

$\text{Ni}(\text{CN})_4^{2-}$  ion is square planar. The relationship in this series between the change in structure and the appearance of electrons in the  $e_g$  subshell has been discussed.<sup>16</sup> It is now of interest to examine the effect of these electrons on the  $\Delta H^\circ$  values for the formation of these complexes from their respective aqueous ions. The  $\Delta H^\circ$  values of  $-85.77$ ,  $-61.5$ , and  $-43.2$  kcal/mol show an increase of 24.3 kcal/mol between  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Co}(\text{CN})_5^{3-}$  and 18.3 kcal/mol between  $\text{Co}(\text{CN})_5^{3-}$  and  $\text{Ni}(\text{CN})_4^{2-}$ . These successive increases in  $\Delta H^\circ$  cannot be accounted for by the decreased number of  $\text{CN}^-$  per  $\text{M}^{2+}$  bonds alone. This is seen by dividing the  $\Delta H^\circ$  value in each case by the number of  $\text{CN}^-$  per  $\text{M}^{2+}$ . One thus obtains  $-14.3$ ,  $-12.3$ , and  $-10.8$  kcal per metal-cyanide bond for  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Co}(\text{CN})_5^{3-}$ , and  $\text{Ni}(\text{CN})_4^{2-}$ , respectively. Two questions now arise.

First, why does the  $\Delta H^\circ$  value per bond decrease in the series and, second, why are the  $\Delta H^\circ$  values per bond only approximately half the differences in the  $\Delta H^\circ$  values per mole in the series? The decrease in the  $-\Delta H^\circ$  value per bond suggests that the successive addition of electrons to the  $e_g$  subshell has a labilizing effect on the metal-cyanide bonds as suggested by Pratt and Williams.<sup>16</sup> The second question indicates that additional factors play a role in increasing the  $\Delta H^\circ$  values per mole in the series. Such energy quantities as ligand field stabilization energies of the complexes and metal ions involved, pairing energies of the metal ions,  $\pi$  bonding, and relative hydration energies are undoubtedly important. Since the magnitudes of most of these terms are unknown for these species in aqueous solution, further interpretation is not attempted here.

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## Kinetics of Formation and Dissociation of Tetracyanonickelate(II) Ion

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The rate of formation of  $\text{Ni}(\text{CN})_4^{2-}$  is a fifth-order reaction, first order in nickel and fourth order in total cyanide; HCN is a reactant as well as  $\text{CN}^-$ . From pH 5.5 to 7.5 the rate expression is  $k_{2,3}[\text{Ni}^{2+}][\text{CN}^-]^2[\text{HCN}]^2$  where  $k_{2,3}$  equals  $1.6 \times 10^{18} \text{ M}^{-4} \text{ sec}^{-1}$  at  $25.0^\circ$ ,  $\mu = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ). Above pH 7.5 the reaction order in  $\text{CN}^-$  is greater than 2 and the reaction order in HCN is less than 2, but the total cyanide dependence remains fourth order. The kinetics of dissociation of  $\text{Ni}(\text{CN})_4^{2-}$  in acid ( $10^{-6}$  to  $2 \text{ M}$   $\text{HClO}_4$ ) indicate the presence of several protonated species including  $\text{HNi}(\text{CN})_4^-$ ,  $\text{H}_2\text{Ni}(\text{CN})_4$ , and  $\text{H}_3\text{Ni}(\text{CN})_4^+$ . Equilibrium studies from pH 4 to 5 confirm the first two acid species with protonation constants  $K_{\text{H}} = 2.5 \times 10^5 \text{ M}^{-1}$  and  $K_{2\text{H}} = 3.0 \times 10^4 \text{ M}^{-1}$ ;  $K_{3\text{H}}$  is estimated to be  $400 \text{ M}^{-1}$  from the kinetic data. The  $\log \beta_4$  value for  $\text{Ni}(\text{CN})_4^{2-}$  is 30.5.

