h about 90% of the starting material was converted to $NF_4W_2O_2F_9$ and to the other products shown in reaction 17. Complete conversion to $NF_4W_2O_2F_9$ was achieved by heating to 180 °C for an additional 4 h.

The ionic structure of NF_4WOF_5 and $NF_4W_2O_2F_9$ in both the solid state and HF solution was demonstrated by vibrational and ^{19}F NMR spectroscopy. The infrared and Raman spectra of solid NF_4WOF_5 and $NF_4W_2O_2F_9$ are shown in Figures 2 and 3, respectively. For comparison, the vibrational spectra of $CsW_2O_2F_9$ are also shown in Figure 3. The observed frequencies, together with their assignments to the NF_4^+,[1,7,9] WOF_5^-,[10,11] and $W_2O_2F_9^-$ [12] ions, are summarized in Table I and clearly establish the nature of these salts in the solid state. In HF solution, however, a significant change was observed. First of all, both NF_4WOF_5 and $NF_4W_2O_2F_9$ were only partially soluble in anhydrous HF. In both cases the insoluble phases were shown by Raman spectroscopy to consist of $NF_4W_2O_2F_9$, and the HF solution showed only NF_4^+ and $W_2O_2F_9^-$ ions. In the HF solution obtained from dissolving NF_4WOF_5, the ratio of NF_4^+:$W_2O_2F_9^-$ was, as expected from eq 18, considerably higher than that found for the $NF_4W_2O_2F_9$ solution. The presence of these ions and the lack of WOF_5^- in these solutions were confirmed by ^{19}F NMR spectroscopy. These spectra showed a triplet of equal intensity at ϕ 215.5 with $J_{NF} = 239.5$ Hz, characteristic for NF_4^+,[1,7] and a singlet at ϕ 54 with two ^{183}W satellites with $J_{^{183}WF} = 84$ Hz, characteristic for $W_2O_2F_9^-$ in HF solution.[12] The latter signal has been attributed to the eight equivalent fluorines of $W_2O_2F_9^-$ with the bridging ninth fluorine undergoing rapid exchange with the HF solvent.[12] This exchange was still rapid at −60 °C, and no evidence for F–F coupling was observed. These Raman and NMR data suggest that NF_4WOF_5 undergoes the solvolysis in anhydrous HF given by eq 18. This solvolysis is analogous to that observed for $CsWOF_5$ in reaction 1 and explains why NF_4WOF_5 could not be prepared by a direct metathesis. Due to their limited solubility in anhydrous HF, some of the $W_2O_2F_9^-$ salt is precipitated out. This was confirmed by ^{19}F NMR peak area measurements on the HF solution of the original NF_4WOF_5 sample; it was shown that the ratio of the fluorines on nitrogen to the equivalent fluorines on tungsten was 1.5:1, indicating that on the basis of (18) about half of the $NF_4W_2O_2F_9$ had precipitated out under the given conditions.

$$2NF_4WO_5 + HF \xrightleftharpoons{HF} NF_4HF_2 + NF_4W_2O_2F_9 \quad (18)$$

Conclusion. The perfluoroammonium cation is capable of forming stable salts derived from the WOF_5^- and the $W_2O_2F_9^-$ anion but rapidly oxidizes the WF_6^- anion to WF_6. The new NF_4WOF_5 and $NF_4W_2O_2F_9$ salts were characterized, and the syntheses and reaction chemistry of tungsten fluoride and oxyfluoride anions were studied in more detail.

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Registry No. NF_4WOF_5, 79028-46-9; $NF_4W_2O_2F_9$, 79056-35-2; $CsWOF_5$, 58341-09-6; $CsW_2O_2F_9$, 79056-36-3; *cis*-$Cs_2WO_2F_4$, 79005-35-9; $CsWF_6$, 19175-38-3; WF_6, 7783-82-6; WOF_4, 52049-91-9.

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Formation Constant of the Tetracyanocuprate(II) Ion and the Mechanism of Its Decomposition

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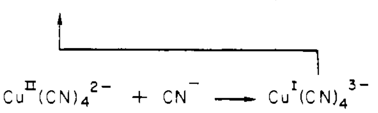
The overall formation constant (β) of tetracyanocuprate(II) ion ($Cu^{II}(CN)_4^{2-}$), which is formed as a reaction intermediate in the anodic oxidation of cyanide ion in the presence of copper ion, has been obtained by measuring the standard electrode potential ($E°$) of the redox couple $Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}$. The results are $E°(Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}) = 0.66$ V vs. NHE and $\beta(Cu^{II}(CN)_4^{2-}) = 10^{22.0}$ M^{-4} at 25 °C. The mechanism of the decomposition of the $Cu^{II}(CN)_4^{2-}$ is discussed by using the $\beta(Cu^{II}(CN)_4^{2-})$ value and the previously obtained kinetic data. It is concluded that a binuclear complex, $Cu^{II}_2(CN)_6^{2-}$, is formed from $Cu^{II}(CN)_4^{2-}$. This complex subsequently decomposes to form $Cu^{I}(CN)_2^-$ and $(CN)_2$, this step being rate determining. The kinetic studies of the chemical reaction between Cu^{2+} and CN^-, which have been reported by several groups of workers, are also interpreted by the same mechanism.

