473. *Kinetics and Equilibria in Copper*(II)*-Cyanide Solutions.*

By J. H. Baxendale and D. T. Westcott.

The equilibria concerned in the formation of $Cu(CN)_3^{2-}$ and $Cu(CN_4)^{3-}$ have been investigated, and the formation constants obtained spectroscopically.

The formation of these copper(I) cyanides in aqueous solution from copper(II) and CN^- is found to be an eighth-order reaction—second order in copper(II) and sixth order in cyanide. The simplest interpretation is that the equilibrium concentration of $Cu(CN)_3^-$ is rapidly established from copper(II) and CN^-. This species then reacts bimolecularly to give $Cu(CN)_2^-$ and $(CN)_2$. However, mechanisms involving other complex copper(II) cyanides can account for the observations equally well.

The oxidation of iodide [1] and thiocyanate [2] ions by iron(III) proceeds *via* the analogous intermediates I_2^- and $(SCN)_2^-$ and involves the ion pairs $Fe^{3+}I^-$ and $Fe^{3+}SCN^-$. The corresponding oxidation of iodide by copper(II) is more complex [3] because of heterogeneous catalysis by solid cuprous iodide. A similar situation exists in the formation of diacetylenes

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[1] Fudge and Sykes, *J.*, 1952, 119.

[2] Betts and Dainton, *J. Amer. Chem. Soc.*, 1953, **75**, 5721.

[3] Kemp and Rohwer, *J. S. African Chem. Inst.*, 1956, **9**, 12.

from monoacetylenes in the presence of copper salts, where the basic reaction is[4] the oxidation of the monoacetylene by copper(II) which is autocatalysed by the copper(I) monoacetylide simultaneously formed. On the other hand, for the oxidation of cyanide to cyanogen in concentrated ammonia solutions, where the copper(II) is present as the ammines and the reaction is homogeneous, Duke and Courtney[5] found a reaction rate of first order in copper(II) and fourth in CN^-, from which they concluded that the slow step involves the species $Cu(CN)_4{}^{2-}$. However, these kinetics could be accounted for equally well in other ways, *e.g.*, by the bimolecular reaction

$$
\begin{aligned}
Cu(CN)_3{}^- + CN^- &\longrightarrow Cu(CN)_3{}^{2-} + CN \\
\text{or} \quad &\longrightarrow Cu(CN)_2{}^- + (CN)_2{}^-
\end{aligned}
$$

Irrespective of the details, however, it appears that, since only one copper(II) atom is concerned in the slow step, a radical or radical ion must be formed as an intermediate.

We have studied the reaction in the absence of ammonia, using very dilute solutions, and have been led to investigate the equilibria in Cu(I) cyanide solutions.

Experimental.—The copper sulphate, potassium cyanide, sodium acetate, and acetic acid used were of analytical grade. Tripotassium cuprocyanide was prepared by Bassett and Corbet's[6] method and recrystallised from aqueous alcohol. The equilibria and kinetics were studied by mixing the required solutions at 25° and measuring their absorptions in 1, 5, or 10 cm. cells held at 25° in the Beckman spectrophotometer.

RESULTS AND DISCUSSION

Equilibria.—In dilute solutions (*ca.* 10 μM) copper(II) reacts rapidly with CN^- to give products, presumably copper(I) cyanides, which absorb appreciably in the region 220—250 mμ. The increase in absorption affords a convenient method of following the reaction at high dilutions. However, the spectrum of the products is a function of the cyanide concentration even when in large excess over copper(II), and also varies with dilution. The spectra of solutions of $CuCl + CN^-$ and of $K_3Cu(CN)_4 + CN^-$ are similar to those of the products and they show similar variations—probably owing to the species $Cu(CN)_2{}^-$, $Cu(CN)_3{}^{2-}$, and $Cu(CN)_4{}^{3-}$ which infrared[7] and E.M.F.[8] measurements have shown to be present.

Fig. 1 shows how the spectrum of $K_3Cu(CN)_4$ solutions changes with concentration. At 3μM and 6μM there is a maximum at 234 mμ which shifts to longer wavelengths when the solution is made 0·01N in potassium hydroxide. A similar shift occurs as the concentration of $K_3Cu(CN)_4$ increases and also (not shown in Fig. 1) when CN^- is added. The effect is no doubt due to the increase in free cyanide ion in each case, for the alkali reverses the hydrolysis of the cyanide ion which occurs appreciably at these concentrations. At higher $K_3Cu(CN)_4$ concentrations the spectrum approaches a limiting form with a maximum at 239 mμ, which is unaffected by CN^- up to about 10^{-3}M (Fig. 1, *B* and Fig. 2, *B*). Increases of CN^- beyond this cause changes in the reverse direction as shown in Fig. 2.

