Acta Chemica Scandinavica A 28 (1974) 13—19

A Stopped-flow Kinetic Study of the Copper(II) Cyanide Reaction in Water and in Aqueous Methanol

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The copper(II) cyanide reaction is second order in copper(II) and inversely proportional to the uncomplexed cyanide. This is attributed to reaction between $Cu(CN)_3^-$ and $Cu(CN)_4^{2-}$. $k_1 = k/[CN^-]$, where k, the observed second order rate constant at 25°C, decreases from 470 $M^{-1}s^{-1}$ in water to 5.6 $M^{-1}s^{-1}$ in 50 % and to 1.23 $M^{-1}s^{-1}$ in 80 %, by weight, methanol. The measurements were made at 25°C, 15°C, and 0°C and at an ionic strength of 0.1 M. The energy of activation in water is 6 ± 1 kcal M^{-1}. The results are correlated with those of earlier workers for water, aqueous methanol, and also aqueous ammonia.

The rate of the reaction

$$2\ Cu(CN)_4^{2-} \rightarrow C_2N_2 + 2\ Cu(CN)_3^{2-} \qquad (1)$$

has previously been measured at low temperatures in aqueous methanol.[1,2] In water the reaction is fast and has hitherto been followed in the presence of a competing ligand [3,4] and in a buffered solution of HCN.[5] The reaction is second order in copper(II).*

The determination of the stoicheiometry and rate, of reactions of labile complexes, usually only enables the composition of the transition state (or reactive intermediate) to be established. However, if alternative pathways lead to impossibly high rate constants, or involve species with improbably large coordination numbers, then it should be possible to identify the reactants. We have studied the copper(II)-cyanide reaction using concentrations which, at about 25°C, gave rates suitable for measurement by the stopped-flow technique. We combine our results with those of earlier workers and attempt to assess the validity of the mechanism we have used in order to correlate all the available experimental data.

EXPERIMENTAL

The chemicals were the same and the solutions were standardised in the same way as in previous papers from this laboratory.[1,2] Ionic strengths were adjusted with sodium *p*-toluene sulphonate.

Kinetic measurements were made with the apparatus described in Ref. 6. The optical absorbance at 535 nm was measured for solutions produced by mixing equal volumes of copper(II) *p*-toluene sulphonate and of sodium cyanide. For any one solution, at constant flow rate, the initial plateau absorption (before stopping the flow) was reproducible, as also was the rate of decay of this absorption (see Figs. 1a and 1b). Second order plots were linear and were constructed as illustrated in Fig. 2. In all cases, some of the copper reacted during mixing and before measurement. This amount of copper was particularly large for the aqueous solutions which were therefore investigated over a series of flow rates. Fig. 3 illustrates that the rate of the homogeneous reaction was independent of flow rate and of stopping time. It is the plateau optical density divided by $\varepsilon = 213$ for minimum initial reduction which is reported in the tables.

RESULTS AND DISCUSSION

The copper(II) in our solutions is almost entirely present as $Cu(CN)_4^{2-}$ (Ref. 1) and the absorbance at 535 nm can be entirely attributed to this species (Refs. 2, 7). Tables 1 and 2 give the total copper concentration in the mixed

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* The data from Ref. 4, which were interpreted by the authors in the terms of a first order rate law is recalculated and discussed later in this paper.

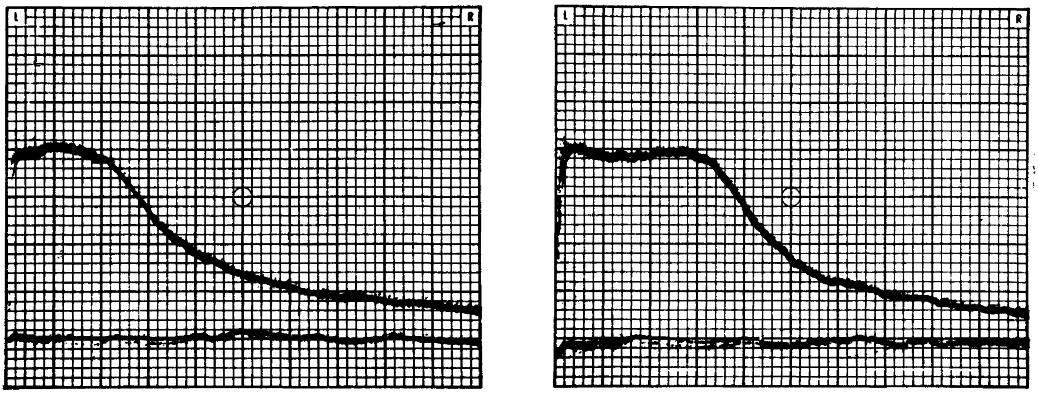

Fig. 1(a) and *Fig. 1(b)*. Oscilloscope traces for Series 24, Table 2, see text.

