Kinetics of Formation of the Tetracyanonickelate(II) Ion

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The formation of Ni(CN)$_6^{4-}$ 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:

\[
\begin{align*}
\text{Ni}^{2+} & \quad + \text{CN}^- & \quad \text{NiCN}^+ & \quad \text{Ni(CN)}_4^{2-} \\
\text{Ni(CN)}_3^{2-} & \quad + \text{CN}^- & \quad \text{Ni(CN)}_4^{2-} \\
\text{Ni(CN)}_4^{2-} & \quad - \text{H}^+ & \quad \text{Ni(CN)}_5^{2-} \\
\text{Ni(CN)}_5^{2-} & \quad - \text{H}^+ & \quad \text{Ni(CN)}_6^{4-} \\
\end{align*}
\]

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

\[
-dX/dt = k_{obs}X
\]

(1)

where

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

\[
k_{obs} = (1 + \beta_1k_6[\text{HCN}]^0\text{H}^{-})/((k_{32} + k_{33}\text{H}^0)^{-1} + [\text{HCN}]k_{12}\text{H}^0 + k_{11}\text{H}^0) + (k_{32}\text{H}^0)^{-1} + [\text{HCN}]k_{12}\text{H}^0 + (k_{33}\text{H}^0)^{-1} + [\text{HCN}]k_{11}\text{H}^0)
\]

(2)

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

\[
k_{32} = (3.4 \pm 0.6) \times 10^{-4} \text{ s}^{-1}; \quad k_{33} = (3.34 \pm 0.16) \times 10^{-2} \text{ s}^{-1} \text{ M}^{-1}; \quad k_{11} = (1.55 \pm 0.15) \times 10^{-4} \text{ s}^{-1}; \quad k_{12} = (5.5 \pm 0.4) \times 10^{-4} \text{ s}^{-1} \text{ M}^{-1}; \quad k_{33} = (0.169 \pm 0.020) \text{ s}^{-1}; \quad k_{33} = (5.6 \pm 1.0) \times 10^9 \text{ s}^{-1}
\]

While $k_{32}$ is a true rate constant, $k_{33} - k_{32}$ are products of rate constants and equilibrium constants. Since the values of these equilibrium constants are unknown the pure rate constants $k_{31} - k_{33}$ cannot be determined.

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

Results from equilibrium measurements on the complex system Ni$^{3+}$–CN$^-$ and kinetic studies of the acid dissociation of Ni(CN)$_4^{2-}$ have been presented in previous papers.

The kinetics of the dissociation and the association of Ni(CN)$_4^{2-}$ have been investigated earlier by Kolski and Margerum. 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. 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 < pH < 7.0, was based on the following grounds: (i) At pH > 4.7 the association to Ni(CN)₄²⁻ is complete at equilibrium and the reaction is not inconveniently slow, (ii) at pH > 7 the reactions are so fast that the accuracy in determining $k_{obs}$ is seriously lowered.

EXPERIMENTAL

Chemicals. Acetic acid (Merek p.a.) and sodium acetate (BDH p.a.). Phosphate buffers were prepared from Na₂HPO₄·2H₂O (BDH p.a.) and Na₂HPO₄·12H₂O (Merek p.a.). Acetate buffers were used in measurements at which 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, 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:

$$C_M \text{Ni(CI)₄} \quad S: [\text{NaClO}_₄ \text{ to } 3.00 \text{M}]$$

$$C_A \text{HCN} \quad \text{buffer NaClO}_₄ \text{ to } 3.00 \text{M ionic strength}$$

Some measurements with buffer in S as well as in T gave concordant results $C_M$ was about $4 \times 10^{-4} - 8 \times 10^{-4}$ M and $C_A$ was varied from $1 \times 10^{-3}$ to $5 \times 10^{-3}$ M. The total concentration of buffer in T was about $1 \times 10^{-3} - 5 \times 10^{-3}$ 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 $K_a$ [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, which has been described briefly in an earlier paper. If the dissociation reactions can be neglected, the following general expression can be deduced:

$$k_{obs} = \frac{\beta \cdot K_{a} [HCN]^4}{h} \left( \frac{1}{k_{00} + k_{21}h + \cdots} + \frac{[HCN]}{k_{10} + k_{21}h} + \frac{[HCN]^2}{k_{20} + k_{31}h} + \frac{[HCN]^3}{k_{30} + k_{33}h + \cdots} \right)^{(3)}$$