### Introduction

Stepwise stability constants for cyanide complexes of nickel are not known because the tetracyano complex is so stable that it forms preferentially when nickel(II) and cyanide ion are mixed. Even solid  $\text{Ni}(\text{CN})_2$  has been shown to consist of  $\text{Ni}^{2+}$  and  $\text{Ni}(\text{CN})_4^{2-}$  ions.<sup>2-4</sup> The  $\log \beta_4$  value is approximately 30 rather than the often quoted estimate of 22.<sup>5</sup> The magnitude of the constant is well established from a wide variety of determinations which have included toxicity,<sup>6</sup> spectrophotometric,<sup>7</sup> kinetic,<sup>8</sup> and potentiometric studies.<sup>9</sup> There are some variations in the  $\beta_4$  value because of differences in ionic strength but there are additional disagreements which we believe can be attributed to

the presence of protonated forms of the complex in some studies.

The overwhelming stability of the diamagnetic  $\text{Ni}(\text{CN})_4^{2-}$  complex compared to lesser cyanide ion complexes with nickel accounts in good measure for the kinetic behavior reported in this work. Four cyanide ions are needed both thermodynamically and kinetically to give the stable diamagnetic square-planar complex. Intermediate species such as  $\text{NiCN}^+$ ,  $\text{Ni}(\text{CN})_2$ , and  $\text{Ni}(\text{CN})_3^-$  are not observed, although they can be assumed to be present as reaction intermediates. An unusually high reaction order results—fifth order overall. Despite the high reaction order the speed of the reaction is great even at low concentrations and stopped-flow methods were used to follow the rate of formation. The kinetics of the formation reaction are extremely interesting for another reason, namely, that hydrocyanic acid is a reactant as well as cyanide ion. Earlier work has shown the important kinetic role of HCN in the formation of mixed cyanide complexes of amino-carboxylate complexes of nickel.<sup>10</sup> The importance

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of protonated species is confirmed in studies of the acid dissociation rate of the tetracyano complex and in equilibrium measurements. The rate of dissociation is quite slow at low acidities with a half-life of approximately 10 hr at pH 5. On the other hand, radiocyanide exchange with  $\text{Ni}(\text{CN})_4^{2-}$  is fast,<sup>11,12</sup> and therefore the exchange must proceed by an association rather than a dissociation mechanism.

### Experimental Section

Sodium cyanide solutions (0.1 M) were standardized by the argentimetric method.<sup>13</sup> The solutions were diluted, adjusted to the desired pH, and placed in a container sealed with a rubber stopper. Samples were withdrawn from this container into the stopped-flow syringe. Nickel perchlorate prepared from  $\text{NiCO}_3$  and  $\text{HClO}_4$  was recrystallized from water. Solutions were standardized by the mole ratio method with standardized NaCN solution. The molar absorptivity of  $\text{Ni}(\text{CN})_4^{2-}$  at 267  $\mu\text{m}$  is  $1.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ .

Equilibrium studies of  $\text{Ni}(\text{CN})_4^{2-}$  at low pH were performed by mixing dilute solutions of  $\text{Na}_2\text{Ni}(\text{CN})_4$  and sodium acetate with  $\text{HClO}_4$ . The reaction vials were filled completely, sealed with paraffin wax, and placed in a thermostated bath at 25.0° for 1 week. The ultraviolet spectrum of each solution then was determined using a Cary 14 spectrophotometer and the pH was measured. All pH values are corrected to give  $-\log [\text{H}^+]$  by subtracting 0.11 from the pH reading.<sup>14</sup>

The rates of formation of  $\text{Ni}(\text{CN})_4^{2-}$  were measured at 267  $\mu\text{m}$  using a Durrum-Gibson stopped-flow apparatus with a 2-cm cell (Kel-F). A Tektronix Model 564 storage scope with a Polaroid camera was used to record the data. All reactions were at 25.0° and the ionic strength was maintained at 0.10 M with  $\text{NaClO}_4$ . The full scale time scans varied from 100 msec to 50 sec and the full-scale transmittance varied from 2 to 60%.

The rates of dissociation of  $\text{Ni}(\text{CN})_4^{2-}$  in acid were much slower and were followed with a Cary 14 spectrophotometer.

Computer programs for the IBM 7094 were used for (1) calculating the fifth-order rate parameters from the % T and time data, (2) calculating the protonation constants of  $\text{Ni}(\text{CN})_4^{2-}$ , and (3) analyzing the pH profile of the acid dissociation rate data.