Introduction

In previous studies of the anodic oxidation of cyanide ion in the presence of copper ion, we have found that copper ion has a marked catalytic effect on this reaction[2a] and that the primary reaction product is cyanogen, which gives various secondary products according to the pH of the solution.[3]

We have proposed the reaction mechanism given by eq 1 and 2 from some electrochemical studies.[2] We have further studied the kinetics of reaction 2 by means of ESR spectroscopy[4,5] and have obtained the rate equation given by eq 3. On the basis of this result, we have proposed two possible



$$Cu^{I}(CN)_4^{3-} \longrightarrow Cu^{II}(CN)_4^{2-} + e^- \quad (1)$$

$$Cu^{II}(CN)_4^{2-} + CN^- \longrightarrow Cu^{I}(CN)_4^{3-} + \tfrac{1}{2}(CN)_2 \quad (2)$$

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[1] (a) Department of Chemistry. (b) Department of Industrial Chemistry.

[2] (a) S. Yoshimura, A. Katagiri, and S. Yoshizawa, *Denki Kagaku oyobi Kogyo Butsuri Kagaku*, **47**, 360 (1979); (b) *ibid.*, **47**, 488 (1979).

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$$v = -\frac{d[\mathrm{Cu^{II}(CN)_4^{2-}}]}{dt} = k_0\frac{[\mathrm{Cu^{II}(CN)_4^{2-}}]^2}{[\mathrm{CN^-}]^2} \qquad (3)$$

mechanisms (A and B) for reaction 2; in these mechanisms, (5a) or (5b) has been considered to be the rate-determining step.

Mechanism A

$$\mathrm{Cu^{II}(CN)_4^{2-} \rightleftarrows Cu^{II}(CN)_3^- + CN^-} \qquad (4a)$$

$$\mathrm{2Cu^{II}(CN)_3^- \rightarrow 2Cu^{I}(CN)_2^- + (CN)_2} \qquad (5a)$$

$$\mathrm{Cu^{I}(CN)_2^- + 2CN^- \rightleftarrows Cu^{I}(CN)_4^{3-}} \qquad (6)$$

Mechanism B

$$\mathrm{2Cu^{II}(CN)_4^{2-} \rightleftarrows Cu^{II}_2(CN)_6^{2-} + 2CN^-} \qquad (4b)$$

$$\mathrm{Cu^{II}_2(CN)_6^{2-} \rightarrow 2Cu^{I}(CN)_2^- + (CN)_2} \qquad (5b)$$

$$\mathrm{Cu^{I}(CN)_2^- + 2CN^- \rightleftarrows Cu^{I}(CN)_4^{3-}} \qquad (6)$$

It is well-known that copper(II) ion reacts with cyanide ion to form cyanogen and a copper(I) species, and evidence for a purple intermediate species, $\mathrm{Cu^{II}(CN)_4^{2-}}$, has been reported.[6] Several kinetic studies have been conducted for this reaction;[7-11] however, there has been disagreement about the reaction mechanism.

We thought that the formation constant of $\mathrm{Cu^{II}(CN)_4^{2-}}$ would give some idea in determining the mechanism of the above reactions involving Cu(II) and $\mathrm{CN^-}$. The formation constant of $\mathrm{Cu^{II}(CN)_4^{2-}}$ has been measured only in a methanol–water mixture at a low temperature (−45 °C),[12] because $\mathrm{Cu^{II}(CN)_4^{2-}}$ is unstable in aqueous solutions at ordinary temperatures. In general, a kinetic method is necessary to determine the formation constant of an unstable reaction intermediate.[13]

In this work we calculate the formation constant of $\mathrm{Cu^{II}(CN)_4^{2-}}$ from the standard electrode potential of the redox couple $\mathrm{Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}}$, which was measured by the current-interrupting method. The mechanism of the decomposition of $\mathrm{Cu^{II}(CN)_4^{2-}}$ and, more generally, the mechanism of the reactions involving Cu(II) and $\mathrm{CN^-}$ are discussed.

