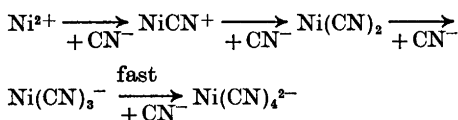


Kinetics of Formation of the Tetracyanonickelate(II) Ion

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The formation of $\text{Ni}(\text{CN})_4^{2-}$ has been investigated spectrophotometrically mainly at 267.5 nm in the pH-range 4.7–7.0. Both conventional spectrophotometry and stopped-flow methods have been applied. The ionic medium was 3.00 M NaClO_4 and the temperature 25.0 °C. The kinetics of the association reactions can in the actual pH-range be described by the following scheme:



On the assumption that all species except $\text{Ni}(\text{CN})_4^{2-}$ and Ni^{2+} are in a steady state the results from both the association and dissociation¹ measurements can be summarized in:

$$-dX/dt = k_{\text{obs}}X \quad (1)$$

where

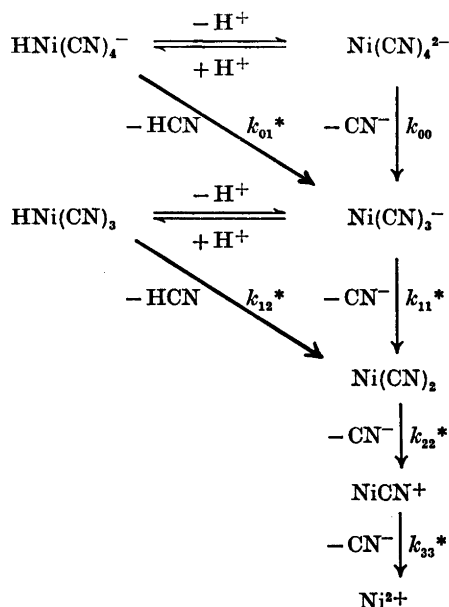
$X = [\text{Ni}(\text{CN})_4^{2-}]$ for dissociation and $[\text{Ni}^{2+}]$ for association and

$$\begin{aligned} k_{\text{obs}} = & (1 + \beta_4 K_a^4 [\text{HCN}]^4 h^{-4}) / \{ (k_{00} + k_{01} h)^{-1} + \\ & [\text{HCN}] (k_{11} h + k_{12} h^2)^{-1} + [\text{HCN}]^2 (k_{22} h^2)^{-1} + \\ & [\text{HCN}]^3 (k_{33} h^3)^{-1} \} \end{aligned} \quad (2)$$

and the corresponding reaction scheme shown beside. (Only the arrows corresponding to dissociation have been marked).

$$\begin{aligned} k_{00} = & (3.4 \pm 0.6) 10^{-4} \text{ s}^{-1}; \quad k_{01} = (3.34 \pm 0.16) 10^{-3} \\ & \text{s}^{-1} \text{ M}^{-1}; \quad k_{11} = (1.55 \pm 0.15) 10^{-5} \text{ s}^{-1}; \quad k_{12} = \\ & (5.5 \pm 0.4) 10^{-5} \text{ s}^{-1} \text{ M}^{-1}; \quad k_{22} = (0.169 \pm 0.020) \\ & \text{s}^{-1}; \quad k_{33} = (5.6 \pm 1.0) 10^3 \text{ s}^{-1} \end{aligned}$$

While k_{00} is a true rate constant, $k_{01} - k_{33}$ are products of rate constants and equilibrium constants. Since the values of these equilibrium constants are unknown the pure rate constants $k_{01}^* - k_{33}^*$ cannot be determined.