A  $\text{p}K_a$  value of 9.0 is used for HCN. This is taken from Anderegg's value<sup>15</sup> of 9.14 at 0.10 M ( $\text{NaNO}_3$ ) and 20° with correction to 25° using  $\Delta H_1 = 10.3 \text{ kcal/mol}$ .<sup>16</sup>

### Results

**Kinetics of Formation of  $\text{Ni}(\text{CN})_4^{2-}$ .**—In order to avoid precipitation of  $\text{Ni}(\text{OH})_2$  and of  $\text{Ni}(\text{CN})_2$  and in order to reduce the speed of the reaction, dilute reactants were used ( $10^{-6}$  to  $3 \times 10^{-4} \text{ M}$ ) in the pH range 5.5–7.5. Under these conditions the reaction followed fifth-order kinetics in accord with eq 1 where  $\text{CN}_T = \text{HCN} + \text{CN}^-$ .

$$\frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} = k_f[\text{Ni}^{2+}][\text{CN}_T]^4 \quad (1)$$

A series of reactions were run with excess cyanide ion in which the total cyanide concentration was varied over a fourfold range at pH 6.8. The order dependence of

the pseudo-first-order rate constant,  $k_0$ , on  $[\text{CN}_T]$  was  $4.08 \pm 0.06$  for the reactions in Table I. The nickel concentration was varied by fourfold for each cyanide concentration to verify the first-order dependence in nickel.

TABLE I<sup>a,b</sup>  
TETRACYANONICKELATE(II) FORMATION RATE STUDIES  
AT 25.0°, pH 6.80 ± 0.10, AND  $\mu = 0.1 \text{ M}$  ( $\text{NaClO}_4$ )

| [Ni-<br>( $\text{ClO}_4$ ) <sub>2</sub> ],<br>M | 10 <sup>5</sup> [ $\text{CN}_T$ ],<br>M | $k_0$ , sec <sup>-1</sup> | 10 <sup>-13</sup> $k_0/[\text{CN}_T]^4$ ,<br>M <sup>-4</sup> sec <sup>-1</sup> |
|---|---|---------------------------|--|
| 3.70  | 9.55                                    | 0.0069                    | 8.3  |
| 5.55  | 9.55                                    | 0.0050                    | 6.0  |
| 7.40  | 9.55                                    | 0.0056                    | 6.7  |
|   |   | Av 0.0055 ± 0.0009        |  |
| 1.85  | 19.10                                   | 0.10                      | 7.7  |
| 3.70  | 19.10                                   | 0.13                      | 9.7  |
| 5.55  | 19.10                                   | 0.12                      | 9.0  |
| 7.40  | 19.10                                   | 0.11                      | 8.3  |
|   |   | Av 0.11 ± 0.02            |  |
| 1.85  | 38.20                                   | 1.6                       | 7.6  |
| 3.70  | 38.20                                   | 1.7                       | 7.8  |
| 5.55  | 38.20                                   | 1.6                       | 7.6  |
| 7.40  | 38.20                                   | 1.5                       | 7.3  |
|   |   | Av 1.6 ± 0.1              | Av 7.9 ± 1.3<br>(for 27 runs)  |

<sup>a</sup> Each  $k_0$  value is the average of 2 or 3 runs. <sup>b</sup> All limits shown are standard deviations.

For conditions in which the total cyanide was not in sufficiently large excess an integrated expression for eq 1 was used to determine the formation rate constant. The integrated rate expression for fourth-order cyanide and first-order nickel dependence is given in eq 2 where  $\alpha = [\text{CN}_T]_{\text{initial}} - 4[\text{Ni}^{2+}]_{\text{initial}}$  and where C is an integration constant relating the species concentrations at time zero. This equation is plotted in Figure 1

$$V = \frac{1}{3\alpha} \left\{ -\frac{1}{[\text{CN}_T]^3} + \frac{3}{2\alpha} \left[ -\frac{1}{[\text{CN}_T]^2} - \frac{2}{\alpha} \left( \frac{1}{[\text{CN}_T]} + \frac{1}{\alpha} \log \frac{[\text{Ni}]}{[\text{CN}_T]} \right) \right] \right\} = kt + C \quad (2)$$

showing the linearity when the reactant ratios are only a factor of 2 greater than the stoichiometric requirements. The data shown in Figure 1 are for the last 50% of the formation of  $\text{Ni}(\text{CN})_4^{2-}$  as observed with the Cary 14. Most of the reactions were followed with the stopped-flow for the first 50%. The two sets of data are in agreement.