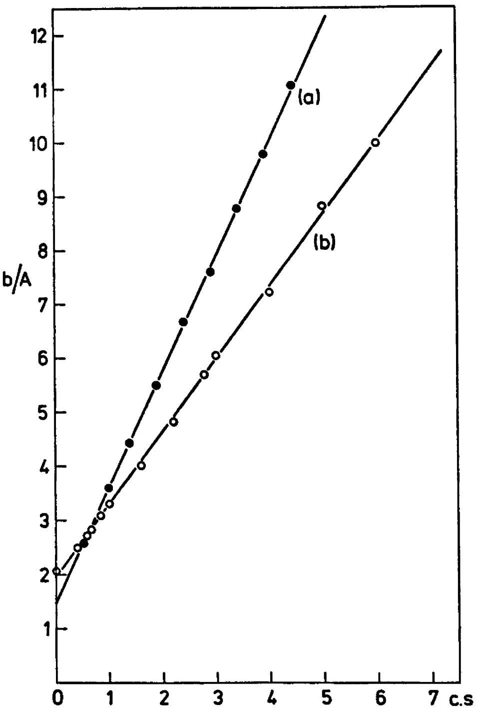

Fig. 2. Second order plots. Ordinate b/A where A is absorbance, abscissa cs where s is seconds. (a) Series 15, Table 1; c = 0.05, b = 0.464. (b) Series 19, Table 1; c = 0.10, b = 0.716.

solutions (C_{Cu}); the uncomplexed cyanide concentration $[CN^-] = (C_{CN^-} - 4C_{Cu})$; together with $\Delta(1/A)/\Delta t = S$, where A is the absorbance per cm cell length (calculated from the measured absorbance and a calibration curve constructed using ferroin solutions), t is seconds. S is therefore equal to k/ε where ε is the molar absorbance of $Cu(CN)_4^{2-}$ and $k(M^{-1}s^{-1})$ the rate constant with respect to the reduction of this species.

The rate constants have an inverse dependence on $[CN^-]$ (see Tables 1 and 3) but S is constant during each run (see Figs. 1 – 3). This means that $[CN^-]$ is constant during any one run in accord with the stoicheiometry given in eqn. 1. Changes due to the equilibrium

$$Cu(CN)_3^{2-} + CN^- \rightleftharpoons Cu(CN)_4^{3-};\ K_4(Cu(I)) \qquad (2)$$

are small.

The value taken for the molar extinction coefficient ε for $Cu(CN)_4^{2-}$, used to calculate $[Cu(CN)_4^{2-}]_0$ given in the tables, was 213 and was obtained in the following way.

It was observed that the plateau absorbance (ΔA_0) decreased, at constant flow rate, with increasing S. For the methanolic solutions (series 1 to 7 in Tables 1 and 3) the amount of this reduction was small enough to allow extrapolation to zero reduction. A plot of $(C_{Cu}/\Delta A_0)^2$ *versus* S is linear and from this ε was calculated to be 213 (intercept $= (1/\varepsilon)^2$; $S \rightarrow 0$). Thus for series 1 to 7, $k = 213\ S\ M^{-1}s^{-1}$. The large amount of initial reduction in aqueous solution precluded accurate extrapolation so that we have used $\varepsilon = 213$ to calculate k throughout. It may be noted that the general trend is the same for all media. This value of 213 is in fair agreement with the results of earlier workers who describe a broad band at 560 nm with ε about 220 at $-30°C$[7] and λ_{max} 535 nm, ε_{max} 172 at $-70°C$.[2]

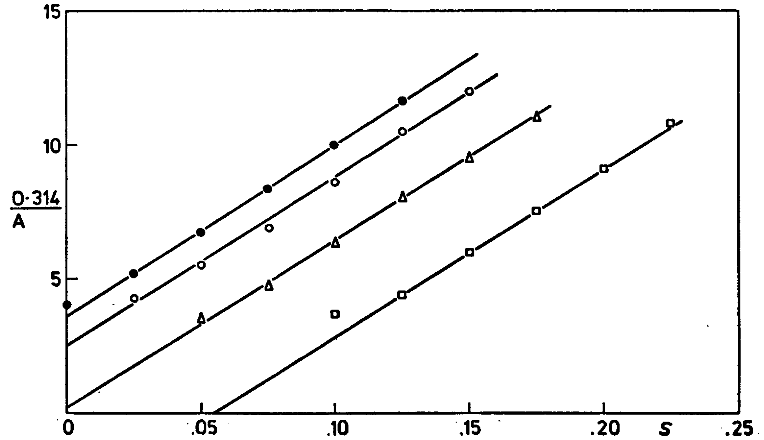

Fig. 3. Series 12, Table 1; see text.

