Kinetics of the Reaction between Copper(II)-Ethylenediaminetetra-acetate Complex and Cyanide

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There have been a number of papers in which the kinetic studies of oxidation-reduction reactions involving metal complexes were dealt with. F. R. Duke and W. G. Courtney[1] studied the reduction of copper(II)-ammine complex with the cyanide ion in solutions containing ammonia in high concentrations, and found that the reaction is of first order on the concentration of the copper(II)-ammine complex and fourth order on that of the cyanide. From the results, they proposed the formation of an activated complex with four cyanides co-ordinated.

Ishibashi, Fujinaga and Sato[2] observed the reduction of copper(II) in the solution containing sodium ethylenediaminetetraacetate (EDTA) and potassium cyanide by following with time the decrease of the polarographic diffusion current due to the copper(II)-EDTA complex. They showed a current-time curve in their paper, but gave no details on the kinetics.

The present investigation was undertaken in order to know the effect of the nature of ligands on the reaction kinetics involving the complex. The kinetics of the reaction of copper(II)-EDTA complex with cyanide is presented in this paper. The second-order dependence on the concentration of copper(II)-EDTA complex clearly indicates that the reduction of the copper(II)-EDTA complex with cyanide ion takes place through reaction paths different from that for the copper(II)-ammine complex.

Experimental

Reagents.—A 0.1 M cupric sulfate solution was prepared by dissolving cupric sulfate which had been purified by recrystallization of the guaranteed reagent, and was standardized by electrogravimetry at a constant potential with the aid of a Yanagimoto automatic potentiostat. Disodium ethylenediaminetetraacetate of guaranteed reagent grade was purified by recrystallization[3] and dissolved in distilled water for a 0.1 M stock solution, the concentration of which was standardized amperometrically against the standardized cupric solution[4]. A stock solution of potassium cyanide was made up by dissolving the guaranteed reagent, its concentration being determined by Liebig and Denigès' method[5] whenever it was used. Sodium carbonate and sodium bicarbonate used for carbonate-bicarbonate buffers and all other chemicals used were of analytical reagent grade.

Apparatus and Procedure.—The rate of the reactions between the Cu(II)-EDTA complex and the cyanide ion was followed by measuring the change of the polarographic diffusion current of the complex as a function of time. The current-time curves were obtained with a Shimadzu pen-recording polarograph Model RP-2 using a dropping mercury electrode as an indicator electrode. The cell was connected with the saturated calomel electrode (S.C.E.) through a Hume and Harris' type salt bridge[6]. When no contamination of the chloride ion was desirable, the intermediate agar plug saturated with potassium chloride was replaced by the one prepared with nearly 1 M potassium nitrate. The dropping mercury electrode used had an m value of 1.69 mg./sec. and a drop time of 4.78 sec., being measured in undeaerated 0.1 M potassium nitrate solution with open circuit at 50 cm. of mercury column at 25°C.

The measurements were made in carbonate-bicarbonate buffers of pH 10 at 25.0°C, unless otherwise stated. The ionic strength was adjusted to be 0.5 with potassium nitrate. Gelatin was added as maximum suppressor by 0.002% in concentration. The pH of the solution was measured with a Hitachi Model EHP-1 pH-meter, immediately after the measurement of the current-time curves, within the accuracy of 0.02 pH unit.

The reaction was initiated by adding a known amount of air-free potassium cyanide solution into the deaerated reaction mixture with the aid of a calibrated syringe at a rate of 1 ml. per second. The solution was thoroughly stirred by

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[1] F. R. Duke and W. G. Courtney, *J. Phys. Chem.*, **56**, 19 (1952).

[2] M. Ishibashi, T. Fujinaga and M. Sato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 696 (1956).

[3] W. J. Blaedel and H. T. Knight, *Anal. Chem.*, **26**, 741 (1954).

[4] N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst* (*Bunseki Kagaku*), **6**, 86 (1957).