The formation rate becomes slower in more acid solutions as  $\text{CN}^-$  is converted to HCN. However, the rate does not decrease as a fourth power of hydrogen ion concentration as would be expected if only cyanide ion reacted. Table II gives the  $k_f$  values between pH 5.6 and 9.2 using excess total cyanide. In Figure 2 the plot of  $\log k_f$  against  $-\log [\text{H}^+]$  gives a slope of 2 rather than a slope of 4. The smaller slope indicates that HCN is a reactant as well as  $\text{CN}^-$ . Equation 3 is the rate expression from pH 5.5 to 7.5. The value of  $k_{2,2}$  is  $1.6 \times 10^{18} \text{ M}^{-4} \text{ sec}^{-1}$ . The rate constant was not

$$\text{rate} = k_{2,2}[\text{Ni}^{2+}][\text{CN}^-]^2[\text{HCN}]^2 \quad (3)$$

affected by changing either the buffer or its concentration.

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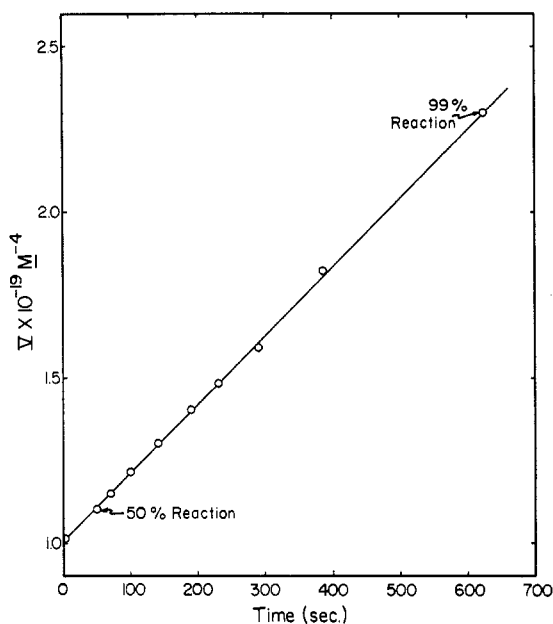


Figure 1.—Plot of the integrated rate expression for the fifth-order reaction ( $V$  in eq 2). The initial concentrations of nickel and  $CN_T$  were  $4.62 \times 10^{-6}$  and  $3.78 \times 10^{-5} M$ , respectively.

TABLE II

pH DEPENDENCE OF TETRACYANONICKELATE(II) FORMATION RATE STUDIES AT 25.0° AND  $\mu = 0.1 M$  ( $NaClO_4$ )

| $-\log [H^+]$ | $10^6[Ni], M$                               | $10^5[CN_T], M$ | $k_f, M^{-4} sec^{-1}$                     |
|---------------|---|-----------------|--|
| 5.64          | 13.90                                       | 45.50           | $(1.4, 4.6) \times 10^{11}$                |
| 6.17          | 4.63  | 22.70           | $(3.9, 3.0) \times 10^{12}$                |
| 6.52          | 4.63  | 22.70           | $1.0 \times 10^{13}$                       |
| 6.54          | 4.63  | 39.00           | $(4.5, 5.2, 5.0) \times 10^{13}$           |
| 6.77          | 4.63  | 22.70           | $(4.3, 4.3) \times 10^{13}$                |
| 6.80          | (average of 27 runs, conditions in Table I) |                 | $7.9 \times 10^{13}$                       |
| 6.95          | 4.63  | 39.00           | $(4.8, 5.9) \times 10^{14}$                |
| 7.07          | 4.63  | 22.70           | $1.1 \times 10^{14}$                       |
| 7.37          | 4.63  | 22.70           | $4.5 \times 10^{14}$                       |
| 7.80          | 4.63  | 3.78            | $2.1 \times 10^{16}$                       |
| 7.90          | 4.63  | 3.84            | $(3.4, 3.8, 4.3, 5.8, 3.5) \times 10^{16}$ |
| 8.46          | 1.85  | 1.47            | $(7.2, 7.8, 8.0) \times 10^{17}$           |
| 8.98          | 1.85  | 1.47            | $(2.5, 2.6, 2.5) \times 10^{18}$           |
| 9.20          | 1.85  | 1.47            | $(2.5, 2.7, 2.9) \times 10^{18}$           |