The kinetic measurements yield a value of the overall stability constant for $\text{Ni}(\text{CN})_4^{2-}$ which is in excellent agreement with the value obtained in previous equilibrium studies.²

Results from equilibrium measurements on the complex system $\text{Ni}^{2+} - \text{CN}^-$ and kinetic studies of the acid dissociation of $\text{Ni}(\text{CN})_4^{2-}$ have been presented in previous papers.^{2,1}

The kinetics of the dissociation and the association of $\text{Ni}(\text{CN})_4^{2-}$ have been investigated earlier by Kolski and Margerum.³ The reaction model proposed by these authors, however, presupposes the existence of protonated nickel cyanide species in high concentrations even at rather low concentrations of hydrogen ions.

This assumption was not confirmed by our equilibrium measurements.³ Since the reaction rate varies strongly in the pH-range examined, both conventional spectrophotometry and stopped-flow techniques have been used. The choice of the pH-interval, $4.7 < \text{pH} < 7.0$, was based on the following grounds: (i) At $\text{pH} > 4.7$ the association to $\text{Ni}(\text{CN})_4^{2-}$ is complete at equilibrium and the reaction is not inconveniently slow, (ii) at $\text{pH} > 7$ the reactions are so fast that the accuracy in determining k_{obs} is seriously lowered.

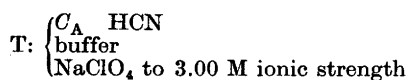
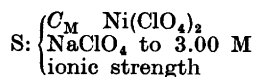
EXPERIMENTAL

Chemicals. Acetate buffers were prepared from acetic acid (Merck *p.a.*) and sodium acetate (BDH *p.a.*). Phosphate buffers were prepared from $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (BDH *p.a.*) and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (Merck *p.a.*). Acetate buffers were used in measurements at which $\text{pH} < 6$ and phosphate buffers at higher values of pH. As to other chemicals see Ref. 1.

Measurements. In the spectrophotometric measurements a Zeiss spectrophotometer PMQ II was used and in the stopped-flow investigations a modified Durrum-Gibson equipment.

The studies were mainly performed at the wavelength 267.5 nm,¹ but a few series were also carried out at 285 nm yielding concordant results.

Within each experimental series pH was kept as constant as possible by means of buffers, while the initial concentration of hydrogen cyanide was varied. The initial nickel concentration was so small, that the concentration of HCN can be regarded as approximately constant in most experimental series. The measurement solutions were obtained by mixing equal volumes of two solutions S and T by means of a glass syringe:



Some measurements with buffer in S as well as in T gave concordant results C_M was about $4 \times 10^{-6} - 8 \times 10^{-5} \text{ M}$ and C_A was varied from 1×10^{-2} to $5 \times 10^{-2} \text{ M}$. The total concentration of buffer in T was about $1 \times 10^{-2} - 5 \times 10^{-2} \text{ M}$. In this region (but not at higher buffer concentrations) the values of k_{obs} were found to be independent of the total buffer concentration within the experimental errors.

The reaction rate is strongly dependent upon the hydrogen ion concentration, h .

Although h is maintained approximately constant by means of the buffers, small deviations may cause substantial changes in reaction rate. Therefore pH was measured in each solution, and the experimental values of the rate constant k_{exp} were corrected to the same value of h , k_{obs} , for corresponding series.

The association reaction showed first order dependence with respect to the nickel(II) ion concentration. Corresponding values of h , $[\text{HCN}]$ and k_{obs} have been collected in Table 1.

CALCULATIONS AND RESULTS

The calculations have been based upon a general reaction scheme proposed by Ekström,⁴ which has been described briefly in an earlier paper.¹ If the dissociation reactions can be neglected, the following general expression can be deduced:

$$k_{\text{obs}} = \left[\frac{\beta_4 K_a^4 [\text{HCN}]^4}{h^4} \right] \left[\frac{1}{k_{00} + k_{01}h + \dots} + \frac{[\text{HCN}]}{k_{10} + k_{11}h \dots} + \frac{[\text{HCN}]^2}{k_{20} + k_{21}h \dots} + \frac{[\text{HCN}]^3}{k_{30} + k_{31}h + \dots} \right]^{-1} \quad (3)$$