Measurement of the Standard Electrode Potential of the Couple $\mathrm{Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}}$

When a constant anodic current is passed through a platinum electrode in a cyanide solution containing copper ion, the electron-transfer reaction eq 1 occurs on the electrode surface and the subsequent chemical reaction, eq 2, occurs in the vicinity of the electrode. After a steady-state condition is reached, a certain distribution of the concentration of $\mathrm{Cu^{II}(CN)_4^{2-}}$ will be set up in the solution. If the current is then interrupted, the electrical double layer will discharge and the potential of the electrode will change suddenly to the quasi-equilibrium value, which is determined by the concentrations of $\mathrm{Cu^{II}(CN)_4^{2-}}$ and $\mathrm{Cu^{I}(CN)_4^{3-}}$ at the electrode surface according to the Nernst equation, eq 7. $E°(\mathrm{Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}})$ is the

$$E = E°(\mathrm{Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}}) + \frac{RT}{F}\ln\frac{[\mathrm{Cu^{II}(CN)_4^{2-}}]_s}{[\mathrm{Cu^{I}(CN)_4^{3-}}]_s} \qquad (7)$$

standard electrode potential of the redox reaction, eq 1, R is the gas constant, F is the Faraday constant, and T is absolute temperature.

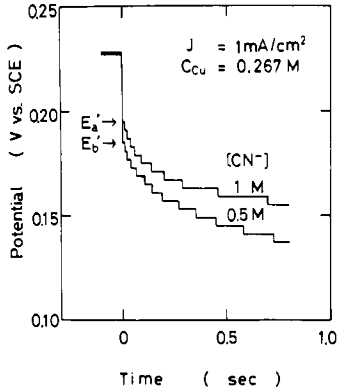

Figure 1. Potential–time curves after interruption of current (measured with digital memory); current density 1 mA cm^{-2}, total copper concentration 0.267 M, and $\mathrm{CN^-}$ concentration (a) 1 M and (b) 0.5 M.

The subscript s indicates the electrode surface. The potential will then change relatively slowly due to the decomposition of $\mathrm{Cu^{II}(CN)_4^{2-}}$. An equilibrium potential, E', which corresponds to $[\mathrm{Cu^{II}(CN)_4^{2-}}]_s$ and $[\mathrm{Cu^{I}(CN)_4^{2-}}]_s$ in a steady-state electrolysis, can be obtained by the extrapolation of the experimental potential–time curve, which is recorded after the interruption of the current, to zero time.

The potential E' may be theoretically formulated for the case in which the electrolysis is conducted in a solution of high cyanide concentration by using a small current density at a planar electrode. Under these conditions, the concentration of $\mathrm{Cu^{I}(CN)_4^{3-}}$ is almost constant throughout the solution and is approximately equal to the total concentration of copper (C_{Cu}), because $\mathrm{Cu^{I}(CN)_4^{3-}}$ is the predominant species of Cu(I) and the concentration of $\mathrm{Cu^{II}(CN)_4^{2-}}$ formed is very small. When the diffusion and reaction of $\mathrm{Cu^{II}(CN)_4^{2-}}$ are taken into account, the differential equation eq 8 holds for the

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - k_2C^2 \qquad (8)$$

concentration (C) of $\mathrm{Cu^{II}(CN)_4^{2-}}$ at the time t and at the distance x from the electrode. D is the diffusion coefficient of $\mathrm{Cu^{II}(CN)_4^{2-}}$, and k_2 is the apparent rate constant for the decomposition of $\mathrm{Cu^{II}(CN)_4^{2-}}$.

The rate constant k_2 is inversely proportional to the square of $[\mathrm{CN^-}]$ (eq 9).[5] Under a steady-state condition, eq 8 gives eq 10. If

$$k_2 = \frac{k_0}{[\mathrm{CN^-}]^2} \qquad (9)$$

$$\frac{d^2C}{dx^2} = \frac{k_2}{D}C^2 \qquad (10)$$

semiinfinite diffusion is assumed, the boundary conditions given by eq 11 and 12 should be satisfied, where J is the current density. The

$$C = [\mathrm{Cu^{II}(CN)_4^{2-}}]_s \quad \frac{dC}{dx} = -\frac{J}{DF} \quad \text{at } x = 0 \qquad (11)$$

$$C = 0 \quad \frac{dC}{dx} = 0 \quad \text{at } x \rightarrow +\infty \qquad (12)$$

differential equation eq 10 may be solved under these boundary conditions to give eq 13. From eq 7, 9, and 13, eq 14 is derived. The

$$[\mathrm{Cu^{II}(CN)_4^{2-}}]_s = \left(\frac{3J^2}{2k_2DF^2}\right)^{1/3} = \left(\frac{3J^2[\mathrm{CN^-}]^2}{2k_0DF^2}\right)^{1/3} \qquad (13)$$

$$E' = E°(\mathrm{Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}}) + \frac{RT}{3F}\ln\frac{3}{2k_0DF^2} + \frac{2RT}{3F}\ln J - \frac{RT}{F}\ln C_{\mathrm{Cu}} + \frac{2RT}{3F}\ln[\mathrm{CN^-}] \qquad (14)$$

standard electrode potential can be determined by the measurement of E'.