<sup>a</sup> Below pH 6 acetic acid-acetate buffer (0.005–0.02 M); above pH 8 borate-boric acid buffer (0.005 M); otherwise  $NaH_2PO_4$  (0.001 M) was used.

Above pH 7.5 the slope in Figure 2 increases approaching a value of 3 and above pH 8.5 the  $k_f$  value begins to level off with pH as would be expected as the degree of protonation of the cyanide diminishes. Low nickel and low cyanide concentrations were necessary to follow the reactions at higher pH and the over-all rates proved to be fifth-order at pH 8.5. The reactions run at pH 9–9.2 showed some evidence of being fifth order, but, because of their speed, the reaction order was not unequivocally established. At the high pH nickel hydrolysis should have some effect and the  $CN^-$  concentration is sufficiently high that some of the lower cyanide complexes of nickel may be present. Therefore, the data at pH 9–9.2 are approximate and the fifth-order constants must be at least this large.

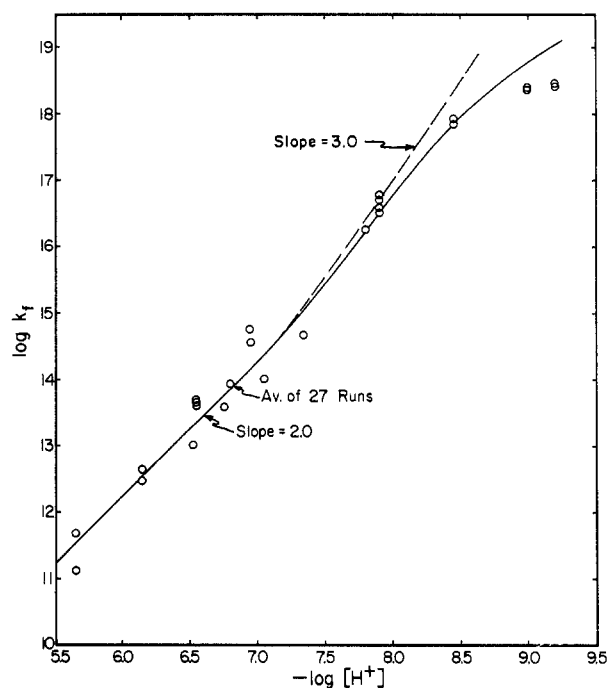


Figure 2.—Dependence of the fifth-order formation rate constant on acidity. Except where noted points are the average of 3 or 4 runs. The solid line is calculated from the following constants:  $k_{2,2} = 1.6 \times 10^{18} M^{-4} sec^{-1}$ ,  $k_{3,1} = 4 \times 10^{19} M^{-4} sec^{-1}$ ,  $k_4 = 6 \times 10^{19} M^{-4} sec^{-1}$ , and  $pK_a = 9.0$ .

Estimated values of  $k_{3,1}$  and  $k_4$  to fit the data from pH 7.5 to 8.5 are  $k_{3,1} \approx 4 \times 10^{19} M^{-4} sec^{-1}$  and  $k_4 \approx 6 \times 10^{19} M^{-4} sec^{-1}$ .