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

$$k_{01} = k_{01} \cdot K_{b0}; \quad k_{11} = k_{11} \cdot K_{00} \cdot K_{a}^{-1}; \quad k_{12} = k_{12} \cdot K_{b0} \cdot K_{a}^{-1}; \quad k_{22} = k_{22} \cdot K_{00} \cdot K_{11} \cdot K_{a}^{-2}; \quad k_{32} = k_{32} \cdot K_{00} \cdot K_{11} \cdot K_{22} \cdot K_{a}^{-3} \text{ where}$$

$$K_{b0} = \frac{[HNi(CN)_{a}^{-}]}{[Ni(CN)_{a}^{-}]} \cdot K_{00} = \frac{[Ni(CN)_{3}^{-}]}{[Ni(CN)_{5}^{-}]} \cdot [Ni]_{eq}$$

$$K_{11} = \frac{[HNi(CN)_{2}^{-}]}{[Ni(CN)_{a}^{-}]} \cdot K_{11} = \frac{[Ni(CN)_{5}^{-}]}{[Ni(CN)_{3}^{-}]} \cdot [Ni]_{eq}$$

$$K_{22} = \frac{[NiCNY]+[CN]_{eq}}{[Ni(CN)_{2}]}$$

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 $k_{01} \cdot k_{12} \cdot k_{22}$ 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 $(k_{00} + k_{33}h + \cdots)^{(1)}$ 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.)

<table>
<thead>
<tr>
<th>[HCN]/mM</th>
<th>$k_{obs}$/s$^{-1}$</th>
<th>[HCN]/mM</th>
<th>$k_{obs}$/s$^{-1}$</th>
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<tr>
<td>$h = 1.932 \times 10^{-4}$ M</td>
<td>4.85</td>
<td>3.35 $\times 10^{-5}$</td>
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<td>9.85</td>
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<td>0.334</td>
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<td>14.85</td>
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<td>15.00</td>
<td>0.981</td>
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<td>19.85</td>
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<td>4.56 $\times 10^{-3}$</td>
<td>25.00</td>
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<tr>
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<td>7.3 $\times 10^{-5}$</td>
<td>5.00</td>
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<td>1.00</td>
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<td>14.85</td>
<td>1.95 $\times 10^{-3}$</td>
<td>15.00</td>
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<td>19.85</td>
<td>4.45 $\times 10^{-3}$</td>
<td>20.00</td>
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<td>24.85</td>
<td>8.69 $\times 10^{-3}$</td>
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<td>7.70</td>
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<td>$h = 7.73 \times 10^{-4}$ M</td>
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<td>5.00</td>
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<td>18.1</td>
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<tr>
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<td>5.00</td>
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<td>5.00</td>
</tr>
<tr>
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<td>0.120</td>
<td>10.00</td>
<td>18.8</td>
</tr>
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<td>15.00</td>
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<td>20.00</td>
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<td>25.00</td>
<td>1.215</td>
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<td></td>
</tr>
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<td>$h = 9.04 \times 10^{-6}$ M</td>
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<td>16.4</td>
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<tr>
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<td>42.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.00</td>
<td>70.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.00</td>
<td>95.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the used pH-range 4.7 < pH < 7. Eqn. (3) can then be transformed to:

\[
\frac{[\text{HCN}^3]}{k_{obs}[h^4]} = \frac{1}{k_{11}'} + \frac{[\text{HCN}]}{2k_{11}^2 + k_{11}'h + \ldots} + \frac{[\text{HCN}^4]}{2k_{11}' + k_{11}'h + \ldots}
\]

where \( k_{ij} = \beta_i K_{ai}^4 k_{ij} \) or \([\text{HCN}] / k_{obs} h^4 = A + B[\text{HCN}] + C[\text{HCN}]^2 \) (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 \( k_{1j}' \) and \( k_{2j}' \), only \( k_{12}' \) and \( k_{23}' \) were significant.