[5] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, N. Y. (1947), p. 282.

[6] D. N. Hume and W. E. Harris, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 465 (1943).

bubbling pure nitrogen gas rapidly for 10 seconds. With this technique, the reproducible current-time curves were obtained from 20 seconds after the initiation of the reaction.

Results and Discussion

The Current-Voltage Curves of the Cu(II)-EDTA Complex in the Absence and the Presence of Potassium Cyanide at pH 10.—Polarographic behavior of the Cu(II)-EDTA complex has been reported by several researchers[7-10]. In Fig. 1 are shown typical examples of the current-voltage curves of 1 mM of Cu(II)-EDTA complex which were obtained in carbonate buffer of pH 10.0 containing 9 mM of EDTA in the absence and the presence of potassium cyanide.

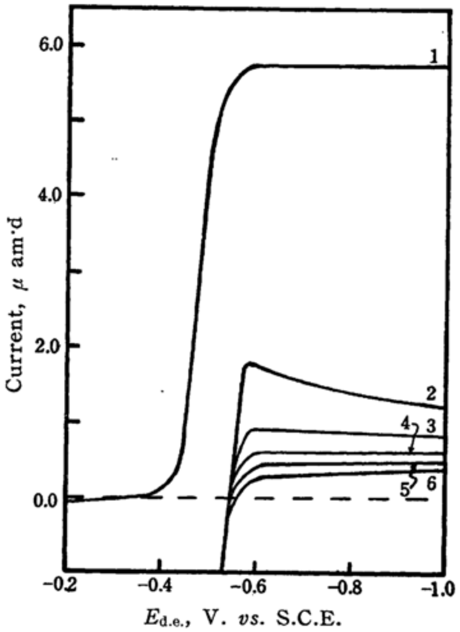

Fig. 1. Current-voltage curves of copper-(II)-EDTA complex obtained in buffer of pH 10 (μ=0.5) before and after the addition of potassium cyanide: curve 1, obtained with the solution containing 0.97×10^{-3} M CuY^{2-}, 8.07×10^{-3} M unchelated EDTA and 0.002% gelatin; curves 2 to 6, recorded successively after the addition of 3.80×10^{-2} M KCN to the solution of curve 1.

In the absence of cyanide, the Cu(II)-EDTA complex gave a well-defined wave with the half-wave potential of −0.46 V. *vs.* S.C.E. and i_d/C of 5.90 μ amp./mM (at −0.74 V. *vs.* S.C.E.) under the experimental condition. (Curve 1). Upon the addition of cyanide whose concentration was greater than the stoichiometric ratio for the Cu(II)-cyanide reaction, the diffusion current of Cu(II)-EDTA complex decreased suddenly to a half of the original magnitude and then gradually to the value of the residual current. Curves 2 to 6 show the current-voltage curves of Cu(II)-EDTA complex which were successively recorded after the addition of potassium cyanide.

The value of i_d/C for Cu(II)-EDTA complex in the presence of excessive cyanide was determined to be 2.95 μ amp./mM by measuring the diffusion currents at −0.74 volt *vs.* S.C.E. with time and by extrapolating those values to zero time. It is interesting to note that the diffusion current of Cu(II)-EDTA complex obtained in the presence of cyanide was a half of that obtained in the absence of cyanide.

Absorptions of Cu(II)-EDTA complex were measured with a Hitachi EPU-2 spectrophotometer in carbonate buffer of pH 10. The absorption maximum was found at 730 mμ, which was slightly different from the value given by Bennett and Schmidt[11]. They stated that the absorption spectra of the chelate at pH 8 and pH 12.5 were similar, both showing a peak at 680 mμ, but they gave no information about the composition of the solution measured. Absorption spectra of the complex were also measured after the addition of potassium cyanide. The absorption maximum was found to shift slightly to shorter wave lengths. From this fact and the statement of Duke and Courtney[1], it was reasonably assumed that the Cu(II) could be represented by the total copper concentration present in the form of Cu(II)-EDTA complex.

