

Kinetics of Dissociation of the Tetracyanonickelate(II) Ion

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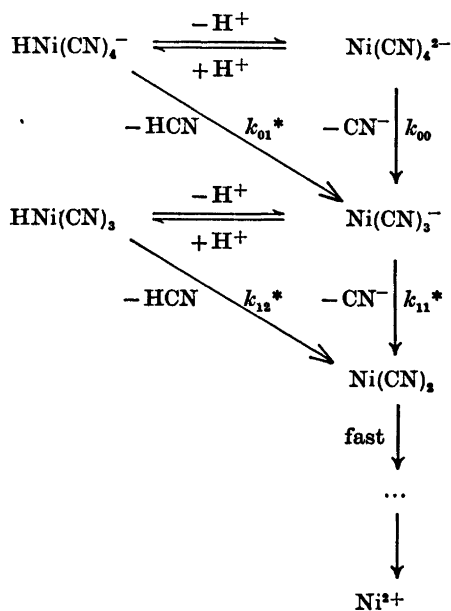
The acid dissociation of $\text{Ni}(\text{CN})_4^{2-}$ has been studied spectrophotometrically mainly at 267.5 nm in the pH range $0 < \text{pH} < 3$. The ionic strength was kept at 3.00 M by means of sodium perchlorate. The temperature was 25.0 °C. The measurements show that the kinetics of dissociation can be adequately described by

$$-d[\text{Ni}(\text{CN})_4^{2-}]/dt = k_{\text{obs}}[\text{Ni}(\text{CN})_4^{2-}]$$

with

$$k_{\text{obs}}^{-1} = (k_{00} + k_{01}h)^{-1} + [\text{HCN}](k_{11}h + k_{12}h^2)^{-1}$$

which corresponds to the following stoichiometric mechanism



In this scheme horizontal arrows represent rapid protonations and deprotonations, and

$$k_{00} = (3.4 \pm 0.6)10^{-4} \text{ s}^{-1};$$

$$k_{01} = (3.34 \pm 0.16)10^{-3} \text{ s}^{-1} \text{ M}^{-1}$$

$$k_{11} = (1.55 \pm 0.15)10^{-5} \text{ s}^{-1};$$

$$k_{12} = (5.5 \pm 0.4)10^{-5} \text{ s}^{-1} \text{ M}^{-1}$$

(The error limits are given as three times the standard deviations). While k_{00} is a true rate constant, k_{01} , k_{11} and k_{12} are products of rate constants and equilibrium constants:

$$k_{01} = k_{01}^* K_{\text{h}0}; \quad k_{11} = k_{11}^* K_{00} K_{\text{a}}^{-1};$$

$$k_{12} = k_{12}^* K_{00} K_{\text{h}1} K_{\text{a}}^{-1}$$

$$\text{where } K_{\text{h}0} = \frac{[\text{HNi}(\text{CN})_4^-]}{[\text{Ni}(\text{CN})_4^{2-}]h}$$

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

$$K_{\text{h}1} = \frac{[\text{HNi}(\text{CN})_3]}{[\text{Ni}(\text{CN})_3^-]h}$$

are equilibrium constants. (K_{a} = dissociation constant for HCN). Since the values of the equilibrium constants $K_{\text{h}0}$, K_{00} and $K_{\text{h}1}$ are unknown the pure rate constants k_{01}^* , k_{11}^* and k_{12}^* cannot be determined.

The kinetics of the formation and dissociation of the tetracyanonickelate(II) ion have previously been investigated by Kolski and Margerum.¹ These authors report an extensive formation of acid nickel cyanide species, $\text{H}_x\text{Ni}(\text{CN})_4^{x-2}$, analogous to those reported, e.g. for the iron(II)-cyanide system.² According to Kolski and Margerum protonated nickel cyanide complexes should in fact be the dominating species at equilibrium at pH < 5.

Our study of the system $\text{Ni}^{2+} - \text{CN}^-$ at equilibrium shows that the only complex existing

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in appreciable concentrations is $\text{Ni}(\text{CN})_4^{2-}$ and that concentrations of NiCN^+ , $\text{Ni}(\text{CN})_2$ and $\text{Ni}(\text{CN})_3^-$ are negligible.³

Our analyses of potentiometric data do not support the suggestion that protonated nickel cyanide species exist at equilibrium and certainly exclude a formation of acid complexes to the extent claimed by Kolski and Margerum.¹

Since we have not been able to find those protonated species which are fundamental parts of the kinetic model proposed by Kolski and Margerum, we considered it important to investigate the kinetics as well.