Table 1.

Number of series	Temperature °C	C_{Cu} mM	$[\mathrm{CN}^-]$ mM	S	$[\mathrm{Cu(CN)}_4{}^{2-}]_0$ mM	$10^{-4}k_{\mathrm{obs}}$ $\mathrm{M}^{-1}\mathrm{s}^{-1}$	$10^{-4}k_{\mathrm{calc}}$ $\mathrm{M}^{-1}\mathrm{s}^{-1}$
Solvent is 50 % by weight methanol-water							
1	25	5.020	13.67	1.99 ± 0.02	1.70	0.0425	0.0410
2	25	5.020	9.22	2.76 ± 0.12	1.51	0.0588	0.0608
3	25	5.020	7.02	3.73 ± 0.24	1.32	0.0795	0.0798
Solvent is 80 % by weight methanol-water							
4	25	3.575	15.10	0.406	2.56	0.0087	0.0088
5	25	3.255	9.48	0.784 ± 0.01	1.63	0.0167	0.0145
6	25	3.575	1.85	4.85 ± 0.01	0.85	0.1032	0.1048
7	25	3.575	1.40	7.32	0.94	0.1560	0.1543
Solvent is water							
8	25	2.085	35.4	53.0	1.10	1.130	1.310
9	25	3.150	25.9	60.6	0.70	1.292	1.815
10	25	3.700	22.0	125.5	0.47	2.680	2.140
11	25	4.175	20.8	112.5	0.48	2.400	2.260
12	25	4.175	10.7	204	0.67	4.350	4.400
13	25	4.080	8.58	282	0.38	6.010	5.470
14	15	2.085	35.4	37.1	0.745	0.790	1.004
15	15	4.175	20.8	94.2	0.833	2.020	1.710
16	15	4.170	19.0	97.8	1.03	2.083	1.870
17	15	4.820	11.2	154.0	1.06	3.280	3.170
18	15	4.175	10.7	137.2	1.25	2.925	3.320
19	0	2.085	35.4	20.1	1.58	0.428	0.510
20	0	4.175	20.8	48.8	1.14	1.255	0.868
21	0	4.175	10.7	78.0	0.98	1.660	1.690
22	0	2.085	8.35	96.2	0.80	2.050	2.110

Ionic strength = 0.10 M

Table 2.

Number of series	Number of runs	Ionic strength	C_{Cu} M	$[\mathrm{CN^-}]$ M	S	$\mathrm{Cu(CN)_4]_0}$	$k_{\mathrm{obs}} \times [\mathrm{CN^-}]$
23	1	0.21	0.0118	0.0428	73.2	1.03	667
24	3	0.25	0.1045	0.0517	55 ± 1	3.44	605
25	4	0.50	0.1045	0.0830	33 ± 3	1.54	583
26	1	0.62	0.0047	0.5540	4.44	3.93	523

Solvent water; 15°C.

The rapid reaction during mixing was also observed at low temperatures [1,2] and was attributed [8] to the more rapid reaction of $[\mathrm{Cu(CN)}_n]^{(n-2)-}$ with $n < 4$ formed in the inhomogeneous solutions. Since the bulk species is $\mathrm{Cu(CN)_4^{2-}}$ and the rate is inversely proportional to $[\mathrm{CN^-}]$, then the composition of the transition state in water must be $[\mathrm{Cu_2(CN)_7}]^{3-}$ (see Tables 1 to 3). The simplest interpretation of this is that it represents reaction of the bulk copper(II) species, *viz.*: $\mathrm{Cu(CN)_4^{2-}}$, with $\mathrm{Cu(CN)_3^-}$ formed according to eqn. 3;

$$\mathrm{Cu(CN)_4^{2-}} \rightleftharpoons \mathrm{Cu(CN)_3^-} + \mathrm{CN^-};\ K_4^{-1}\ (\mathrm{Cu(II)}) \qquad (3)$$