From this observation, it may be concluded that a one-electrotron reduction of Cu(II)-EDTA complex occurs in the solution containing cyanide ions. The cupric copper was reduced with one-electron transfer to the cuprous copper, which reacted immediately with the cyanide ion to form a very stable cuprous cyanide complex. The latter gives no polarographic wave at potentials less negative than the decomposition potentials of alkali metal

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[7] R. L. Pecsok, *Anal. Chem.*, **25**, 561 (1953).

[8] K. Bril and P. Krumholz, *J. Phys. Chem.*, **58**, 339 (1954).

[9] W. Furness, P. Crawshaw and W. C. Davies, *Analyst*, **74**, 629 (1949).

[10] T. Yoshino, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 131 (1957).

[11] M. C. Bennett and N. O. Schmidt, *Trans. Faraday Soc.*, **51**, 1412 (1955).

[12] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience Publishers, New York (1952), p. 494.

ions[12]. The rate of the chemical reaction between cuprous copper and cyanide ion may be much faster than that of the electrochemical reduction of cuprous copper to copper amalgam.

The Reaction Kinetics.—The diffusion current-time relations were obtained at various concentrations of cupric copper, cyanide and EDTA. Typical examples are given in Fig. 2.

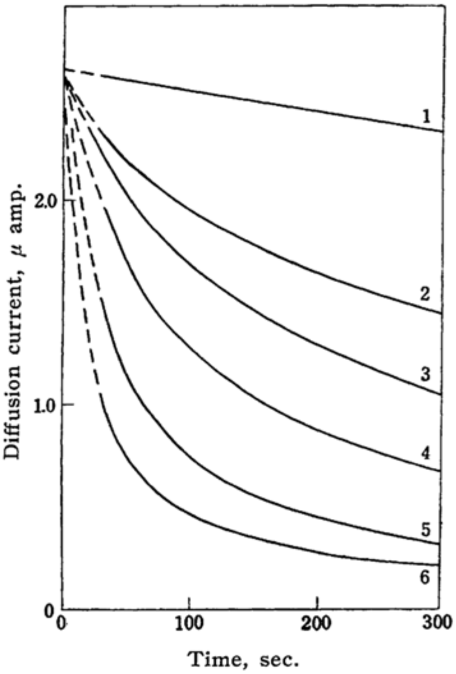

Fig. 2. The diffusion current-time relation of the reaction between CuY^{2-} and CN^-, measured at −0.74 volt *vs.* S.C.E. in buffer of pH 9.95 of ionic strength 0.5 at 25°C. The initial concentration: CuY^{2-}, 0.969×10^{-3} M; unchelated EDTA, 8.069×10^{-3} M. The concentration of KCN added: 1, 1.88×10^{-2} M; 2, 2.84×10^{-2} M; 3, 3.31×10^{-2} M; 4, 3.78×10^{-2} M; 5, 4.73×10^{-2} M; 6, 5.65×10^{-2} M.

Two reaction mechanisms were assumed and compared with experimental results. Mechanism A:

$$2\,CuY^{2-} \underset{k_2}{\overset{k_1}{\rightleftarrows}} CuYCu + Y^{4-} \quad \text{(rapid)} \qquad (1)$$

$$CuYCu + n\,CN^- \xrightarrow{k_3} Cu(CN)_n{}^{2-n} + CuY^{2-} \quad \text{(slow)} \qquad (2)$$

$$Cu(CN)_n{}^{2-n} \longrightarrow \text{Cu(I)-cyano complex} + 1/2(CN)_2 \quad \text{(rapid)} \qquad (3)$$

The rate of the decrease of CuY^{2-} concentration may be written as

$$-\frac{d[CuY^{2-}]}{dt} = \frac{k_1k_3[CuY^{2-}]^2[CN^-]^n}{k_2[Y^{4-}] + k_3[CN^-]^n} \qquad (4)$$