The acid dissociation of $\text{Ni}(\text{CN})_4^{2-}$ is a rather slow process and is well suited for study by conventional spectrophotometric techniques. In our studies of the association reaction, to be published in a later paper, stopped-flow methods have been used in addition.

The present paper describes the dissociation measurements.

EXPERIMENTAL

Chemicals. Perchloric acid, sodium perchlorate, sodium cyanide, and nickel(II) perchlorate were obtained as described in previous papers.^{3,4} Stock solutions of $\text{Na}_2\text{Ni}(\text{CN})_4$ were prepared in two ways: (1) directly from calculated amounts of sodium cyanide and nickel(II) perchlorate solution and (2) from solid $\text{Na}_2\text{Ni}(\text{CN})_4$ prepared by a modification of the procedure described by Fernelius *et al.*⁵ Since the precipitate of $\text{Ni}(\text{CN})_2$ was difficult to filter, centrifugation was used instead.

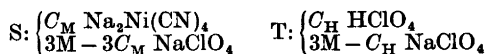
No difference between the results obtained using the different stock solutions could be found.

Measurements. An absorption spectrum for $\text{Ni}(\text{CN})_4^{2-}$ was recorded as described previously³ using a Hitachi EPS-3T spectrophotometer. This spectrum showed three absorbance peaks at 267.5, 285 and 310 nm, respectively. 267.5 nm was chosen as a suitable wavelength for measurements. At 267.5 nm CN^- , HCN and Ni^{2+} have negligible absorbances.

For the kinetic measurements a Zeiss PMQ II spectrophotometer equipped with 1–5 cm Beckman quartz cuvettes was used. The molar absorptivity for $\text{Ni}(\text{CN})_4^{2-}$ at 267.5 nm was determined to $1.06 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

The rate dependence on the species $\text{Ni}(\text{CN})_4^{2-}$, H^+ , Ni^{2+} and HCN (or CN^-) has been investigated.

In the first series of measurements $[\text{H}^+]$ was kept constant within each series. The solutions were obtained by mixing equal volumes of two solutions S and T by means of a glass syringe.

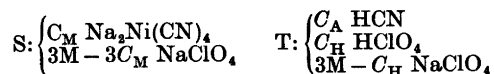


C_M was about $2 \times 10^{-5} - 2 \times 10^{-4} \text{ M}$ and C_H was varied from $2 \times 10^{-3} \text{ M}$ to 2 M . These measurements indicated an approximate first order reaction with respect to $\text{Ni}(\text{CN})_4^{2-}$. When the logarithm of the absorbance was plotted against the reaction time, however, a systematic deviation from linearity was obtained. This deviation might be suspected to depend on HCN being formed in the course of the reaction which might retard the dissociation.

Measurements with varying initial concentrations of HCN showed that HCN strongly retarded the reaction.

A check showed that the presence of Ni^{2+} did not affect the reaction rate.

The measurement solutions were now designed in the following way:



The values of C_M and the cuvette length l were chosen so that an initial absorbance between 0.4 and 0.8 was obtained.

The measurement series were performed at the following hydrogen ion concentrations: $[\text{H}_3\text{O}^+]$: 1.000 M; 0.750 M; 0.500 M; 0.375 M; 0.250 M; 0.1000 M; 0.0750 M; 0.0500 M; 0.0250 M; 0.0100 M; 0.00750 M; 0.00500 M; 0.00250 M; 0.00100 M. Since the values of C_M have been kept very low compared to C_H the hydrogen ion concentration can be regarded as constant within each series. For each value of $[\text{H}_3\text{O}^+]$ about 5–10 measurements were performed with different values of the initial hydrogen cyanide concentration, C_A . The absorbance A was measured as a function of the reaction time t until $A \approx 0.1$ and corrected for the small absorbance A_∞ measured after completion of the reaction.

CALCULATIONS AND RESULTS

The calculations have been based upon a general model described by Ekström.⁶ The reaction scheme (Fig. 1) is valid for both dissociation and association.

This reaction scheme may be regarded as composed of fast protonation equilibria (vertical rows) and slower reactions implying gain or loss of cyanide ions (horizontal rows). (In Fig. 1 only the arrows corresponding to dissociation have been marked).