Thus

$$k_1 = k_t/K_4(\mathrm{Cu(II)})\ \text{(see Table 3)} \qquad (4)$$

where k_t is the true rate constant for the reaction between $\mathrm{Cu(CN)_3^-}$ and $\mathrm{Cu(CN)_4^{2-}}$. The small change in k_1, with change of ionic strength from 0.2 to 0.6 M, parallels that found for the stability constants of other cyanide complexes.*

Using k_1 from series $(8-13)$, $(14-18)$, and $(19-22)$ in Table 1, then the energy of activation, E_A, is 6 ± 1 kcal $\mathrm{M^{-1}}$. Using reaction rate theory, then $E_A = \Delta H^* + RT$, and from the above treatment, $\Delta H^* = \Delta H_4 - \Delta H_t^*$ where

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* *E.g.*, $K_4(\mathrm{Cu(I)})$ (eqn. 2) is 200 ($\Delta H_4^\circ = 6.7$ kcal) at 15°C and is, within the experimental error, constant between ionic strengths of 0.2 and 1.0.[9] $K_4(\mathrm{Cu(I)})$ is about 300 at 15°C and an ionic strength of 0.1.[10] $K_4(\mathrm{Cu(II)})$ is of course much larger than this (see text).

Table 3.

Series	Range of $[\mathrm{CN^-}]$ M	Solvent	Rate law: $k = k_1/[\mathrm{CN^-}] + k_2/[\mathrm{CN^-}]^2$
1 to 3	0.01367 to 0.00702	50 % wt. Methanol – water (25°C)	$k_{\mathrm{calc}} = 5.6/[\mathrm{CN^-}]$
4 to 7	0.01510 to 0.00140	80 % wt. Methanol – water (25°C)	$k_{\mathrm{calc}} = 1.23/[\mathrm{CN^-}] + 0.0013/[\mathrm{CN^-}]^2$
8 to 13	0.0354 to 0.00858	Water (25°C)	$k_{\mathrm{calc}} = 470/[\mathrm{CN^-}]$
14 to 18	0.0354 to 0.0107	Water (15°C)	$k_{\mathrm{calc}} = 355/[\mathrm{CN^-}]$
19 to 22	0.0354 to 0.00835	Water (0°C)	$k_{\mathrm{calc}} = 181/[\mathrm{CN^-}]$

Table 4. $C_{\mathrm{Cu}} = 1.25 \times 10^{-3}$ M; $C_{\mathrm{NH_3}} = 12.5$ M. 0°C. Ionic strength 1.0 M with $\mathrm{NaNO_3}$. Data from Fig. 1, Ref. 4. For calculation of k see text. $k_{\mathrm{average}} = 2.2 \times 10^8\ \mathrm{M^{-1}s^{-1}}$.

	$C_{\mathrm{CN^-}}/C_{\mathrm{Cu}}$	$C_{\mathrm{CN^-}}/C_{\mathrm{NH_3}}$	$k\ \mathrm{M^{-1}s^{-1}}$	10^{8}-$k/[\mathrm{CN^-}]^4$
a	12	1.2×10^{-3}	11.3	2.48
b	8	8×10^{-4}	2.28	2.28
c	6	6.25×10^{-4}	0.93	2.94
d	5	5×10^{-4}	0.3	1.97

ΔH_t^* is the true activation enthalpy. Similarly, the abnormally low value for the frequency factor corresponding to k_1 results from the composite form of this rate constant.

The only stability constant for Cu(II)$-$CN$^-$ equilibria which has been reported, is that of Bjerrum and Paterson, who found the decadic logarithm of the overall stability constant (β_4) to be 26.7 in 60 % methanol-water at -45°C. We use this value, later in the discussion, to check the plausibility of the values we now estimate for β_4 in water at 0°C and at 25°C.