If the condition, $k_2[Y^{4-}] \gg k_3[CN^-]^n$, is fulfilled, eq. 4 can be simplified as

$$-\frac{d[CuY^{2-}]}{dt} = \frac{k_1k_3}{k_2}\,\frac{[CuY^{2-}]^2[CN^-]^n}{[Y^{4-}]} \qquad (5)$$

Mechanism B:

$$CuY^{2-} \underset{k_2'}{\overset{k_1'}{\rightleftarrows}} Cu^{2+} + Y^{4-} \quad \text{(rapid)} \qquad (6)$$

$$Cu^{2+} + n'CN^- \xrightarrow{k_3'} Cu(CN)_{n'}{}^{2-n'} \quad \text{(slow)} \qquad (7)$$

$$Cu(CN)_{n'}{}^{2-n'} \longrightarrow \text{Cu(I)-cyano complex} + 1/2(CN)_2 \quad \text{(rapid)} \qquad (8)$$

The rate of the decrease of CuY^{2-} concentration can be derived as

$$-\frac{d[CuY^{2-}]}{dt} = \frac{k_1'k_3'}{k_2'}\,\frac{[CuY^{2-}][CN^-]^{n'}}{[Y^{4-}]} \qquad (9)$$

In mechanisms A and B, the difference is in the reaction orders on the concentrations of the CuY^{2-} and the cyanide ion. Therefore, the reaction rate can be written in general as

$$-\frac{d[CuY^{2-}]}{dt} = \frac{k_1k_3}{k_2}\,\frac{[CuY^{2-}]^m[CN^-]^n}{[Y^{4-}]} \qquad (10)$$

In the reaction mixture of pH 10, the Cu(II)-EDTA complex exists only in the form of CuY^{2-}. The formation of $CuY(OH)^{3-}$ is considered to be negligible[11]. On the other hand, the cyanide exists in the forms of cyanide ion CN^- and hydrogen cyanide HCN at pH 10, and the unchelated ethylenediaminetetra-acetate, in the forms of HY^{3-} and Y^{4-} ions. The concentration of CN^-, therefore, was calculated from the total concentration of free cyanide and the dissociation constant of hydrogen cyanide, and that of Y^{4-}, from the total concentration of unchelated EDTA and the fourth dissociation constant of EDTA. The value of 4×10^{-10} was used for K_{HCN}[13] and the activity coefficient of cyanide ion, f_{CN^-}, at the given ionic strength was estimated. The fourth dissociation constant of EDTA used in this calculation was $10^{-9.53}$ which is the hybrid constant obtained by Carini and Martell[14] at ionic strength 0.5 at 25°C. The concentration of each species at a given time was calculated from the stoichiometric relation,

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[13] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York (1952), p. 137.

[14] F. F. Carini and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5745 (1952).

$$\mathrm{CuY^{2-}+4\ CN^-=Cu(CN)_3{}^{2-}+1/2(CN)_2+Y^{4-}}$$

and the observed concentration of $\mathrm{CuY^{2-}}$. Eq. 10 can be rewritten as

$$\log\left(-\frac{\mathrm{d}[\mathrm{CuY^{2-}}]}{\mathrm{d}t}\right)+\log[\mathrm{Y^{4-}}]-m\log[\mathrm{CuY^{2-}}]$$
$$=\log\frac{k_1k_3}{k_2}+n\log[\mathrm{CN^-}] \qquad (11)$$