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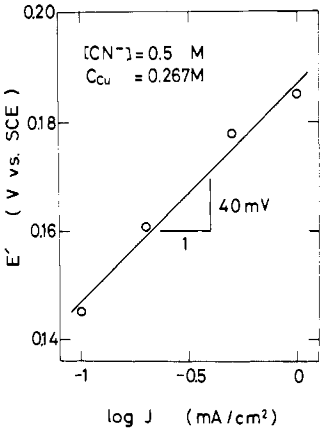

Figure 2. Relationship between E' and the logarithm of current density, J (mA cm^{-2}); CN^- concentration 0.5 M and total copper concentration 0.267 M.

Experimental Section

An H-type cell with a glass frit separator was used for measurements. A platinum plate was used as the working electrode. It was partly covered by silicone insulation so that its effective surface area was 1 cm^2. The reference electrode was a saturated calomel electrode, whose potential was 0.245 V vs. NHE. The counterelectrode was a platinum plate. A homemade constant-current source, a digital memory (Iwatsu-denshi DM-301), and a pen-writing recorder were used for the electrochemical measurement. Reagent grade potassium cyanide, copper(I) cyanide, and sodium hydroxide were used without further purification. Solutions were prepared that contained copper(I) cyanide and potassium cyanide of different concentrations and sodium hydroxide as a supporting electrolyte. The concentration of sodium hydroxide was always 1 M. Since the predominant species of copper(I) was $Cu^I(CN)_4^{3-}$ under the conditions of the present work,[14] the concentrations of $Cu^I(CN)_4^{3-}$ and CN^- were calculated by the equations $[Cu^I(CN)_4^{3-}] = C_{Cu}$ and $[CN^-] = C_{CN^-} - 4C_{Cu}$, where C_{Cu} and C_{CN^-} are the concentrations of total copper(I) and total cyanide, respectively. Nitrogen gas was passed through the solution to remove dissolved oxygen. The measurements were carried out at 25 °C in stationary solutions.

Concentrations are expressed in the units of M = mol dm^{-3} throughout this work.

Results

A constant anodic current was applied at the platinum electrode in a solution containing copper(I) and CN^-. After a steady state was reached, the current was interrupted, and the potential of the electrode was recorded as a function of time. Curves a and b in Figure 1 show the potential change for two different CN^- concentrations under otherwise the same conditions. Although the potential values in the steady-state current flow agreed in both cases, the potential change after the interruption of the current was slower for the higher concentration of CN^-. This corresponds to the fact that the rate of the decomposition of $Cu^{II}(CN)_4^{2-}$ decreases as $[CN^-]$ increases. The E' values were obtained by the extrapolation of curves a and b.

The theoretical equation eq 14 can be applied to the E' values measured under different conditions. Figure 2 shows E' measured at different current densities, J. A straight line with a slope of 40 mV/decade shows the theoretical relationship between E' and log J as expected from eq 14. Figures 3 and 4 show E' measured at different concentrations of total copper (C_{Cu}) and of cyanide ion ($[CN^-]$), respectively. Data points can be approximated by the straight lines with slopes of −60 and 40 mV/decade, respectively, as expected from eq 14. Large deviation of one point at $[CN^-] = 0.1$ M in Figure 4 may be caused by an error introduced on the extrapolation of the potential–time curve, due to the considerably high rate of the decomposition of $Cu^{II}(CN)_4^{2-}$. The standard electrode potential for the redox couple $Cu^{II}(CN)_4^{2-}/Cu^I(CN)_4^{3-}$ is calculated from the above results by using eq 14:

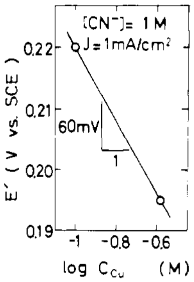

Figure 3. Relationship between E' and the logarithm of total copper concentration (M); CN^- concentration 1 M and current density 1 mA cm^{-2}.

$$E°(Cu^{II}(CN)_4^{2-}/Cu^I(CN)_4^{3-}) = 0.66 \text{ V vs. NHE } (25\ °C) \tag{15}$$