**Protonation Constants.**—The fact that the formation rate depended on  $[HCN]^2$  suggested that the reaction product might be  $H_2Ni(CN)_4$ . Although acid forms of tetracyanonickelate have been reported,<sup>3</sup> their stability constants were not known and such species were not taken into account in potentiometric measurements<sup>9</sup> of the  $\beta_4$  value. We equilibrated dilute solutions of  $Ni(CN)_4^{2-}$  at pH 4–5 (see Table III)

TABLE III

EQUILIBRIUM CONDITIONS FOR  $Ni(CN)_4^{2-}$  AND ACID AT 25.0°,  $\mu = 0.1 M$  ( $NaClO_4$ ),  $[AcT] = 0.01 M$ ,  $[Ni_T] = (8.0-8.3) \times 10^{-6} M$ ,  $[CN_T] = (3.2-3.3) \times 10^{-5} M$ , AND  $\log K_a = 9.0$

| $-\log [H^+]$ | $\log \frac{[\text{all forms of } Ni(CN)_4]}{[Ni^{2+}][CN^-]^4}$ | $\log [\beta_4(1 + K_H[H^+] + K_HK_{2H}[H^+]^2)]^a$ |
|---------------|--|---|
| 5.08          | 30.9   | 31.0  |
| 4.88          | 31.2   | 31.2  |
| 4.73          | 31.5   | 31.4  |
| 4.55          | 31.7   | 31.6  |
| 4.43          | 32.0   | 31.8  |
| 4.20          | 32.3   | 32.2  |
| 3.99          | 32.5   | 32.5  |

<sup>a</sup> These values are calculated using the following constants and are the best fit to match the experimental values in column 2:  $\log \beta_4 = 30.5 \pm 0.3$ ,  $\log K_H = 5.4 \pm 0.2$ , and  $\log K_HK_{2H} = \log \beta_{2H} = 9.9 \pm 0.2$ .

and used spectrophotometric measurements to calculate the stability constant. The second column in Table III shows that a constant value cannot be obtained for  $\beta_4$  if protonated species are not taken into account. As seen in the next section, the dissociation

kinetics in stronger acid also gave evidence of protonated species. The dissociation is slow enough at pH 1 to permit spectral scans which showed no shifts in wavelength or relative intensity of the characteristic tetracyanonickelate peaks at 267, 285, and 310  $m\mu$ . Extrapolation of the acid dissociation rate data to zero time gave molar absorptivities at 267  $m\mu$  identical with that expected for the initial  $\text{Ni}(\text{CN})_4^{2-}$  present in solution. Hence we conclude that the molar absorptivities of the protonated complexes are the same as that for  $\text{Ni}(\text{CN})_4^{2-}$  at these wavelengths. The best fit for the data in Table III required two acids,  $\text{HNi}(\text{CN})_4^-$  and  $\text{H}_2\text{Ni}(\text{CN})_4$ . Attempts to fit the data using fewer protonation constants did not give satisfactory results. The computer fit gave a  $\log \beta_4$  value of 30.5,  $\log K_H = 5.4$  and  $\log K_{2H} = 4.5$ , where  $K_H = [\text{HNi}(\text{CN})_4^-]/[\text{H}^+][\text{Ni}(\text{CN})_4^{2-}]$  and  $K_{2H} = [\text{H}_2\text{Ni}(\text{CN})_4]/[\text{H}^+][\text{HNi}(\text{CN})_4^-]$ . The third column in Table III shows the agreement between the calculated values and the experimental values of

$$\frac{[\text{H}_2\text{Ni}(\text{CN})_4] + [\text{HNi}(\text{CN})_4^-] + [\text{Ni}(\text{CN})_4^{2-}]}{[\text{Ni}^{2+}][\text{CN}^-]^4}$$

found in the second column using  $\text{p}K_a = 9.0$  for HCN.

Over most of the pH range used in the formation kinetic studies the product was  $\text{Ni}(\text{CN})_4^{2-}$  despite the fact that two HCN molecules were involved in the reaction. The acid constants are consistent with the dissociation rate data.

**Kinetics of Acid Dissociation.**—The rate of dissociation of tetracyanonickelate is first order in the complex and depends on the acidity (Table IV).