If the reaction proceeded through mechanism A or B, a plot of the left-hand side of eq. 11 against $\log[\mathrm{CN^-}]$ should give a straight line with slope of n, when m in the left-hand side of eq. 11 is 2 for mechanism A and 1 for mechanism B. This relation was examined by introducing $[\mathrm{CuY^{2-}}]$, $[\mathrm{Y^{4-}}]$, $[\mathrm{CN^-}]$ and $-\frac{\mathrm{d}[\mathrm{CuY^{2-}}]}{\mathrm{d}t}$ at $t=120$(sec.) on the concentration-time curves obtained with varied concentrations of cyanide but at the constant initial concentrations of $\mathrm{CuY^{2-}}$ and EDTA. As seen in Fig. 3, eq. 11 is satisfied when m is 2, the plot of the left-hand side of eq. 11 against $\log[\mathrm{CN^-}]_{t=120}$ giving a straight line with a slope of 4.1 (A in Fig. 3). The corresponding plot with $m=1$, on the other hand, gave no straight line (B in Fig. 3). This is a clear indication of the fact that mechanism B does not explain the reaction kinetics.

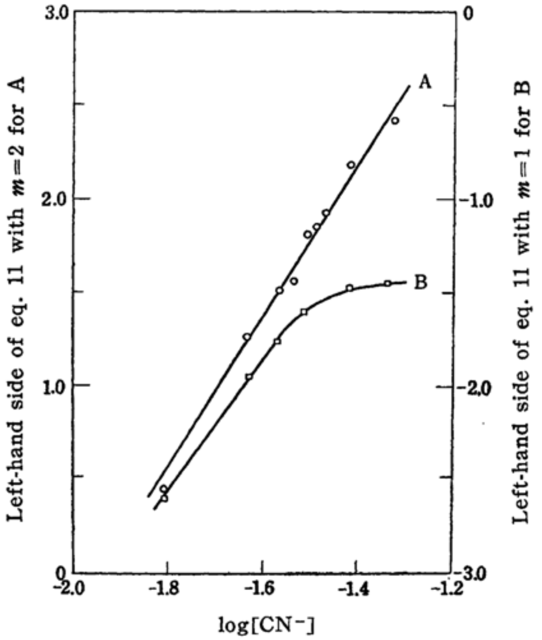

Fig. 3. Plot of the left-hand side of eq. 11 against $\log[\mathrm{CN^-}]$ with $m=2$ (curve A) and $m=1$ (curve B).

Substituting $n=4$, eq. 10 may be written as

$$\log\left(-\frac{\mathrm{d}[\mathrm{CuY^{2-}}]}{\mathrm{d}t}\right)+\log[\mathrm{Y^{4-}}]-4\log[\mathrm{CN^-}]$$
$$=\log\frac{k_1k_3}{k_2}+m\log[\mathrm{CuY^{2-}}] \qquad (12)$$

Although m was decided to be 2 from the treatment mentioned above, the left-hand side of eq. 12 was plotted against $\log[\mathrm{CuY^{2-}}]$ using the values of $-\frac{\mathrm{d}[\mathrm{CuY^{2-}}]}{\mathrm{d}t}$, $[\mathrm{Y^{4-}}]$, $[\mathrm{CN^-}]$ and $[\mathrm{CuY^{2-}}]$ which were obtained at various t's on one concentration-time curve and also at $t=120$ (sec.) on several concentration-time curves recorded with varied initial concentrations of $\mathrm{CuY^{2-}}$ but at the constant initial concentrations of cyanide and EDTA. As shown in Fig. 4, the plot gave a straight line with a slope of 2.1, which definitely showed that the reaction is second order on the $\mathrm{CuY^{2-}}$ concentration.