From what is known about this system[7,8] it is reasonable to suppose that the effects arise from the changes in the species concerned in the equilibria:

$$Cu(CN)_2{}^- + CN^- \xrightleftharpoons{K_1} Cu(CN)_3{}^{2-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$Cu(CN)_3{}^{2-} + CN^- \xrightleftharpoons{K_2} Cu(CN)_4{}^{3-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

On this basis the spectrum at low CN^- concentrations corresponds to that of $Cu(CN)_2{}^-$ (Fig. 1, *A*). This passes to that of $Cu(CN)_3{}^{2-}$ with increasing CN^- (Fig. 1, *B*; Fig. 2, *B*),

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[4] Baxendale and Westcott, unpublished work.

[5] Duke and Courtney, *J. Phys. Chem.*, 1952, **56**, 19.

[6] Bassett and Corbet, *J.*, 1924, **125**, 1660.

[7] Penneman and Jones, *J. Chem. Phys.*, 1956, **24**, 293.

[8] Kunschert, *Z. anorg. Chem.*, 1904, **41**, 359.

and with further increases moves towards that of $Cu(CN)_4^{3-}$, although the latter is not attained at the concentrations used. Quantitative analysis of the spectra confirms this. If we assume equilibrium (1) to be responsible for the changes shown in Fig. 1, then the amount of $Cu(CN)_3^{2-}$ present when the concentration of $K_3Cu(CN)_4$ is initially c is given by

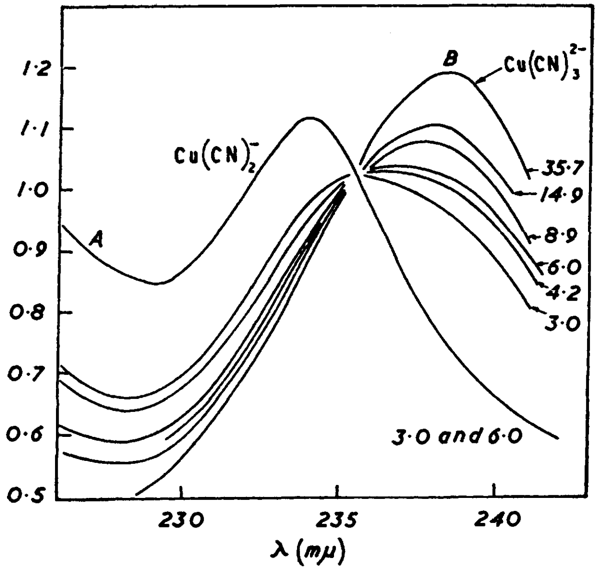


FIG. 1. *Change in absorption of* $K_3Cu(CN)_4$ *with concentration (given in* μM*). Curve B was unchanged when* $1{\cdot}2 \times 10^{-3}$M-CN^- + 0·1N-KOH *were present. All other solutions except those giving curve A contained* 0·01N-KOH.

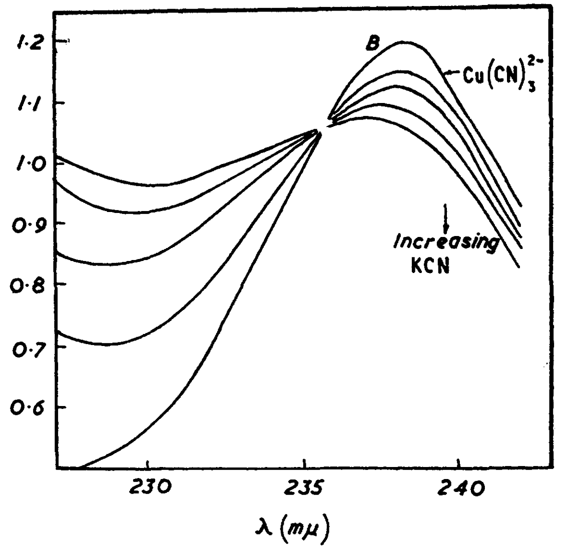


FIG. 2. *Change in absorption of* 6μM-$K_3Cu(CN)_4$ *with added* KCN. *All solutions contained* 0·01N-KOH. KCN *concentrations* are 1, 2, 5, 15, *and* 20 mM, *the absorption at* 239 mμ *decreasing as* KCN *increases.*

$$[Cu(CN)_3^{2-}] = c(\varepsilon - \varepsilon_2)/(\varepsilon_3 - \varepsilon_2)$$

where ε is the absorption coefficient of the solution, ε_2 and ε_3 those for $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$, all measured at the same wavelength. The calculated values of K_1 from this by using the data at 239 mμ are given in the Table and are reasonably consistent.