It should be noticed that it is not possible to distinguish between on the one hand a successive loss of CN^- and H^+ and on the other

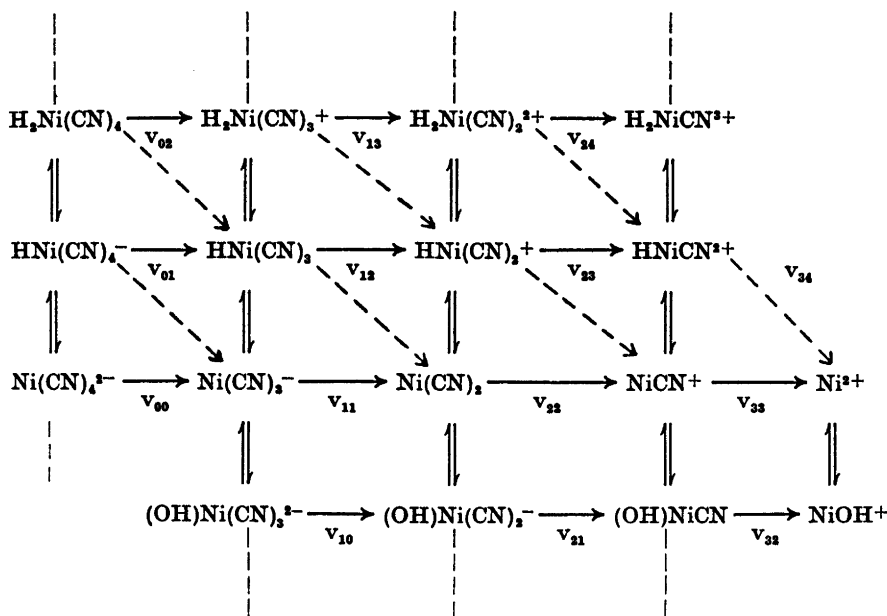


Fig. 1. A general model for possible dissociation and association reactions Ni²⁺ – Ni(CN)₄²⁻.

hand a direct loss of HCN. Thus for instance the reactions



may be substituted by $\text{HNi(CN)}_4^- \rightarrow \text{Ni(CN)}_3^- + \text{HCN}$ (note the dashed arrows in Fig. 1).

With the assumption that all species except Ni(CN)₄²⁻ and Ni²⁺ are in a steady state it can be shown⁶ that the total reaction rate, v , is given by:

$$v = [(v_{00} + v_{01} + \dots)^{-1} + (v_{10} + v_{11} + \dots)^{-1} + (v_{20} + v_{21} + \dots)^{-1} + (v_{30} + v_{31} + \dots)^{-1}]^{-1} \quad (1)$$

where $v = -\frac{d[\text{Ni(CN)}_4^{2-}]}{dt}$ and

$$v_{ij} = k_{ij}h^j[\text{HCN}]^{-i}[\text{Ni(CN)}_4^{2-}](1 - QK^{-1})$$

$$v = \frac{[\text{Ni(CN)}_4^{2-}]}{N} - \frac{[\text{Ni(CN)}_4^{2-}]Q}{NK} \quad (2)$$

where $N = \frac{1}{k_{00} + k_{01}h + k_{02}h^2 + \dots} +$

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

$Q = \frac{[\text{Ni}^{2+}][\text{CN}^-]^4}{[\text{Ni(CN)}_4^{2-}]}$ and K is the corresponding

equilibrium constant (*i.e.* $K = 1/\beta_4$); ($h = [\text{H}_3\text{O}^+]$).

In the right hand member of eqn. (2) the first term represents the forward reactions (the dissociation reactions) and the second term the backward reactions (the association reactions). If the backward reactions can be neglected we thus obtain for the dissociation reactions:

$$v_d = -\frac{d[\text{Ni(CN)}_4^{2-}]}{dt} = k_{\text{obs}}[\text{Ni(CN)}_4^{2-}] \quad (3)$$

$$\text{where } k_{\text{obs}} = \frac{1}{N([\text{HCN}], h)} \quad (4)$$

Analogously we obtain for the association reactions:

$$v_a = \frac{[\text{Ni(CN)}_4^{2-}]Q\beta_4}{N([\text{HCN}], h)} = \frac{\beta_4[\text{Ni}^{2+}][\text{CN}^-]^4}{N([\text{HCN}], h)}$$

$$= \frac{\beta_4 K_a^4 [\text{HCN}]^4 [\text{Ni}^{2+}]}{h^4 N([\text{HCN}], h)} \text{ or}$$

$$v_a = -d[\text{Ni}^{2+}]/dt = k_{\text{obs}}[\text{Ni}^{2+}] \quad (5)$$

$$\text{where } k_{\text{obs}} = \frac{\beta_4 K_a^4 [\text{HCN}]^4}{h^4 N([\text{HCN}], h)} \quad (6)$$