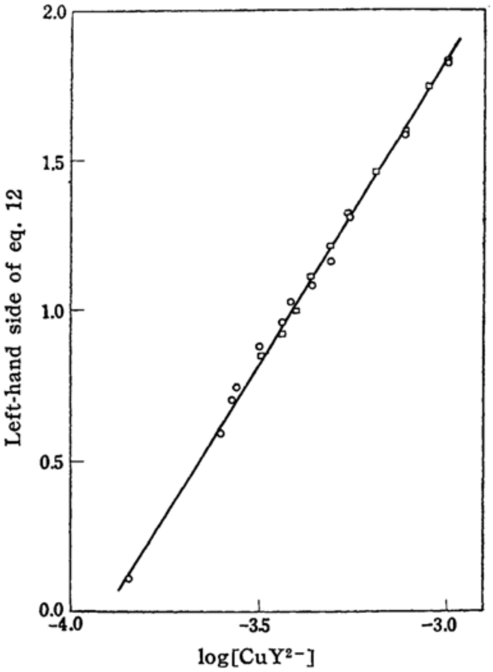

Fig. 4. Plot of the left-hand side of eq. 12 against $\log[\mathrm{CuY^{2-}}]$: □, values obtained at various t's on one concentration-time curve; ○, values obtained at $t=120$(sec.) on various concentration-time curves.

The diffusion current-time curves were also recorded at various initial concentrations of EDTA but at the constant initial concentrations of $\mathrm{CuY^{2-}}$ and cyanide. Eq. 10 is rearraged as

$$\log\left(-\frac{d[\mathrm{CuY^{2-}}]}{dt}\right)-2\log[\mathrm{CuY^{2-}}]$$
$$-4\log[\mathrm{CN^{-}}]=\log\frac{k_1k_3}{k_2}-\log[\mathrm{Y^{4-}}] \quad (13)$$

where 2 is substituted for m and 4, for n. The left-hand side of eq. 13 was plotted against $\log[\mathrm{Y^{4-}}]$ with the values obtained at $t=120$ (sec.). The plot gave a straight line with a slope of -0.95 (Fig. 5), and confirmed the first-order dependence on the reciprocal of the $\mathrm{Y^{4-}}$ concentration.

The rate constant for the overall reaction, k_1k_3/k_2, was calcuated from the concentration-time curves obtained under various conditions (Table I), and determined to be 6.8×10^7 $\mathrm{l.^4\ mole^{-4}\ sec.^{-1}}$

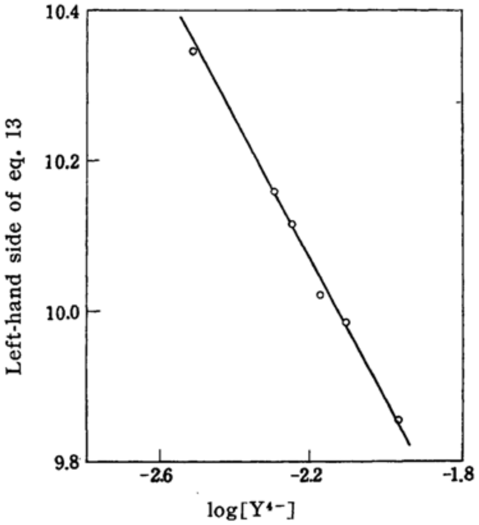

Fig. 5. Plot of the left-hand side of eq. 13 against $\log[\mathrm{Y^{4-}}]$.

TABLE I
DETERMINATION OF THE OVERALL RATE CONSTANT, k_1k_3/k_2

$[\mathrm{CuY^{2-}}]$ $\times10^4$, M	$[\mathrm{Y^{4-}}]$ $\times10^3$, M	$[\mathrm{CN^{-}}]$ $\times10^2$, M	(k_1k_3/k_2) $\times10^{-7}$, $\mathrm{l.^4\ mole^{-4}\ sec.^{-1}}$
3.18_7	6.63	2.89	6.85
3.25_4	6.71	3.20	6.55
4.81_4	6.50	2.94	7.13
4.91_6	6.93	3.11	6.70
5.25_5	6.55	3.27	6.65
5.45_8	6.45	2.96	6.91
7.69_5	6.28	3.05	6.63
10.00	6.11	3.13	6.60
4.33_9	6.54	2.93	6.94
4.33_9	6.97	3.09	6.72
5.18_7	8.22	3.09	6.15
2.20_4	5.46	3.82	7.11
5.83_1	6.51	3.29	6.84
3.96_6	6.57	2.92	6.31
6.37_3	6.05	2.31	6.16

Mean 6.8×10^7 $\mathrm{l.^4\ mole^{-4}\ sec.^{-1}}$

In similar experiments carried out at pH 9.2 the rate of the reaction showed a second-order depence on the $\mathrm{CuY^{2-}}$ concentration, a fourth-order depence on the cyanide ion concentration and a first-order dependence on the reciprocal of the $\mathrm{Y^{4-}}$ concentration. The value of k_1k_3/k_2 obtained at pH 9.2 was in fair agreement with that obtained at pH 10.0.