The following constants were obtained from the graphical calculations:

\( k_{11}' = (2.10 \pm 0.20) \times 10^{-12} \text{ s}^{-1} \); \( k_{12}' = (2.36 \pm 0.30) \times 10^{-11} \text{ s}^{-1} \); \( k_{23}' = (7.8 \pm 1.5) \times 10^{-4} \text{ s}^{-1} \).

The error limits represent graphically determined maximum errors. From the dissociation measurements \( k_{11} = 1.55 \times 10^{-4} \text{ s}^{-1} \) was calculated.

The values of \( k_{11} \) and \( k_{11}', k_{11} \) above yield \( \beta_i K_{ai}^4 = 1.394 \times 10^{-7} \) which gives \( k_{12} = (0.169 \pm 0.020) \text{ s}^{-1} \) and \( k_{23} = (5.6 \pm 1.0) \times 10^{-4} \text{ s}^{-1} \).

Furthermore, using the value \( K_a = 3.28 \times 10^{-10} \text{ M} \), determined in earlier measurements, we get a value of the overall stability constant for Ni(CN)$_4^2$:

\( \beta_i = (1.20 \pm 0.12) \times 10^{21} \text{ M}^{-4} \) in very good agreement with the value \( 1.25 \pm 0.09 \times 10^{21} \text{ M}^{-4} \) obtained in earlier equilibrium studies.

For the association reactions eqn. (3) can be rearranged to give \( k_{obs} \) as a function of [CN$^-$_]{\text{2}}:

\[
k_{obs} = \beta_i [\text{CN}^-]^2 \left[ \frac{1}{K_{a}^4 k_{11}} + \frac{[\text{CN}^-]}{K_{a}^4 k_{22}} + \frac{[\text{CN}^-]^2}{K_{a}^4 k_{23}} \right]^{-1}
\]

Using the values of the constants \( \beta_i, K_a, k_{11}, k_{22} \) and \( k_{23} \), \( k_{obs} \) was computed as a function of [CN$^-$_] from eqn. (5). In Fig. 1 the calculated curve \( k_{obs} = f([\text{CN}^-]) \) is represented and in the same diagram some experimental data are plotted.
Fig. 1. The full-drawn curve represents \( lg k_{obs} \) calculated from eqn. (5). The experimental values of \( lg [CN^-] \), \( lg k_{obs} \) are denoted by O (this work) and \( \triangle \) (from the work of Kolksi and Margerum). \( k_{obs} \) in s\(^{-1} \) and [CN\(^-\)] in M.

From results of the kinetics reported by Kolski and Margerum for the formation of Ni(CN)\(_4\)\(^{2-}\) some values of \( lg[CN^-], lg k_{obs} \) 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\(^{3+}\) and Ni(CN)\(_4\)\(^{2-}\) exist in substantial concentrations. Although the complexes NiCN\(^+\), Ni(CN)\(_2\)\(^{2-}\) and Ni(CN)\(_3\)\(^{-}\) are so weak compared to Ni(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 HNi(CN)\(_6\)\(^{-}\) and HNi(CN)\(_4\)\(^{-}\) 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 Ni(CN)\(_4\)\(^{2-}\).

The results from the measurements on the association from Ni\(^{2+}\) to Ni(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 HNi(CN)\(_4\)\(^{+}\).

Fig. 1 shows, however, that the experimental material is well described without assuming the formation of such species.

The path via HNi(CN)\(_4\) which was found in the dissociation measurements cannot be detected in the association studies. The reason for this is immediately clear from an inspection of eqn. 2, in which \( k_{14} > k_{15} \) in the whole range 4.7 < pH < 7.0 (The term \( k_{15} \) corresponds to the reaction path via HNi(CN)\(_4\), and \( k_{14} \) to the direct loss or uptake of CN\(^-\)).

In Fig. 1 a comparison can be drawn between the values of \( lg[CN^-], lg k_{obs} \) obtained in the present work and by Kolski and Margerum. 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 \( \beta_4 \) 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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