TABLE IV<sup>a</sup>  
ACIDITY EFFECTS ON THE DISSOCIATION RATE OF  
TETRACYANONICKELATE(II) AT 25.0° AND  $\mu = 0.1 M$  ( $\text{NaClO}_4$ )

| $-\log [\text{H}^+]$ | $10^5 [\text{Ni}(\text{CN})_4^{2-}]$<br>M | $k_d, \text{sec}^{-1}$ | $-\log [\text{H}^+]$ | $10^5 [\text{Ni}(\text{CN})_4^{2-}]$<br>M | $k_d, \text{sec}^{-1}$ |
|----------------------|---|------------------------|----------------------|---|------------------------|
| -0.06                | 4.50                                      | $4.3 \times 10^{-3}$   | 2.52                 | 6.47                                      | $2.2 \times 10^{-4}$   |
| 0.24                 | 8.32                                      | $2.3 \times 10^{-3}$   | 2.68                 | 1.45                                      | $3.1 \times 10^{-4}$   |
| 0.40                 | 7.41                                      | $1.8 \times 10^{-3}$   | 2.90                 | 0.53                                      | $3.4 \times 10^{-4}$   |
| 0.60                 | 3.23                                      | $1.1 \times 10^{-3}$   | 3.10                 | 4.16                                      | $2.4 \times 10^{-4}$   |
| 0.88                 | 4.16                                      | $1.1 \times 10^{-3}$   | 3.12                 | 1.76                                      | $1.7 \times 10^{-4}$   |
| 1.11                 | 4.16                                      | $9.8 \times 10^{-4}$   | 3.46                 | 0.77                                      | $2.8 \times 10^{-4}$   |
| 1.32                 | 8.06                                      | $6.1 \times 10^{-4}$   | 3.65                 | 2.05                                      | $1.0 \times 10^{-4}$   |
| 1.62                 | 0.78                                      | $5.3 \times 10^{-4}$   | 3.90                 | 2.20                                      | $6.9 \times 10^{-5}$   |
| 1.71                 | 6.64                                      | $5.1 \times 10^{-4}$   | 3.92                 | 0.89                                      | $1.5 \times 10^{-4}$   |
| 1.88                 | 7.52                                      | $4.4 \times 10^{-4}$   | 4.13                 | 2.33                                      | $5.0 \times 10^{-5}$   |
| 1.90                 | 4.16                                      | $4.7 \times 10^{-4}$   | 4.48                 | 0.96                                      | $5.9 \times 10^{-5}$   |
| 1.95                 | 0.30                                      | $4.6 \times 10^{-4}$   | 4.53                 | 2.47                                      | $2.6 \times 10^{-5}$   |
| 2.20                 | 1.03                                      | $4.1 \times 10^{-4}$   | 4.80                 | 2.52                                      | $2.3 \times 10^{-5}$   |
| 2.35                 | 4.16                                      | $3.6 \times 10^{-4}$   | 4.83                 | 1.01                                      | $4.8 \times 10^{-5}$   |
| 2.43                 | 0.40                                      | $4.2 \times 10^{-4}$   | 4.90                 | 8.32                                      | $1.9 \times 10^{-5}$   |

<sup>a</sup>  $k_d$  is independent of buffer concentration (0.005–0.03 M acetic acid–sodium acetate from pH 3.5 to 5.0).

The observed first-order dissociation rate constant,  $k_d$ , is plotted in Figure 3. The value of  $k_d$  has a complex dependence on acidity but at a given pH it is independent of buffer concentration. From eq 3 a slope of  $-2$  would be expected in Figure 3. This is shown as a dashed line. The deviation at high acidity is partly explained by the presence of  $\text{HNi}(\text{CN})_4^-$