Integration of eqn. (3) yields $\ln [\text{Ni(CN)}_4^{2-}]_t = \ln [\text{Ni(CN)}_4^{2-}]_0 - k_{\text{obs}}t$, if k_{obs} is constant. At the

Table 1. Corresponding values of initial hydrogen cyanide concentration, $[\text{HCN}]_0$, and observed rate constant, k°_{obs} , for the different measurement series. (Within every series the hydrogen ion concentration h is constant). $\Delta k = 100 \times (k_{\text{obs}} - k_{\text{calc}})/k_{\text{calc}}$.

$[\text{HCN}]_0/\text{mM}$	$k^{\circ}_{\text{obs}}/\text{s}^{-1}$	$\Delta k/\%$	$[\text{HCN}]_0/\text{mM}$	$k^{\circ}_{\text{obs}}/\text{s}^{-1}$	$\Delta k/\%$
$h = 1.000 \text{ M}$			10.0	1.717×10^{-4}	+7.3
30.0	1.456×10^{-3}	+1.8	8.0	2.064×10^{-4}	+9.3
20.0	1.814×10^{-3}	+1.0	6.50	2.420×10^{-4}	+10.9
15.0	2.027×10^{-3}	-1.6	5.00	2.593×10^{-4}	+0.4
8.00	2.584×10^{-3}	-0.4	4.00	3.274×10^{-4}	+11.0
5.00	2.862×10^{-3}	-1.9	3.00	3.695×10^{-4}	+7.6
3.00	3.160×10^{-3}	-0.7	2.00	4.50×10^{-4}	+9.7
1.000	3.330×10^{-3}	-4.8	1.000	5.45×10^{-4}	+6.7
0.400	3.260×10^{-3}	-9.6	0.500	6.20×10^{-4}	+6.6
0	3.580×10^{-3}	-2.7	0.100	7.06×10^{-4}	+8.0
			0	7.08×10^{-4}	+4.8
$h = 0.750 \text{ M}$			$h = 0.0750 \text{ M}$		
30.0	9.47×10^{-4}	+0.3	20.0	6.87×10^{-5}	+5.1
20.0	1.165×10^{-3}	-4.1	15.0	8.76×10^{-5}	+4.2
15.0	1.402×10^{-3}	-1.1	8.00	1.412×10^{-4}	+0.7
8.00	1.880×10^{-3}	+1.5	5.00	2.091×10^{-4}	+6.5
5.00	2.200×10^{-3}	+3.3	3.00	2.918×10^{-4}	+8.9
3.00	2.435×10^{-3}	+2.8	1.00	4.54×10^{-4}	+7.6
1.000	2.661×10^{-3}	-0.2			
$h = 0.500 \text{ M}$			$h = 0.0500 \text{ M}$		
30.0	5.15×10^{-4}	-2.4	20.0	4.43×10^{-5}	+6.0
20.0	6.67×10^{-4}	-4.6	15.0	5.77×10^{-5}	+6.4
15.0	7.42×10^{-4}	-11.1	8.00	9.91×10^{-5}	+6.4
8.00	1.049×10^{-3}	-8.7	5.00	1.440×10^{-4}	+7.3
5.00	1.294×10^{-3}	-5.5	3.00	2.012×10^{-4}	+5.8
3.00	1.516×10^{-3}	-3.4	1.000	3.388×10^{-4}	+3.9
1.000	1.753×10^{-3}	-4.7	0	5.11×10^{-4}	+0.7
0	1.954×10^{-3}	-2.8			
$h = 0.375 \text{ M}$			$h = 0.0250 \text{ M}$		
30.0	3.487×10^{-4}	-0.7	20.0	2.102×10^{-5}	+4.7
20.0	4.47×10^{-4}	-5.7	15.0	2.803×10^{-5}	+6.3
15.0	5.70×10^{-4}	-0.9	8.00	5.11×10^{-5}	+9.1
8.00	7.58×10^{-4}	-7.6	5.00	7.72×10^{-5}	+9.7
5.00	1.011×10^{-3}	-0.9	3.00	1.200×10^{-4}	+13.6
3.00	1.094×10^{-3}	-7.0	1.000	2.566×10^{-4}	+21.3
1.000	1.358×10^{-3}	-4.7	0	5.22×10^{-4}	+22.9
$h = 0.250 \text{ M}$			$h = 0.0100 \text{ M}$		
30.0	2.019×10^{-4}	+0.2	15.0	1.027×10^{-5}	-1.2
20.0	2.772×10^{-4}	-0.4	12.0	1.229×10^{-5}	-4.8
15.0	3.404×10^{-4}	-1.1	8.00	1.840×10^{-5}	-3.4
8.00	4.94×10^{-4}	-3.8	6.00	2.557×10^{-5}	+2.4
5.00	6.16×10^{-4}	-5.4	5.00	3.265×10^{-5}	+10.5
3.00	7.65×10^{-4}	-3.5	4.00	3.728×10^{-5}	+2.9
1.000	9.55×10^{-4}	-5.8	2.00	6.77×10^{-5}	+2.5
0	1.139×10^{-3}	-3.2	1.00	1.138×10^{-4}	+1.3
			0.800	1.306×10^{-4}	-0.0
			0.600	1.555×10^{-4}	-0.3
			0.400	2.006×10^{-4}	+3.6
			0.200	2.690×10^{-4}	+5.4
			0.100	3.299×10^{-4}	+8.7
			0	3.988×10^{-4}	+6.5
$h = 0.1000 \text{ M}$					
50.0	4.21×10^{-5}	+6.7			
40.0	4.95×10^{-5}	+1.7			
30.0	6.58×10^{-5}	+3.8			
20.0	9.42×10^{-5}	+3.8			