In this calculation, the value $k_0 = 74$ M s^{-1} obtained in the previous work is used. Since the diffusion coefficient of $Cu^{II}(CN)_4^{2-}$ is not known, a value of 1×10^{-5} cm^2 s^{-1} is assumed. (This value is estimated from the diffusion coefficients of Cu^{2+} ($D = 0.72 \times 10^{-5}$ cm^2 s^{-1})[15] and $Cu^{II}(NH_3)_4^{2+}$ ($D = 0.95 \times 10^{-5}$ cm^2 s^{-1}),[16] both of which have the same square-planar configuration as $Cu^{II}(CN)_4^{2-}$.) A comparison of the diffusion coefficients of different metal complex ions suggests that the uncertainty of the estimated D value is probably less than the factor of 2, which would cause a maximum error of 0.006 V in $E°$.

The largest value of the steady-state concentration of $Cu^{II}(CN)_4^{2-}$ can be calculated from eq 13 for the largest values of J and $[CN^-]$. It is 5.9×10^{-3} M in the case of $J = 1$ mA cm^{-2} and $[CN^-] = 1$ M and still negligible in the total copper concentration ($C_{Cu} = 0.1$ M at least). This justifies the above approximation of $[Cu^I(CN)_4^{3-}] = C_{Cu}$.

Formation Constant of $Cu^{II}(CN)_4^{2-}$. The formation constant of $Cu^{II}(CN)_4^{2-}$ can be calculated from the $E°(Cu^{II}(CN)_4^{2-}/Cu^I(CN)_4^{3-})$ value obtained above and the other known data. Equations 16, 17, 18, and 19 hold for the

$$E = E°(Cu^{2+}/Cu^+) + \frac{RT}{F} \ln \frac{[Cu^{2+}]}{[Cu^+]} \tag{16}$$

$$E = E°(Cu^{II}(CN)_4^{2-}/Cu^I(CN)_4^{3-}) + \frac{RT}{F} \ln \frac{[Cu^{II}(CN)_4^{2-}]}{[Cu^I(CN)_4^{3-}]} \tag{17}$$

$$\beta(Cu^I(CN)_4^{3-}) = \frac{[Cu^I(CN)_4^{3-}]}{[Cu^+][CN^-]^4} \tag{18}$$

$$\beta(Cu^{II}(CN)_4^{2-}) = \frac{[Cu^{II}(CN)_4^{2-}]}{[Cu^{2+}][CN^-]^4} \tag{19}$$

equilibria among the species Cu^+, Cu^{2+}, $Cu^I(CN)_4^{3-}$, and $Cu^{II}(CN)_4^{2-}$, in an aqueous solution. $E°(Cu^{2+}/Cu^+)$ is the standard electrode potential for the redox couple Cu^{2+}/Cu^+, and $\beta(Cu^I(CN)_4^{3-})$ and $\beta(Cu^{II}(CN)_4^{2-})$ are the overall formation constants of the complexes $Cu^I(CN)_4^{3-}$ and $Cu^{II}(CN)_4^{2-}$, respectively. Equation 20 is derived from eq 16–19. On the substitution of $10^{30.53}$ M^{-4} (25 °C)[14] for $\beta(Cu^I(CN)_4^{3-})$,

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$$\beta(\mathrm{Cu^{II}(CN)_4{}^{2-}}) = \beta(\mathrm{Cu^{I}(CN)_4{}^{3-}}) \times \exp\left\{\frac{F}{RT}(E^\circ(\mathrm{Cu^{2+}/Cu^{+}}) - E^\circ(\mathrm{Cu^{II}(CN)_4{}^{2-}/Cu^{I}(CN)_4{}^{3-}}))\right\} \quad (20)$$

0.153 V (25 °C)[17] for $E^\circ(\mathrm{Cu^{2+}/Cu^{+}})$, and 0.66 V for $E^\circ(\mathrm{Cu^{II}(CN)_4{}^{2-}/Cu^{I}(CN)_4{}^{3-}})$ (25 °C), the value given by eq 21 is obtained.

$$\beta(\mathrm{Cu^{II}(CN)_4{}^{2-}}) = 10^{22.0}\ \mathrm{M^{-4}}\ (25\ °\mathrm{C}) \quad (21)$$

Bjerrum[18] has estimated $[\mathrm{Cu^{II}(CN)_4{}^{2-}}] = 10^{25}\ \mathrm{M^{-4}}$ for aqueous solutions at 25 °C from the consideration of the relationship between the formation constants of cyano complexes and ammine complexes of different metals. Paterson and Bjerrum[12] have obtained the value $\beta(\mathrm{Cu^{II}(CN)_4{}^{2-}}) = 10^{26.7}\ \mathrm{M^{-4}}$ in a methanol (60 wt %)-water mixture at −45 °C from a EMF measurement. Under these conditions, the complex is relatively stable. The value of $\beta(\mathrm{Cu^{II}(CN)_4{}^{2-}})$ obtained in the present work is considerably smaller than the above two values.