While k_{00} is a true rate constant, $k_{01} - k_{33}$ are products of rate constants and equilibrium constants:

$$k_{01} = k_{01}^* K_{h0}; \quad k_{11} = k_{11}^* K_{00} K_a^{-1}; \quad k_{12} = k_{12}^* K_{00} K_{h1} K_a^{-1}; \quad k_{22} = k_{22}^* K_{00} K_{11} K_a^{-2}; \quad k_{33} = k_{33}^* K_{00} K_{11} K_{22} K_a^{-3} \text{ where}$$

$$K_{h0} = \frac{[\text{HNi}(\text{CN})_4^-]}{[\text{Ni}(\text{CN})_4^{2-}]h}; \quad K_{00} = \frac{[\text{Ni}(\text{CN})_3^-]_{\text{eq}}[\text{CN}^-]_{\text{eq}}}{[\text{Ni}(\text{CN})_4^{2-}]_{\text{eq}}}$$

$$K_{h1} = \frac{[\text{HNi}(\text{CN})_3]}{[\text{Ni}(\text{CN})_3^-]h}; \quad K_{11} = \frac{[\text{Ni}(\text{CN})_2]_{\text{eq}}[\text{CN}^-]_{\text{eq}}}{[\text{Ni}(\text{CN})_3^-]_{\text{eq}}}$$

$$K_{22} = \frac{[\text{NiCN}^+]_{\text{eq}}[\text{CN}^-]_{\text{eq}}}{[\text{Ni}(\text{CN})_2]_{\text{eq}}}$$

are equilibrium constants. K_a = dissociation constant for HCN. Since the values of the equilibrium constants above except K_a are unknown the pure rate constants $k_{01}^* - k_{33}^*$ cannot be determined. (Only those of the constants k_{ij} in the general expression (3) that have been found to be relevant in the actual dissociation - and association measurements have been defined above in terms of rate constants and equilibrium constants.)

Some preliminary calculations showed that the term $(k_{00} + k_{01}h + \dots)^{-1}$ can be neglected

Table 1. Corresponding values of hydrogen cyanide concentration and observed rate constant, k_{obs} , for the different measurement series. (Within each series the hydrogen ion concentration, h , is constant.)

[HCN]/ mM	$k_{\text{obs}}/\text{s}^{-1}$	[HCN]/ mM	$k_{\text{obs}}/\text{s}^{-1}$
$h = 1.932 \times 10^{-5}$ M		$h = 1.500 \times 10^{-6}$ M	
4.85	3.35×10^{-5}	5.00	5.18×10^{-2}
9.85	2.85×10^{-4}	10.00	0.334
14.85	1.000×10^{-3}	15.00	0.981
19.85	2.27×10^{-3}	20.00	1.94
24.85	4.56×10^{-3}	25.00	3.09
$h = 1.545 \times 10^{-5}$ M		$h = 9.68 \times 10^{-7}$ M	
4.85	7.3×10^{-5}	5.00	0.170
9.85	5.42×10^{-4}	10.00	1.00
14.85	1.95×10^{-3}	15.00	2.62
19.85	4.45×10^{-3}	20.00	4.95
24.85	8.69×10^{-3}	25.00	7.70
$h = 9.66 \times 10^{-6}$ M		$h = 8.41 \times 10^{-7}$ M	
4.85	2.79×10^{-4}	5.00	0.283
9.70	1.99×10^{-3}	10.00	1.68
14.85	7.16×10^{-3}	15.00	4.13
19.85	1.71×10^{-2}	20.00	7.69
		25.00	11.3
$h = 7.73 \times 10^{-6}$ M		$h = 6.17 \times 10^{-7}$ M	
4.85	3.95×10^{-4}	5.00	0.688
9.85	3.45×10^{-3}	10.00	3.25
14.85	1.17×10^{-2}	15.00	7.64
19.85	2.60×10^{-2}	20.00	13.9
25.00	5.50×10^{-2}	25.00	18.1
$h = 4.56 \times 10^{-6}$ M		$h = 4.14 \times 10^{-7}$ M	
4.85	2.30×10^{-3}	5.00	1.52
9.85	1.54×10^{-2}	10.00	6.62
15.00	5.14×10^{-2}	15.00	13.6
20.00	1.18×10^{-2}	20.00	21.3
25.00	0.219		
$h = 2.324 \times 10^{-6}$ M		$h = 2.208 \times 10^{-7}$ M	
5.00	1.85×10^{-2}	5.00	5.31
10.00	0.120	10.00	18.8
15.00	0.332	15.00	34.3
20.00	0.698	20.00	49.3
25.00	1.215		
		$h = 9.04 \times 10^{-8}$ M	
		5.00	16.4
		10.00	42.9
		15.00	70.6
		20.00	95.5