Table 1. Continued.

[HCN] ₀ /mM	$k^{\circ}_{\text{obs}}/s^{-1}$	$\Delta k/\%$
$h = 7.50 \times 10^{-3}$ M		
2.00	5.37×10^{-5}	+4.6
1.50	6.75×10^{-5}	+3.4
0.800	1.101×10^{-4}	+3.9
0.300	2.076×10^{-4}	+8.9
$h = 5.00 \times 10^{-3}$ M		
2.00	3.517×10^{-5}	-1.0
1.50	4.46×10^{-5}	-2.8
0.800	7.47×10^{-5}	-3.3
0.500	1.044×10^{-4}	-4.6
0.300	1.471×10^{-4}	-2.9
0	3.45×10^{-4}	-3.6
$h = 2.50 \times 10^{-3}$ M		
2.00	1.708×10^{-5}	-7.7
1.50	2.136×10^{-5}	-11.9
0.800	3.817×10^{-5}	-11.0
0.500	6.10×10^{-5}	-4.5
0.300	7.67×10^{-5}	-19.2
0	2.992×10^{-4}	-14.4
$h = 1.00 \times 10^{-3}$ M		
3.00	5.00×10^{-6}	-2.2
2.00	8.62×10^{-6}	+13.3
1.50	1.119×10^{-5}	+11.2
1.00	1.338×10^{-5}	-10.1
0.800	1.572×10^{-5}	-14.6
0.600	2.104×10^{-5}	-12.7
0.400	3.050×10^{-5}	-12.7
0.200	5.27×10^{-5}	-17.0
0.100	8.41×10^{-5}	-21.5
0	2.873×10^{-4}	-16.6

actual wavelength only $\text{Ni}(\text{CN})_4^{2-}$ absorbs light and the absorbance

$$A = \epsilon_{\text{Ni}(\text{CN})_4^{2-}} [\text{Ni}(\text{CN})_4^{2-}] l$$

Thus

$$\ln A_t = \ln A_0 - k_{\text{obs}} t \quad (7)$$

If $\ln A_t$ is plotted as a function of t a straight line with the slope k_{obs} is obtained for every measurement series, provided that h and [HCN] are constant within the series. While h can be considered to be constant to a good approximation, [HCN] varies somewhat since it is formed from $\text{Ni}(\text{CN})_4^{2-}$. If HCN has been added initially, the deviation from linearity can be kept very small. However, k_{obs} was determined both at $t=0$ corresponding to $[\text{HCN}] = [\text{HCN}]_0$

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Table 2. Supplementary values of (h , k°_{obs} , Δk) at $[\text{HCN}]_0 = 0$. (For definitions see Table 1).

h/M	0.800	0.660	0.400	0.0800	0.0660	0.0400	0.0066	0.0040
$k^{\circ}_{\text{obs}}/s^{-1}$	3.105×10^{-3}	2.583×10^{-3}	1.729×10^{-3}	5.88×10^{-4}	6.01×10^{-4}	5.20×10^{-4}	4.02×10^{-4}	3.37×10^{-4}
$\Delta k/\%$	+3.0	+1.5	+3.1	-3.3	+7.1	+9.6	+10.7	-4.9

and $k_{\text{obs}} = k^{\circ}_{\text{obs}}$, and also after a few half times when $[\text{HCN}] \approx [\text{HCN}]_0 + 4[\text{Ni}(\text{CN})_4^{2-}]_0$ and $k_{\text{obs}} \approx k^{\circ}_{\text{obs}}$.