Mechanism of the Decomposition of Cyanocopper(II) Complexes. At first, mechanism A will be discussed in detail. Since reaction 5a is rate determining, the reaction rate can be expressed by eq 22, where k_a is the true rate constant of

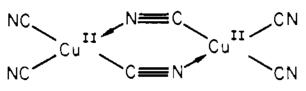
$$v = k_a[\mathrm{Cu^{II}(CN)_3{}^{-}}]^2 \quad (22)$$

reaction 5a. With use of the stepwise formation constant of $\mathrm{Cu^{II}(CN)_4{}^{2-}}$ (K_4), eq 22 is transformed to eq 23. As $k_a/K_4{}^2$

$$v = \frac{k_a}{K_4{}^2}\,\frac{[\mathrm{Cu^{II}(CN)_4{}^{2-}}]^2}{[\mathrm{CN^-}]^2} \quad (23)$$

is equal to k_0 (=74 M s^{-1}), the k_a value can be calculated if K_4 is known. The constant K_4 is estimated to be $\sim 10^{4.3}$–$10^{4.5}$ M^{-1} from $\beta(\mathrm{Cu^{II}(CN)_4{}^{2-}})$ and the formation constants of amminecopper(II) complexes and chlorocopper(II) complexes, both of which have the same configuration as $\mathrm{Cu^{II}(CN)_4{}^{2-}}$ (see Appendix). Therefore, k_a should be $\sim 10^{10.9}$–$10^{10.5}$ M^{-1} s^{-1}. This value is comparable to the rate constants of the diffusion-controlled reactions such as those between $\mathrm{H_3O^+}$ and $\mathrm{OH^-}$ and between $\mathrm{H_3O^+}$ and $\mathrm{F^-}$ in aqueous solutions.[19] The k_a value seems to be impossibly large for the rate constant of the reaction between complex ions that have the same charge. Mechanism A can therefore be eliminated.

Mechanism B seems more realistic, although there is no positive evidence for the binuclear complex, $\mathrm{Cu^{II}{}_2(CN)_6{}^{2-}}$. Two possible structures of the $\mathrm{Cu^{II}{}_2(CN)_6{}^{2-}}$ complex are shown by **1** and **2**. The structure **1** is expected from the facts that copper(II) ion can form polynuclear complexes with chloride and bromide ions as bridge ligands and that cyanide ion can act as a bridge group of the type M–C–N–M between metal ions such as Cu(I), Ag(I), and Ni(II).[20] The other structure **2** is postulated from the analogy with the well-known bridged structure of some binuclear metal carbonyls. This structure appears to be the transition state in the process in which the two bridging cyanide groups form a bond to give a cyanogen (N≡C—C≡N) molecule. The equilibrium between $\mathrm{Cu^{II}{}_2(CN)_6{}^{2-}}$ and other copper(II) complexes can be expected from the fact that most copper(II) complexes are very labile.[21]



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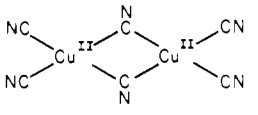

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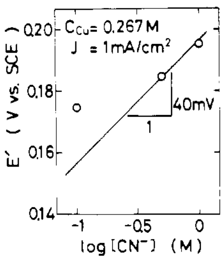

Figure 4. Relationship between E' and the logarithm of CN$^-$ concentration (M); total copper concentration 0.267 M and current density 1 mA cm^{-2}.

Kinetics and Mechanism of the Reactions between Cu(II) and CN$^-$. Several groups of workers have studied the kinetics of the reactions between $\mathrm{Cu^{2+}}$ or Cu(II) complexes and CN$^-$ ion under different conditions:

$$\mathrm{Cu(II) + CN^- \rightarrow Cu(I) + {}^1/_2(CN)_2} \quad (24)$$

Some of them have obtained rate equations that are similar in that the reaction rate is proportional to the square of the concentration of the predominant copper(II) species, although different reaction mechanisms have been proposed. It may reasonably be assumed that different copper(II) species were in equilibrium in each case above, because most Cu(II) complexes are very labile.[21] If such an assumption is made, the reported rate equations may be rewritten as eq 25. It is

$$v = 2\frac{\mathrm{d}[(\mathrm{CN})_2]}{\mathrm{d}t} = k_r[\mathrm{Cu^{2+}}]^2 \quad (25)$$

valuable to calculate the apparent rate constant, k_r, from experimental results obtained for the wide range of conditions and to discuss reaction mechanisms.