Equilibrium constant for the reaction $Cu(CN)_2^- + CN^- \rightleftharpoons Cu(CN)_3^{2-}$.

(Data from Fig. 1.)

Total Cu^I (μM)	$10^{-3}\varepsilon_{239}$	$(CN)_3^{2-}$ (%)	$10^{-5}K_1$	Total Cu^I (μM)	$10^{-3}\varepsilon_{239}$	$(CN)_3^{2-}$ (%)	$10^{-5}K_1$
3·0	9·4	48	2·0	8·9	10·5	72	2·2
4·2	9·85	58	2·3	14·9	10·9	80·5	2·3
6·0	10·1	63	2·1	35·7	11·8	100	—

Similarly, for the spectra of Fig. 2 it is easily shown that if equilibrium (2) is responsible for the variations, then we should have

$$b/(\varepsilon - \varepsilon_3) = (b + 1/K_2)/(\varepsilon_4 - \varepsilon_3)$$

where $b = [CN^-]$ and ε_4 is the absorption coefficient of $Cu(CN)_4^{3-}$. Hence a plot of $b/(\varepsilon - \varepsilon_3)$ against b should be linear, as is found (Fig. 3). This line gives $K_2 = 55$, and the Table gives $K_1 = 2{\cdot}2 \times 10^5$. Using infrared absorption with concentrations higher by a factor of 10^4 than those used here, Penneman and Jones [7] obtained $K_1 = 4 \times 10^4$ and $K_2 = 131$ in terms of concentrations at 29°. In terms of activities they estimated $K_2 = 39$ and $K_1 = 2{\cdot}4 \times 10^4$.

FIG. 3.

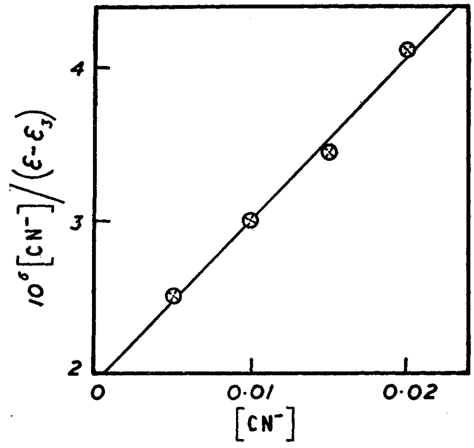
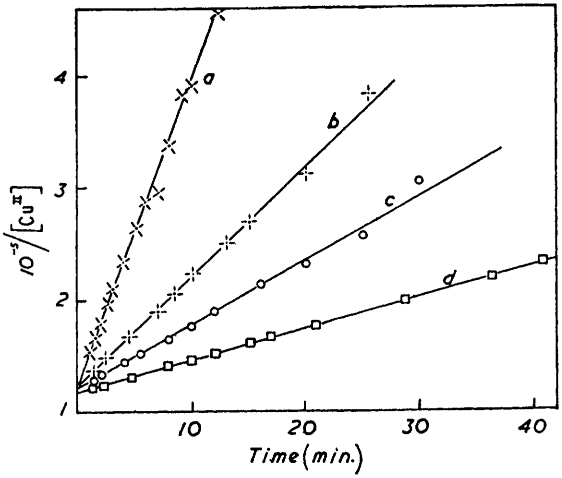


FIG. 4. *Second-order plots for reaction of copper*(II) *with cyanide ion at* pH 5·05 *for various values of* $[CN^-]$: *a*, 2·40; *b*, 2·04; *c*, 1·80; *d*, 1·56 mM.