Within the measurement errors both sets of ($[\text{HCN}]$, k_{obs}) gave the same set of rate constants, k_{ij} , see below. In Table 1 the corresponding values of (h , $[\text{HCN}]_0$ and k°_{obs}) for the different series have been collected. Table 2 contains some complementary values of (h , k°_{obs}) at $[\text{HCN}]_0 = 0$.

For series with the same hydrogen ion concentration k_{obs}^{-1} was plotted as a function of $[\text{HCN}]$. These plots yielded straight lines, *i.e.* at constant h : $k_{\text{obs}}^{-1} = A + B[\text{HCN}]$ where A and B are constants whose values depend on h .

When A^{-1} was plotted as a function of h (Fig. 2) a straight line was obtained implying that $k_{0i} = 0$ for $i \geq 2$. From the intercept and slope of this line k_{00} and k_{01} were determined.

The corresponding analyses of B as a function of h showed that only k_{11} and k_{12} were significant *i.e.* $(Bh)^{-1} = k_{11} + k_{12}h$ (Fig. 3).

The results can be summarized in the following equation

$$k_{\text{obs}} = \{(k_{00} + k_{01}h)^{-1} + [\text{HCN}](k_{11}h + k_{12}h^2)^{-1}\}^{-1} \quad (8)$$

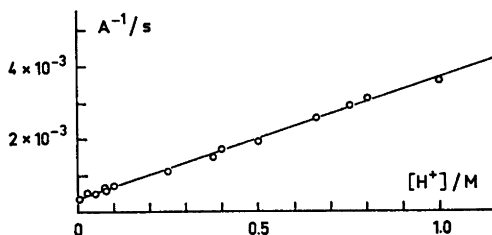


Fig. 2. Determination of k_{00} and k_{01} from a plot of A^{-1} as a function of $[\text{H}^+]$. (A is defined from $k_{\text{obs}}^{-1} = A + B[\text{HCN}]$).

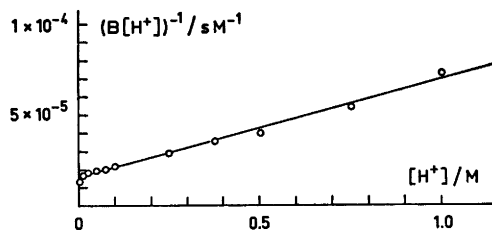


Fig. 3. Determination of k_{11} and k_{12} from a plot of $(B[\text{H}^+])^{-1}$ as a function of $[\text{H}^+]$. (B is defined from $k_{\text{obs}}^{-1} = A + B[\text{HCN}]$).

with

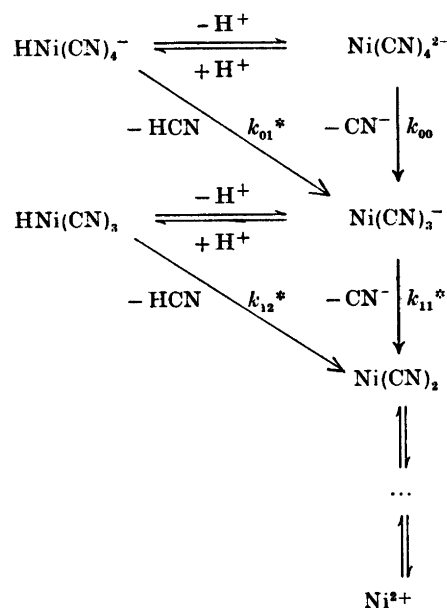
$$k_{00} = (3.41 \pm 0.6)10^{-4} \text{ s}^{-1};$$

$$k_{01} = (3.34 \pm 0.16)10^{-3} \text{ M}^{-1}$$

$$k_{11} = (1.55 \pm 0.15)10^{-5} \text{ s}^{-1};$$

$$k_{12} = (5.47 \pm 0.4)10^{-5} \text{ s}^{-1} \text{ M}^{-1}$$

(The errors are given as three times the standard deviations in the constants obtained from the linear plots described above). The corresponding reaction scheme is shown in Scheme 1.