It has been reported that some metal-EDTA complex ions, such as $\mathrm{PbY^{2-}}$, $\mathrm{CoY^{-}}$ and $\mathrm{HgY^{2-}}$, react with excessive metal ions to form salt-like compounds of the formula of MYM-type[15-17]. On the other hand, there has been no report in which the compounds of MYM (or MYM')-type are confirmed to be present in the solution at an appreciable concentration. Bennett and Wise[18] concluded from their polarographic investigation that there is no measurable quantity of CuYCd in the solution containing Cu(II), Cd(II) and EDTA. Some experiments carried out in this study were not successful in showing the existence of CuYCu in the solution. Nevertheless, it would not be unreasonable to consider that CuYCu exists, more or less, in the solution containing $\mathrm{CuY^{2-}}$, CuYCu being in equilibrium with $\mathrm{CuY^{2-}}$ according to the reaction 1.

It might be interesing to note that the reaction of Cu(II)-ammine complexes and cyanide ion is first order on the concention of the complexes[1], while the reaction of Cu(II)-EDTA complex and cyanide ion is second order on the concentration of the complex. The reason is not quite understood at present and it is also difficult to speculate upon the form of the activated complex. However, the greater stability of the ethylenediaminetetra-acetate complex owing to the chelate formation may be unfavorable for the reaction which takes place through the dissociation process, and the reaction between CuYCu and cyanide may favor the formation of an activated complex which leads to the spontaneous reduction of cupric to cuprous copper.

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[15] N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, **31**, 283 (1958).

[16] G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

[17] R. W. Schmid and C. N. Reilley, *J. Am. Chem. Soc.*, **78**, 5513 (1956).

[18] M. C. Bennett and W. S. Wise, *Trans. Faraday Soc.*, **52**, 696 (1956).

Summary

The reaction between copper(II)-ethylenediaminetetra-acetate complex and cyanide ion has been investigated by measuring the change of the polarographic diffusion current of the complex as a function of time after the initiation of reaction.

The rates of the reaction obtained with various concentrations of Cu(II)-EDTA complex, cyanide and unchelated EDTA showed that the reaction is of second order on the concentration of the Cu(II)-EDTA complex, fourth order on that of the cyanide and first order on the reciprocal of that of the unchelated EDTA. The reaction mechanism proposed is

$$2\ \mathrm{CuY}^{2-} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{CuYCu} + \mathrm{Y}^{4-}$$

$$\mathrm{CuYCu} + 4\ \mathrm{CN}^- \xrightarrow{k_3} \mathrm{Cu(CN)}_4{}^{2-} + \mathrm{CuY}^{2-}$$

(rate-determining)

$$\mathrm{Cu(CN)}_4{}^{2-} \longrightarrow \mathrm{Cu(I)\text{-}cyano\ complex} + 1/2(\mathrm{CN})_2$$

and the rate of the reaction is expressed as

$$-\frac{d[\mathrm{CuY}^{2-}]}{dt} = \frac{k_1 k_3}{k_2} \frac{[\mathrm{CuY}^{2-}]^2[\mathrm{CN}^-]^4}{[\mathrm{Y}^{4-}]}$$

The value of k_1k_3/k_2 was determined to be 6.8×10^7 $\mathrm{l.}^4$ mole^{-4} $\mathrm{sec.}^{-1}$ in a carbonate-bicarbonate buffer of pH 10.0, at ionic strength 0.5 and at 25°C.

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