus hydrogen ion concentration for the ligand exchange reaction. [PVA Cu\textsubscript{4+}(OH)\textsuperscript{2+}] = 5 x 10\textsuperscript{-4} M; [Cu\textsuperscript{2+}] = 5 x 10\textsuperscript{-4} M; $\mu$ = 0.1 (KCl); 25°C

**Figure 6** Plot of $k_3$ as a function of hydrogen ion concentration for the ligand exchange reaction. [PVA Cu\textsubscript{4+}(OH)\textsuperscript{2+}] = 5 x 10\textsuperscript{-4} M; [Cu\textsuperscript{2+}] = 5 x 10\textsuperscript{-4} M; $\mu$ = 0.1 (KCl); 25°C
Kinetics of ligand exchange reaction: C.-L. Ku et al.

it is evident that \( k_2 \) and \( k_3 \) are linearly related to the hydrogen ion concentration. They can be expressed by equations (7) and (8), respectively:

\[
k_2 = 3.78 \times 10^{12}[H^+] + 5.04 \quad (7)
\]

\[
k_3 = 5.17 \times 10^{14}[H^+] + 482 \quad (8)
\]

Substituting equations (7) and (8) into equation (6), we obtain the following rate expression:

\[
\frac{dE_{PVA-Cu.(OH)_{2n-2}^2}}{dt} = 3.78 \times 10^{12} [H^+][CN^-][PVA-Cu.(OH)_{2n-2}^2] \quad (9)
\]

Mechanism of the ligand exchange reaction

The rate law of the ligand exchange reaction between PVA, Cu(OH)_{2n-2} complex and cyanide anion, as given in equation (9), may be described by the following mechanisms with four paths.

For paths 1 and 2, the reactions are initiated by the attack of \( H^+ \) on the polynuclear copper complex \( Cu_{n}(OH)_{2n-3} \) included inside the PVA chain.

Path 1. The rate law of path 1 is:

\[
r = 3.78 \times 10^{12} [H^+][CN^-][PVA-Cu_{n}(OH)_{2n-2}^2] \quad (10)
\]

The proposed mechanism is as follows:

\[
PVA-Cu_{n}(OH)_{2n-2}^2 + H^+ \rightarrow PVA + Cu_{n-1}(OH)_{2n-3} + H_2O \quad (equilibrium)
\]

\[
Cu_{n}(OH)_{2n-3} + CN^- \rightarrow CU_{n-1}(OH)_{2n-4} + OH^- \quad (RDS)
\]

\[
CuCN^+ + CN^- \rightleftharpoons Cu(CN)_2^2 (10a)
\]

where \( K_1 \) is the equilibrium constant of step 1 and \( k_1 \) is the rate constant of the rate-determining step (RDS) and \( k_1K_1/[H_2O] = 3.78 \times 10^{13} \text{s}^{-1} \text{M}^{-1} \).

Once protonated, the unstable intermediate \( Cu_{n}(OH)_{2n-3} \) escapes from the PVA chain to the bulk water and subsequently they are taken up by \( CN^- \) to form \( CuCN^+ \). This step is considered to be the rate-determining step. After several post-equilibrium steps, \( Cu(CN)^2^- \) is formed. Finally, the intermediate \( Cu(CN)_2^2 \) complex undergoes a redox reaction to form \( Cu(CN)_3^2^- \). The evidence of \( Cu(CN)_3^2^- \) will be explained in the following section.

Path 2. The rate law of path 2 is:

\[
r = 5.17 \times 10^{14}[H^+][CN^-][PVA-Cu_{n}(OH)_{2n-2}^2] \quad (11)
\]

The proposed mechanism is as follows:

\[
PVA-Cu_{n}(OH)_{2n-2}^2 + H^+ \rightarrow PVA + Cu_{n-1}(OH)_{2n-3}(H_2O) \quad (equilibrium)
\]

\[
PVA-Cu_{n}(OH)_{2n-3}(H_2O) + CN^- \rightarrow PVA + CuCN^+ + Cu_{n-1}(OH)_{2n-4} + OH^- + H_2O \quad (RDS)
\]

The next reaction steps are as given in equation (10a).

In the above equations, \( K_2 \) is the equilibrium constant of step 1, \( k_2 \) is the rate constant for the rate-determining step and \( k_2K_2 = 5.17 \times 10^{14} \text{s}^{-1} \text{M}^{-2} \).

After protonation, the intermediate, \( PVA-Cu_{n}(OH)_{2n-3}(H_2O) \), is formed inside the PVA chain. Then the \( CN^- \) diffuses into the PVA chain and attacks the \( Cu(OH) \) bond of \( Cu_{n}(OH)_{2n-3} \) resulting in the formation of intermediate \( CuCN^+ \). This step is considered to be the rate-determining step. The final product is still \( Cu(CN)_3^2^- \).