Scheme 1.

In order to check how close the constants $k_{00} - k_{12}$ describe the measurement data k_{calc} were calculated from eqn. (8) for the actual values of h and HCN and were compared to the values of k_{obs} obtained experimentally (Tables 1, 2).

The experimental errors can be expected to be about $\pm(5-10)\%$. (At the lowest values of h the errors can be assumed to be larger). From Table 1 it is obvious that the experimental material is well described by the calculated constants.

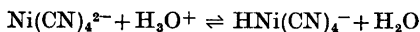
(The values of k_{obs} could alternatively be calculated from the integrated rate expression. Combining eqns. (3) and (8) and integrating we get

$$\ln x - k_1 x = -k_2 t + \ln a - k_1 a$$

Here x = concentration of $\text{Ni}(\text{CN})_4^{2-}$ at time t . a = concentration of $\text{Ni}(\text{CN})_4^{2-}$ at $t=0$. k_1 and k_2 contain the constants $k_{00} - k_{12}$ as parameters and are functions of h . k_1 and k_2 can be determined for each experiment (h being constant within each experiment). From the corresponding values of h , k_1 and k_2 the constants $k_{00} - k_{12}$ can be determined.

However, in the present measurements the cyanide concentration was approximately constant within each series. Hence, nearly linear plots were obtained at the determination of the values of k_{obs} permitting a good accuracy in the evaluation of both k_{obs}^0 and k_{obs}^∞ . The numerically more simple method using initial rates was therefore preferred for the calculations).

Our previous measurements³ show clearly that the species $\text{H}_i\text{Ni}(\text{CN})_4^{2-i}$ ($i = 1-4$) exist at most to a very small extent at equilibrium. Our present kinetic measurements, however, indicate that $\text{HNi}(\text{CN})_4^-$ is kinetically significant. Therefore, we decided to make a supplementary investigation of the formation of $\text{HNi}(\text{CN})_4^-$. According to Kolski and Margerum,¹ the equilibrium constant for the reaction



is

$$K_{\text{H}} = 2.5 \times 10^5 \text{ M}^{-1}$$

Thus $\text{Ni}(\text{CN})_4^{2-}$ should possess obvious base properties. We added $\text{Na}_2\text{Ni}(\text{CN})_4$ to a solution of perchloric acid for which pH had been measured and measured pH in the solution soon after mixing. The concentration of the perchloric acid was chosen so that only a slow disintegration of $\text{Ni}(\text{CN})_4^{2-}$ could be expected. The concentrations before possible reaction were: $[\text{H}_3\text{O}^+] = 0.50 \text{ mM}$; $[\text{Ni}(\text{CN})_4^{2-}] = 1.00 \text{ mM}$.

Before addition of $[\text{Ni}(\text{CN})_4^{2-}]$ we measured $-\lg [\text{H}_3\text{O}^+] = 3.30$. Accepting the value of K_{H} postulated by Kolski and Margerum we should expect a value of $-\lg [\text{H}_3\text{O}^+] \approx 5.40$ after addition of $\text{Na}_2\text{Ni}(\text{CN})_4$ corresponding to a change in electromotive force of about 124 mV. We measured a change in emf of less than 1 mV, indicating a negligible formation of $\text{HNi}(\text{CN})_4^-$. The results of this experiment thus support the results from our previous equilibrium measurements.³

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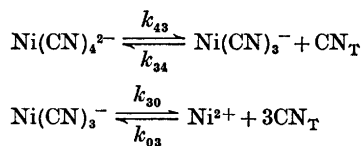
DISCUSSION

The results from our experiments thus show that the acid dissociation of $\text{Ni}(\text{CN})_4^{2-}$ can be described by a rather simple model with two types of reaction paths, implying loss of HCN and loss of CN^- , respectively. As mentioned above it is not possible to distinguish between a loss of HCN and successive losses of CN^- and H^+ . The former model, however, seems to be more attractive from a chemical point of view.

Our measurements show further that protonated nickel cyanide species are not present in detectable concentrations. Hence, the results from our measurements on the dissociation of $\text{Ni}(\text{CN})_4^{2-}$ indicate a kinetic model quite different from that proposed by Kolski and Margerum.¹

When our investigations of the dissociation of $\text{Ni}(\text{CN})_4^{2-}$ were completed, and we were analyzing the results from our measurements on the association reactions, the results of an investigation of the kinetics of the tetracyanonickelate(II) ion by Crouse and Margerum⁷ were published. In this paper a study of the dissociation of $\text{Ni}(\text{CN})_4^{2-}$ by means of I_2 as a scavenger for cyanide is described. The authors find that the rate constant for this reaction does not depend on pH when $\text{pH} > 3$. Their method is not applicable at lower values of pH.