in the used pH-range $4.7 < \text{pH} < 7$. Eqn. (3) can then be transformed to

$$\frac{[\text{HCN}]^3}{k_{\text{obs}}h^4} = \frac{1}{k_{10}' + k_{11}'h + \dots} + \frac{[\text{HCN}]}{k_{20}' + k_{21}'h + \dots} + \frac{[\text{HCN}]^2}{k_{30}' + k_{31}'h + \dots}$$

where $k_{ij}' = \beta_4 K_a^4 k_{ij}$ or

$$[\text{HCN}]^3/k_{\text{obs}}h^4 = A + B[\text{HCN}] + C[\text{HCN}]^2 \quad (4)$$

where A , B and C are constants with values depending on h .

From eqn. (4) values of A , B and C were first determined for series of measurements with the same value of h . Then A^{-1} was plotted against h yielding a straight line through the origin, indicating that among all k_{ij}' only k_{11}' is detectable in the investigated pH-range. Analogous analyses of B^{-1} and C^{-1} as functions of h indicated that among the possible constants k_{2j}' and k_{3j}' only k_{22}' and k_{33}' were significant.

The following constants were obtained from the graphical calculations:

$$k_{11}' = (2.16 \pm 0.20)10^{-12} \text{ s}^{-1}; \quad k_{22}' = (2.36 \pm 0.30)10^{-8} \text{ s}^{-1}; \quad k_{33}' = (7.8 \pm 1.5)10^{-4} \text{ s}^{-1}.$$

The error limits represent graphically determined maximum errors. From the dissociation measurements¹ $k_{11} = 1.55 \times 10^{-5} \text{ s}^{-1}$ was calculated.

The values of k_{11} and k_{11}' above yield $\beta_4 K_a^4 = 1.394 \times 10^{-7}$ which gives $k_{22} = (0.169 \pm 0.020) \text{ s}^{-1}$ and $k_{33} = (5.6 \pm 1.0)10^3 \text{ s}^{-1}$.

Furthermore, using the value $K_a = 3.28 \times 10^{-10} \text{ M}$, determined in earlier measurements,² we get a value of the overall stability constant for Ni(CN)₄²⁻: $\beta_4 = (1.20 \pm 0.12)10^{31} \text{ M}^{-4}$ in very good agreement with the value $(1.25 \pm 0.09) \times 10^{31} \text{ M}^{-4}$ obtained in earlier equilibrium studies.²

For the association reactions eqn. (3) can be rearranged to give k_{obs} as a function of $[\text{CN}^-]$:

$$k_{\text{obs}} = \beta_4 [\text{CN}^-]^3 \left[\frac{1}{K_a k_{11}} + \frac{[\text{CN}^-]}{K_a^2 k_{22}} + \frac{[\text{CN}^-]^2}{K_a^3 k_{33}} \right]^{-1} \quad (5)$$

Using the values of the constants β_4 , K_a , k_{11} , k_{22} and k_{33} , k_{obs} was computed as a function of $[\text{CN}^-]$ from eqn. (5). In Fig. 1 the calculated curve $\lg k_{\text{obs}} = f(\lg [\text{CN}^-])$ is represented and in the same diagram some experimental data are plotted.