Kinetics.—Preliminary experiments showed that Cu^{2+} and CN^- at concentrations *ca.* 10 μM react completely within the time required to measure the absorption of the mixture. The reaction is much slower in acid solutions and very sensitive to acid and cyanide concentrations. Convenient reaction times were obtained at about pH 4·7 with *ca.* 10^{-5}M-copper(II) and 10^{-3}M-cyanide. Buffers were made up with 0·01M-sodium acetate and acetic acid to give pH 4·75 and 5·05. Perchloric acid was added in equimolar amounts to the potassium cyanide to avoid changes in pH due to the latter.

In these conditions the final product has maximum absorption at 234 mμ and is therefore in the form $Cu(CN)_2^-$. The reaction was followed by measuring the absorption at this wavelength, and the amount of copper(II) present calculated from this and the absorption of the final products. Fig. 4 shows that at pH 5·05 with cyanide in large excess, good second-order plots in copper(II) are obtained, *i.e.*,

$$-\,d[Cu^{II}]/dt = k_1[Cu^{II}]^2$$

At the same cyanide concentration a five-fold increase in initial copper(II) gave the same value of k_1. The latter was also unaffected by the presence or absence of air, or by the presence of the products of a previous reaction.

Reactions at pH 4·75 are also of second order in copper(II). Fig. 5 shows that k_1 is proportional to [cyanide] ^{6} at both pH's, *i.e.*,

$$-\,d[Cu^{II}]/dt = k_2[Cu^{II}]^2[\text{cyanide}]^{\,6}$$

where k_2 is the slope of the lines in Fig. 5 and increases with pH.

At these pH's the cyanide will be present almost entirely as HCN, and it seems probable that pH affects the rate *via* the equilibrium

$$HCN \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + CN^-$$

because the cyanide reacts in the CN^- form. In this case, since $K_a = 10^{-9}$, we would expect k_2 to vary as $1/[H^+]^6$, which is approximately true for the two pH's in Fig. 5. Hence the overall rate equation

$$-\,d[Cu^{2+}]/dt = k_3[Cu^{2+}][CN^-]^6$$

would account for the experimental observations.

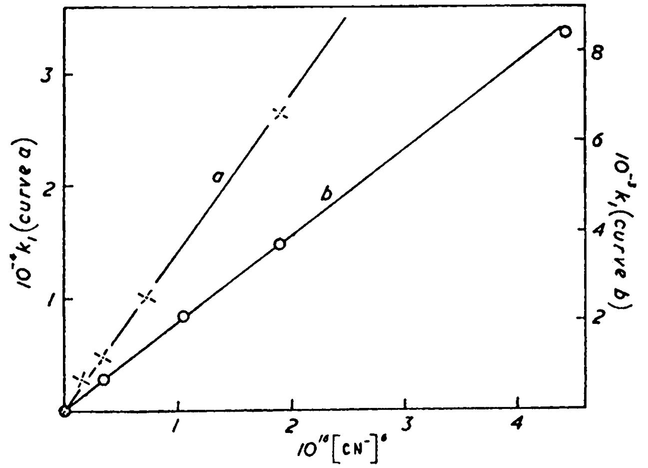


FIG. 5. *Dependence of second-order rate constant,* k_1, *on* $[CN^-]$ *at a,* pH 5·05; *b,* pH 4·75.

This very high order in CN^- probably arises because the reacting species in the rate-determining step are present in equilibrium with Cu^{2+} and CN^-. Thus, suppose the slow step is

$$2Cu(CN)_3^- \longrightarrow 2Cu(CN)_2^- + (CN)_2$$

and $Cu(CN)_3^-$ is formed *via* the rapidly established equilibria

$$Cu^{2+} + CN^- \rightleftharpoons CuCN^+$$

$$CuCN^+ + CN^- \rightleftharpoons Cu(CN)_2$$

$$Cu(CN)_2 + CN^- \rightleftharpoons Cu(CN)_3^-$$

Then

$$[Cu(CN)_3^-] = K_3[Cu^{2+}][CN^-]^3$$

and the observed rate equation would follow provided that only a small fraction of the copper(II) is present in the form of complex ions.

However, if we assume that the extent of complex-ion formation is small, the same kinetics would be given if the slow step involved any two ions having between them a total of six CN^-, *e.g.*, $Cu(CN)_2$ and $Cu(CN)_4^{2-}$. This does not exhaust the possibilities, for if the copper(II) is present predominantly as one of the lower complex ions, say $CuCN^+$, then reaction between two $Cu(CN)_4^{2-}$ or between $Cu(CN)^+$ and $Cu(CN)_6^{4-}$ would give the same kinetics.

THE UNIVERSITY, MANCHESTER.

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