Crouse and Margerum propose the following reaction model.



A steady state approximation in $\text{Ni}(\text{CN})_3^-$ leads to $k_{\text{obs}} = k_{43}k_{30}/(k_{34}[\text{CN}]_T + k_{30})$ where k_{30} , k_{34} and k_{43} may depend on $[\text{H}^+]$. However, Crouse and Margerum have not determined the dependence on $[\text{H}^+]$ or the corresponding mechanism. From their measurements a constant value of $k_{43} = 4.8 \times 10^{-4} \text{ s}^{-1}$ is obtained at $\text{pH} > 3$. The expression above may be rearranged to

$$k_{\text{obs}}^{-1} = \left(\frac{1}{k_{43}} + \frac{k_{34}}{k_{43}k_{30}} [\text{CN}_T] \right) \quad (9)$$

A comparison of our eqn. (8) with Crouse's and Margerum's eqn. (9) shows that they are

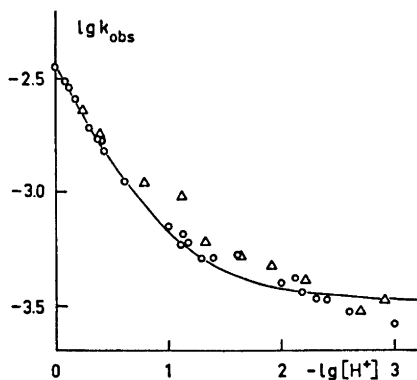


Fig. 4. The hydrogen ion dependence of the rate constant k_{obs} at zero hydrogen cyanide concentration. The full-drawn curve represents $\lg k_{\text{calc}}$ calculated from eqn. (8). The experimental values of k_{obs} are denoted by \circ (this work) and \triangle (according to Kolski and Margerum¹). ($[\text{H}^+]$ in M and k_{obs} in s^{-1}).

identical if the following relations between their parameters hold:

$$k_{43} = k_{00} + k_{01}h \text{ and } k_{34}/k_{43}k_{30} = (k_{11}h + k_{12}h^2)^{-1}$$

When cyanide is removed by iodine the association reactions can be neglected and $k_{\text{obs}} \approx k_{43}$. At low values of h , $k_{43} \approx k_{00}$. Thus under the experimental conditions used by Crouse and Margerum only the reaction $\text{Ni}(\text{CN})_4^{2-} \rightarrow \text{Ni}(\text{CN})_3^-$ is significant. This explains the constant value of k_{obs} obtained by these authors. The agreement between the values of $k_{43} = 4.8 \times 10^{-4} \text{ s}^{-1}$ at $\text{pH} > 3$ given by Crouse and Margerum and our value of $k_{00} = 3.82 \times 10^{-4} \text{ s}^{-1}$ is good considering the large differences in the ionic media.

In Fig. 4 experimental and calculated values of $\lg k_{\text{obs}}$ at $[\text{HCN}] = 0$ are plotted against $-\lg [\text{H}^+]$. The experimental values obtained by Kolski and Margerum are plotted in the same diagram showing on the whole a good agreement.

The experiments performed by Kolski and Margerum,¹ as well as those performed by Crouse and Margerum⁷ can be satisfactorily explained using the reaction model described in the present paper.

In our investigations of the association reactions to $\text{Ni}(\text{CN})_4^{2-}$ (Ref. 8), k_{11}' , k_{22}' and k_{33}' were determined ($k_{ii}' = \beta_4 K_a^4 k_{ii}$). We obtained

$\beta_4 K_a^4 k_{11} = 2.16 \times 10^{-12} \text{ s}^{-1}$. Using $K_a = 3.28 \times 10^{-10} \text{ M}$ (Ref. 4) and $k_{11} = 1.55 \times 10^{-5} \text{ s}^{-1}$ from the dissociation reactions we get $\beta_4 = (1.20 \pm 0.12) \times 10^{21} \text{ M}^{-4}$ from our kinetic measurements, in excellent agreement with the value $(1.25 \pm 0.09) \times 10^{21} \text{ M}^{-4}$ obtained from the equilibrium measurements.³

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