Nord and Matthes[8] have measured the transient concentration of the intermediate $\mathrm{Cu^{II}(CN)_4{}^{2-}}$ by means of a visible spectrometer in the reaction between $\mathrm{Cu^{2+}}$ and CN$^-$ and have obtained the rate equation eq 26. They have reported the

$$v = k_2[\mathrm{Cu^{II}(CN)_4{}^{2-}}]^2 \quad (26)$$

value k_2 for several different CN$^-$ concentrations at 25 °C. Equation 26 is transformed to eq 27 by using eq 19. As the

$$v = k_2(\beta(\mathrm{Cu^{II}(CN)_4{}^{2-}}))^2[\mathrm{CN^-}]^8[\mathrm{Cu^{2+}}]^2 \quad (27)$$

apparent rate constant, k_r, corresponds to $k_2(\beta(\mathrm{Cu^{II}(CN)_4{}^{2-}}))^2[\mathrm{CN^-}]^8$, it is calculated as shown in the first section of Table I.

Baxendale and Westcott[9] have conducted the reaction between $\mathrm{Cu^{2+}}$ and CN$^-$ in weakly acidic solutions, where most of the cyanide was present in the form of HCN. They have followed the change of the concentration of the reaction product, $\mathrm{Cu^{I}(CN)_2{}^{-}}$, by means of a UV spectrometer and have obtained the rate equation, eq 25, and k_r values at 25 °C for different concentrations of total cyanide and for two different pH values. Their results are shown in the second section of Table I. In the calculation of [CN$^-$], the acid dissociation constant of hydrocyanic acid ($K_a = 10^{-9.21}$)[22] is used.

Tanaka et al.[10] have studied the kinetics of the reaction between (ethylenediaminetetraacetato)copper(II) complex

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Table I. Second-Order Rate Constant k_r Calculated from Various Kinetic Data

Data from Table I, Ref 8

$10^3[CN^-]$/M	$10^{-4}k_2$/$M^{-1}\ s^{-1}$	k_r/$M^{-1}\ s^{-1}$
35.4	1.130	2.8×10^{36}
25.9	1.292	2.6×10^{35}
22.0	2.680	1.5×10^{35}
20.8	2.400	8.4×10^{34}
10.7	4.350	7.5×10^{32}
8.58	6.010	1.8×10^{32}

Data from Figure 5, Ref 9

$10^7[CN^-]$/M	$10^3[HCN]$/M	pH	k_r/$M^{-1}\ s^{-1}$
1.08	1.56	5.05	4.5×10
1.25	1.80	5.05	7.8×10
1.41	2.04	5.05	1.7×10^2
1.66	2.40	5.05	4.3×10^2
0.63	1.81	4.75	4.7×10
0.75	2.17	4.75	1.4×10^2
0.83	2.40	4.75	2.5×10^2
0.96	2.76	4.75	5.5×10^2

Data from Table I, Ref 10

$10^2[CN^-]$/M	$10^3[Y^{4-}]$/M	$10^{-7}k_Y$/$M^{-4}\ s^{-1}$	k_r/$M^{-1}\ s^{-1}$
2.31	6.05	6.16	4.2×10^{36}
2.89	6.63	6.85	1.3×10^{37}
3.29	6.51	6.84	2.1×10^{37}
3.82	5.46	7.11	3.3×10^{37}

Data from Figure 6, Ref 5

$[CN^-]$/M	k_2/$M^{-1}\ s^{-1}$	k_r/$M^{-1}\ s^{-1}$
1.00	74	7.4×10^{45}
2.00	18.2	4.7×10^{47}
3.00	8.2	5.4×10^{48}

($Cu^{II}Y^{2-}$) and cyanide by measuring the decrease of the $Cu^{II}Y^{2-}$ concentration by polarography. They have obtained the experimental rate equation eq 28. Equation 28 can be

$$v = k_Y \frac{[Cu^{II}Y^{2-}]^2[CN^-]^4}{[Y^{4-}]} \qquad (28)$$

transformed to eq 29, in which $\beta(Cu^{II}Y^{2-})$ is the formation

$$v = k_Y(\beta(Cu^{II}Y^{2-}))^2[Y^{4-}][CN^-]^4[Cu^{2+}]^2 \qquad (29)$$

constant of the $Cu^{II}Y^{2-}$ complex. In this case, the constant k_r corresponds to $k_Y(\beta(Cu^{II}Y^{2-}))^2[Y^{4-}][CN^-]^4$ and is calculated from the reported data, where $\beta(Cu^{II}Y^{2-}) = 10^{18.8}\ M^{-1}$ (25 °C)[23] is used. The result is shown in the third section of Table I.