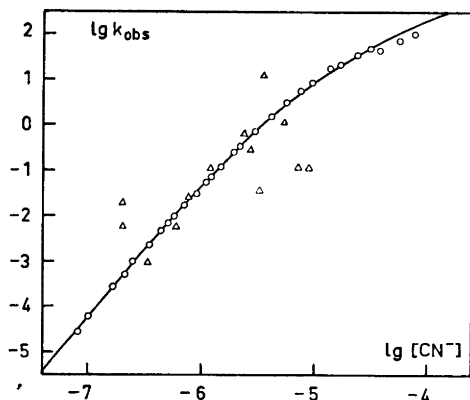


Fig. 1. The full-drawn curve represents $\lg k_{\text{obs}}$ calculated from eqn. (5). The experimental values of ($\lg [\text{CN}^-]$, $\lg k_{\text{obs}}$) are denoted by O (this work) and Δ (from the work of Kolski and Margerum³). (k_{obs} in s^{-1} and $[\text{CN}^-]$ in M).

From results of the kinetics reported by Kolski and Margerum³ for the formation of $\text{Ni}(\text{CN})_4^{2-}$ some values of ($\lg [\text{CN}^-]$, $\lg k_{\text{obs}}$) were calculated. These values have been plotted in Fig. 1 for comparison.

DISCUSSION

The results from the equilibrium and kinetic measurements on the nickel cyanide system can be summarized as follows: At equilibrium only Ni^{2+} and $\text{Ni}(\text{CN})_4^{2-}$ exist in substantial concentrations. Although the complexes NiCN^+ , $\text{Ni}(\text{CN})_2$ and $\text{Ni}(\text{CN})_3^-$ are so weak compared to $\text{Ni}(\text{CN})_4^{2-}$, that they cannot be proved to exist at equilibrium, they are undoubtedly kinetically significant.

A description of the dissociation measurements also requires reaction paths *via* $\text{H}\text{Ni}(\text{CN})_4^-$ and $\text{H}\text{Ni}(\text{CN})_3$ existing either as intermediate species or as activated complexes. The studies at equilibrium, however, clearly indicate that protonated species do not occur in measurable amounts. Nor can any sign of intermediates be detected from the change of light absorption spectrum during a kinetic run. These spectra indicate the presence of only Ni^{2+} and $\text{Ni}(\text{CN})_4^{2-}$.

The results from the measurements on the association from Ni^{2+} to $\text{Ni}(\text{CN})_4^{2-}$ can be described within the experimental errors by

means of a model, where only successive additions of CN^- are assumed to take place. It cannot be excluded that a minor part of the reaction might occur with addition of HCN , *i.e.* *via* the species HNiCN^{2+} and $\text{H}\text{Ni}(\text{CN})_3^+$. Fig. 1 shows, however, that the experimental material is well described without assuming the formation of such species.

The path *via* $\text{H}\text{Ni}(\text{CN})_3$ which was found in the dissociation measurements¹ cannot be detected in the association studies. The reason for this is immediately clear from an inspection of eqn. 2, in which $k_{11}h \gg k_{12}h^2$ in the whole range $4.7 < \text{pH} < 7.0$ (The term $k_{12}h^2$ corresponds to the reaction path *via* $\text{H}\text{Ni}(\text{CN})_3$ and $k_{11}h$ to the direct loss or uptake of CN^-).

In Fig. 1 a comparison can be drawn between the values of ($\lg [\text{CN}^-]$, $\lg k_{\text{obs}}$) obtained in the present work and by Kolski and Margerum.³ From Fig. 1 it can be concluded that their results can be satisfactorily described by the present reaction model in the range of cyanide concentration where the scattering of their data is moderate.

The value of β_4 determined kinetically agrees closely with the value obtained in the equilibrium measurements.

Thus the present investigations on dissociation and association give results considerably different from those obtained by Kolski and Margerum concerning both the kinetics and the complex species existing at equilibrium.

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