Path 3. The rate law of path 3 is:

\[
r = 5.04 [CN^-][PVA-Cu_{n}(OH)_{2n-2}^2] \quad (12)
\]

The proposed mechanism is as follows:

\[
PVA-Cu_{n}(OH)_{2n-2}^2 + H^+ \rightarrow PVA + Cu_{n-1}(OH)_{2n-3} \quad (equilibrium)
\]

\[
Cu_{n}(OH)_{2n-3} + CN^- \rightarrow Cu_{n-1}(OH)_{2n-4} + OH^- \quad (RDS)
\]

\[
CuCN^+ + CN^- \rightleftharpoons Cu(CN)_2^2 (10a)
\]

\[
Cu(CN)_3^2^- \rightleftharpoons Cu(CN)_2^2 + \frac{1}{2}(CN)_2 \quad (10a)
\]

In the above equations, \( K_3 \) is the equilibrium constant of step 1, \( k_3 \) is the rate constant for the rate-determining step and \( k_3K_3 = 5.04 \text{s}^{-1} \).

After protonation, the intermediate \( Cu_{n}(OH)_{2n-3} \) released from PVA chain combines with \( CN^- \) in the bulk water to form \( CuCN^+ \). The final product is \( Cu(CN)_3^2^- \).

Path 4. The rate law of path 4 is:

\[
r = 482[CN^-][PVA-Cu_{n}(OH)_{2n-2}^2] \quad (13)
\]

The proposed mechanism is as follows:

\[
PVA-Cu_{n}(OH)_{2n-2}^2 + CN^- \rightarrow PVA + CuCN^+ + Cu_{n-1}(OH)_{2n-3} + OH^- \quad (RDS)
\]

The next reaction steps are as given in equation (10a). In the above equations, \( K_4 \) is the equilibrium constant of step 1, \( k_4 \) is the rate constant for the rate-determining step and \( k_4 = 482 \text{s}^{-1} \text{M}^{-1} \). The formation of intermediate, \( CuCN^+ \), through the bimolecular ligand exchange reaction between \( PVA-Cu_{n}(OH)_{2n-2}^2 \) and \( CN^- \) is the rate-determining step. The final product is \( Cu(CN)_3^2^- \).
In the absence of PVA, the u.v.-visible spectrum of the aqueous solution of freshly prepared Cu$_4$(OH)$_8$O$_2$- (or Cu(OH)$_2$) dissolved in an excess of CN$^-$ shows an absorption peak at 238 nm which is believed to be the charge transfer band of Cu(CN)$_3$$^{2-}$.

The increases in the concentrations of either the cyanide or PVA-Cu$_4$(OH)$_8$O$_2$- result in an increase in absorption intensity at 238 nm and a decrease in absorbances at 260, 370 and 620 nm. The effects reflect that the excess of CN$^-$ destroys the Cu-OH band of PVA-Cu$_4$(OH)$_8$O$_2$- complex and subsequently forms Cu(CN)$_3$$^{2-}$. These results support the evidence for step 2 (RDS) of path 3.

The absorption spectrum for the increase in concentration of the cyanide in PVA Cu$_4$(OH)$_8$O$_2$- solution at pH 12.0 is shown in Figure 7. In this figure, the diminution in 620 nm has been measured with a different absorption scale in comparison with that in 260 and 370 nm. Furthermore, the absorption intensity is invoked with the help of the slope ratio method to deduce the composition of product for the reaction between PVA Cu$_4$(OH)$_8$O$_2$- and CN$^-$. The combining ratio between CN and Cu is found to be 2.7. Thus the final product may be inferred as Cu(CN)$_3$$^{2-}$.

CONCLUSIONS

The kinetics of the ligand exchange reaction of the green PVA Cu$_4$(OH)$_8$O$_2$- complex with CN$^-$ has been studied by a stopped-flow method at pH 11.6-12.6, $\mu$ = 0.1 (KCl) and 25 C. The substitution reaction proceeds simultaneously through four different reaction paths. The cluster model structure of the green PVA Cu$_4$(OH)$_8$O$_2$- complex is used to interpret these four paths. The Cu(CN)$_3$$^{2-}$ is inferred as the final product of the ligand substitution reaction.

ACKNOWLEDGEMENTS

The financial support of the National Research Council of the R.O.C. under Grant NSC 78-0208-M 005-02 is gratefully acknowledged. The authors thank Professor Andrew Yeh (Chung-Yuan Christian University) for help in carrying out the stopped-flow measurements.

REFERENCES

1 Kuhn, W. and Toth, I. Z. Naturwissenschaften, 1963, 18A, 112
2 Hojo, N. and Shira, H. Vippon Kaigaku Kaishi 1972, 1316
4 Chen, J.H and Huang, L. P. J. Chem. Soc. 1988, 38, 273
6 Nishimura, M., Oake, K. and Murakami, K. Polymer, 1989, 30, 1540