We have obtained[5] the same rate equation as that obtained by Nord and Matthes (eq 26), which can be transformed to eq 27. The constant k_r is shown in the fourth section of Table I.

Figure 5 shows a plot of the logarithm of k_r against the logarithm of $[CN^-]$. All points substantially lie on a single straight line, which is expressed by eq 30. As the constant

$$\log k_r = 6.17 \log [CN^-] + 45.9 \qquad (30)$$

k_r is regarded as proportional to the sixth power of $[CN^-]$, the reaction rate can be described by eq 31, which was first reported by Baxendale and Westcott.[9] The result indicates that all the reactions considered have the same rate-determining step. According to the discussion in the previous section, it is concluded that the chemical reaction between the Cu^{2+} or Cu(II) complex and CN^- proceeds by the mechanism shown in eq 32 and 5b. Reaction 32 is in equilibrium, and reaction 5b is rate determining.

$$v = k[CN^-]^6[Cu^{2+}]^2 \qquad (31)$$

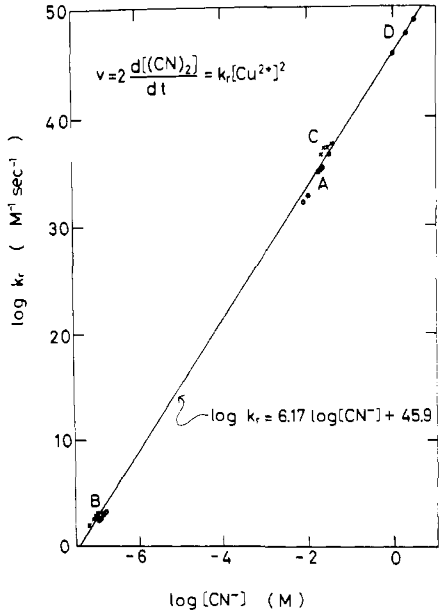

Figure 5. Relationship between the logarithm of k_r ($M^{-1}\ s^{-1}$) and the logarithm of CN^- concentration (M): A, data by Nord and Matthes;[8] B, data by Baxendale and Westcott[9] (○, pH 5.05; ×, pH 4.75); C, data by Tanaka et al.;[10] D, data by Yoshimura et al.[5]

$$2Cu(II) + 6CN^- \rightleftharpoons Cu^{II}_2(CN)_6^{2-} \qquad (32)$$

$$Cu^{II}_2(CN)_6^{2-} \rightarrow 2Cu^I(CN)_2^- + (CN)_2 \qquad (5b)$$

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Appendix

In general, the stepwise formation constant (K_i) of a metal complex decreases monotonically as the number (i) of the ligands increases, unless there is an abrupt change in coordination number or in electronic structure of the metal ion or there is a special steric effect, at a certain stage of complexation. The decrease in K_i values can be partly explained by statistical factors determined by the numbers of ligands and of water molecules in the complexes.[20] For example, the ratios of successive K_i values of amminecopper(II) complexes ($K_1 = 10^{3.99}$, $K_2 = 10^{3.34}$, $K_3 = 10^{2.73}$, $K_4 = 10^{1.97}$) are $K_2/K_1 = 0.224$, $K_3/K_2 = 0.245$, and $K_4/K_3 = 0.174$, and those of chlorocopper(II) complexes ($K_1 = 10^{0.0}$, $K_2 = 10^{-0.7}$, $K_3 = 10^{-1.5}$, $K_4 = 10^{-2.3}$) are $K_2/K_1 = 0.20$, $K_3/K_2 = 0.16$, and $K_4/K_3 = 0.16$, whereas the ratios $K_2/K_1 = 0.375$, $K_3/K_2 = 0.444$, and $K_4/K_3 = 0.375$ are theoretically expected from the statistical factors for the four-coordinate complexes. If the ratios of K_i of cyanocopper(II) complexes are assumed to be equal to those of amminecopper(II) complexes or chlorocopper(II) complexes, we obtain a set of values $K_1 = 10^{6.48}$, $K_2 = 10^{5.85}$, $K_3 = 10^{5.22}$, and $K_4 = 10^{4.46}$ or $K_1 = 10^{6.6}$, $K_2 = 10^{5.9}$, $K_3 = 10^{5.1}$, and $K_4 = 10^{4.3}$ for cyanocopper(II) complexes. We can therefore estimate the K_4 value of $Cu^{II}(CN)_4^{2-}$ to be $\sim 10^{4.3}$–$10^{4.5}$.

Registry No. $Cu^{II}(CN)_4^{2-}$, 36580-69-5.

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