For the Cu(II)$-$CN$^-$$-H_2$O system, Baxendale gave graphically recorded results (Figs. 4 and 5, Ref. 5) for 25°C with $[\text{CN}^-] \sim 10^{-7}$ and at pH 5.05 and 4.75. He showed that the reaction was second order in copper(II) and that the composition of the transition state, under his conditions, was $[\text{Cu}_2(\text{CN})_6]^{2-}$. From his figures we find that $\log k - 6 \log [\text{CN}^-] = 43.4$ for both pH. k is the second order rate constant, M^{-1} s^{-1}, and [CN$^-$] has been calculated from C_{CN^-} using $\text{p}K_{\text{HCN}} = 9.21$. Following our interpretation, the reactants either (a) are both Cu(CN)$_3^-$, so that

$$k[\text{Cu(CN)}_3^-]^2 = k_t\beta_3^2[\text{CN}^-]/(C_{\text{Cu}} - ([\text{Cu(CN)}_3^-])^2$$

and since $[\text{Cu(CN)}_3^-] \ll C_{\text{Cu}}$,

then $\log k_t + 2 \log \beta_3 = 43.4$,

or (b) are Cu(CN)$_4^{2-}$ and Cu(CN)$_2$, resulting in the substitution of $\log \beta_4 + \log \beta_2$ for $2 \log \beta_3$. Considering first (a), then since the limiting value of $k_t \approx 10^{10}$, $\beta_3 < 10^{16.7}$. Using the β_4/β_3 ratio of the Cu(II)$-$NH$_3$ system[11] we find $\beta_4 \geq 10^{20}$ and $K_4 \approx 10^4$. Considering (b), then an analogous treatment gives $\beta_4 \geq 10^{21}$. In both (a) and (b) $\log \beta_n \times 1/n \approx 5$ and we use this approximated value below. That $\log \beta_4 \approx 20$ is reasonable as it would not be expected to be very different from the $\log \beta_4$ values for Zn(II) and Cd(II), which are 17 and 18, respectively.[12] Also, combining $\log \beta_4 = 20$ at 25°C with $\log \beta_4 = 26.7$ at -45°C gives $\Delta H_{1-4} = -30$ kcal M^{-1} which is about the same as that for Cd(II) (29 kcal M^{-1}). We do not know the solvent effect on β_4 but believe that it cannot be large.

Using K_4 at 24°C $= 10^4$ then k_t, defined by eqn. 4, for the reaction between Cu(CN)$_4^{2-}$ and Cu(CN)$_3^{2-}$ $\approx 10^7$ M^{-1}s^{-1}. The decrease in reaction rate with increase in coordination number is also found for other redox reactions involving coordinated CN$^-$ and also Cl$^-$ and has been attributed to stabilisation of the reactive intermediate by bridging.

The data in Refs. 3 and 4 can also be satisfactorily accounted for using $\log \beta_n \times 1/n = 5$. Thus, Tanaka *et al.*[3] measured the rate of cyanide oxidation by copper(II) in the presence of excess ethylenediamine tetraacetate anion (Y^{4-}) and at 25°C with an ionic strength of 0.5 found that

$$-\text{d}[\text{CuY}^{2-}]/\text{d}t = 6.8 \times 10^7 \frac{[\text{CN}^-]^4[\text{CuY}^{2-}]^2}{[\text{Y}^{4-}]} \tag{5}$$

Here the bulk species is CuY^{4-} but with [CN$^-$] large enough to ensure that $n = 4$ for the very small concentration of Cu(CN)$_n^{(n-2-)}$. We rewrite eqn. 5 as

$$\begin{aligned} -\text{d}C_{\text{Cu}}/\text{d}t &= k_t[\text{Cu(CN)}_4^{2-}][\text{CuY}^{2-}] \\ &= k\frac{[\text{CN}^-]^4}{[\text{Y}^{4-}]} \times C_{\text{Cu}}^2 \end{aligned} \tag{6}$$

where $\log_{10} k = \log_{10} k_t + \log \beta_4 - \log \beta_{\text{Y}^{4-}}$. $\log \beta_{\text{Y}^{4-}} a$ is 18.5[12] so that using $\log \beta_4 \approx 20$ gives $k_t \approx 10^6$ M^{-1}s^{-1}.

We would expect analogous behaviour for the Cu(II)$-$CN$^-$$-NH_3$ system studied by Duke and Courtney,[4] and therefore reexamined their experimental data as recorded in Fig. 1 of Ref. 4. The results of our calculations are given in Table 4 of the present paper. We find that for solution *a* then a plot of $1/C_{\text{Cu}}$ *vs.* *t* (sec) is linear for all of the 97 % of the reaction measured. Solution *b* gives a similar second order plot for about the first half life, while the other second order rate constants were obtained from initial slopes. We agree with the authors that the transition state contains four cyanide ions but find that it should be formulated as $[\text{Cu}_2(\text{CN})_4(\text{NH}_3)_n]^{2-}$. Here n is presumably 4 or 5. Substitution of 4 for the coordination number of the bulk species (5) does not affect the following conclusions. From Table 4 and following our treatment,

$$\log \beta_4(\text{CN}^-) - \log \beta_5(\text{NH}_3) + \log k_t = 8.34 + 5 \log a_{\text{NH}_3}.$$

Since $\log \beta_5 + 5 \log_{10} a_{\text{NH}_3} = 20.4$[11] then using $\log \beta_4 \approx 21$ at 0°C gives $k \approx 10^8$ M^{-1-}s^1 which is again less than the diffusion controlled limiting value. For this NH$_3$$-CN^-$ system the rate decreases enormously when the ratio of coordinated cyanide:copper becomes less than two. We therefore believe that the first formed products of the second order reaction are the mixed Cu(I) cyanoammonia complexes $CuCN(NH_3)_n$ and that the probable reactants are both the mixed Cu(II) complex $Cu(CN)_2(NH_3)_2$. Any extra stability (over the statistical values) associated with these mixed complexes would lower the calculated k.

Data in aqueous methanol. In aqueous methanol at 25°C, except at the very lowest $[CN^-]$, the rate is again dominated by the k_1 term corresponding to reaction of $Cu(CN)_3^-$ with $Cu(CN)_4^{2-}$ (see Table 3). Increasing the concentration of methanol decreases the rate as also was found by Mønsted and Bjerrum.[2] These latter authors observed that, except for very high methanol content, then the linear log k *vs.* D^{-1} relation, theoretically expected, was not strictly obeyed. This behaviour is usual for systems where "specific solvation" can be postulated. Throughout this paper we have adopted the usual convention of omitting solvent molecules and written $Cu(CN)_3^-$ and $Cu(CN)_4^{2-}$ for the reacting species. The maximum coordination number for copper(II) in solution is, however, probably five [13] so that both inner and outer coordinated solvent may play an important role in the transition state. Change in reactivity accompanying change of composition of coordinated solvent would mean that the dependence of rate on methanol content of the solvent would no longer be expected to reflect only macroscopic properties of the solvent, but would also follow the dependence known for activity coefficients of inner solvated ions. This would lead to a decrease of log k proportional to decreasing x where x is the mol fraction of the more strongly coordinated solvent,[14,15] in this case water. The extensive data in Ref. 2 do show this trend. Specific solvation can also explain changes in E_A, which increases from 6 kcal M^{-1} in water to 11.9 kcal M^{-1} in 50 % methanol [2] and to 14 kcal M^{-1} in 80 % methanol.[2]

In neither of the mixtures at $-20°C$ and $-28°C$ was the rate found to be strictly proportional to $1/[CN^-]$. This may reflect the presence of a k_0 term corresponding to reaction between two $Cu(CN)_4^{2-}$ complexes.† Since, however, the low temperature work was made with free cyanide 0.027 to 0.074 M, so that a large fraction of the sodium *p*-toluene sulphonate used to adjust the ionic strength to 0.1 was replaced by cyanide, it may well, as pointed out by the authors, reflect an opposing medium effect.

For 50 % methanol at $-28°C$ then k_1 (as defined in Table 3 and calculated from $k_1 = 5.6$ at 25°C together with $E_A = 11.9$ kcal M^{-1}) is 0.073 $M^{-1}s^{-1}$. The product of the observed rate constant and the free cyanide ($k[CN^-]$) is 0.043, 0.073, and 0.105 for $[CN^-] = 0.028$, 0.0508, and 0.0736, respectively. For 80 % methanol E_A is 14.0 kcal M^{-1} and using $k_1 = 1.23$ at 25°C gives $k_1 = 0.0178$ at $-20.5°C$. At this temperature $k[CN^-]$ is 0.0185, 0.0230, and 0.0279 for $[CN^-] =$ 0.0273, 0.0501, and 0.0729, respectively. It is therefore possible that only the k_1 term appears at low temperatures also and that the deviation with increasing $[CN^-]$ represents a kinetic salt effect. If this is so then the large changes in E_A can be attributed, as above, to change in $\Delta H^* = \Delta H_4 - \Delta H_t^*$.

Acknowledgement. The authors thank Professor Jannik Bjerrum for invaluable discussions both during the course of the work and during the preparation of the manuscript.

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† If this is so, then it is difficult to understand the disappearance of the k_1 term (see later discussion). However, the data can be reproduced using a $[CN^-]^{-\frac{1}{2}}$ dependence, possibly reflecting the protonation of the transition state in methanol-rich solvents at low temperatures.

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Received August 13, 1973.