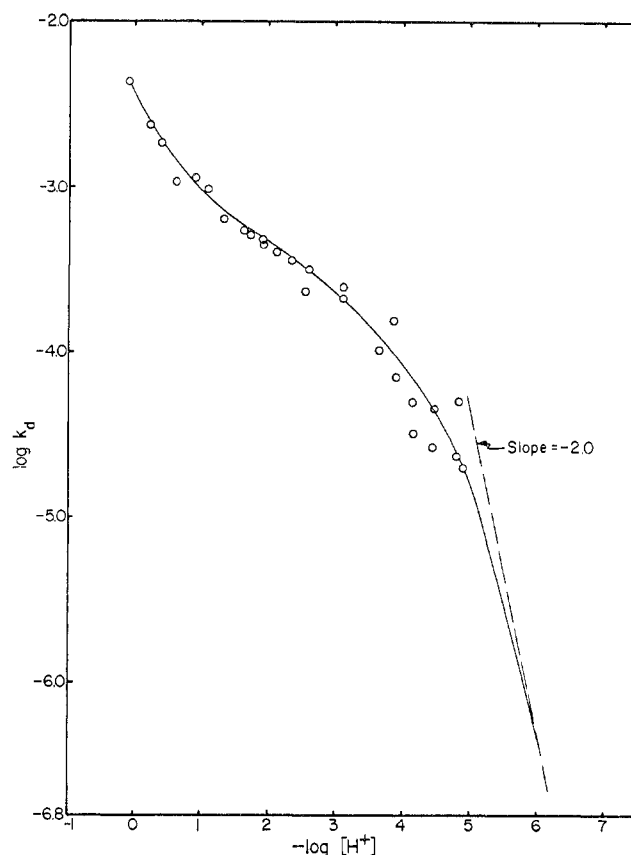
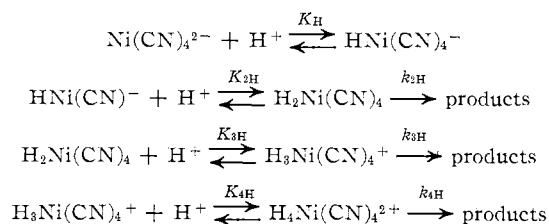


Figure 3.—Observed first-order dissociation rate constant,  $k_d$ , in  $\text{HClO}_4$  solutions. Initial  $[\text{Ni}(\text{CN})_4^{2-}]$  was  $(4-8) \times 10^{-6} M$ , the ionic strength was  $0.1 M$  ( $\text{NaClO}_4 + \text{HClO}_4$ ) up to pH 1 at 25.0°. The solid curve was calculated from  $K_H = 2.5 \times 10^5 M^{-1}$ ,  $K_{2H} = 3 \times 10^4 M^{-1}$ ,  $K_{3H} = 400 M^{-1}$ ,  $k_{2H} = 9.2 \times 10^{-5} \text{ sec}^{-1}$ ,  $k_{3H} = 5.2 \times 10^{-4} \text{ sec}^{-1}$ , and  $k_{4H}K_{4H} = 3.3 \times 10^{-3} M^{-1} \text{ sec}^{-1}$ .

and  $\text{H}_2\text{Ni}(\text{CN})_4$ . These acid species can account for the decrease in the slope from pH 5 to 4 but two additional rate constants and one more acidity constant are necessary to establish the experimental curve. A mechanism consistent with the formation kinetics and with the protonation constants for  $\text{Ni}(\text{CN})_4^{2-}$  is



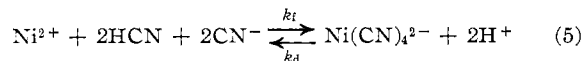
This mechanism gives the following expression for  $k_d$

$$k_d = \frac{K_H K_{2H} k_{2H} [\text{H}^+]^2 + K_H K_{2H} K_{3H} k_{3H} [\text{H}^+]^3 + \frac{K_H K_{2H} K_{3H} K_{4H} k_{4H} [\text{H}^+]^4}{1 + K_H [\text{H}^+] + K_H K_{2H} [\text{H}^+]^2 + K_H K_{2H} K_{3H} [\text{H}^+]^3}}{1 + K_H [\text{H}^+] + K_H K_{2H} [\text{H}^+]^2 + K_H K_{2H} K_{3H} [\text{H}^+]^3} \quad (4)$$

The solid line in Figure 3 is the best fit of eq 4 using  $K_H$  and  $K_{2H}$  as given in Table III and  $\log K_{3H} = 2.6 \pm 0.4$ . The rate constants are  $k_{2H} = 9.2 \times 10^{-5} \text{ sec}^{-1}$ ,  $k_{3H} = 5.2 \times 10^{-4} \text{ sec}^{-1}$ , and  $K_{4H}k_{4H} = 3.3 \times 10^{-3} M^{-1} \text{ sec}^{-1}$ . The value of  $k_d$  does not level off even at 2 M  $\text{HClO}_4$  and hence  $K_{4H}$  could not be determined. The product of  $k_H^{\text{H}_2\text{Ni}(\text{CN})_4} = K_{4H}k_{4H}$  was obtained.

### Discussion

The formation and dissociation kinetics agree with a mechanism in which four cyanides and one nickel are present during the rate-determining step. In the vicinity of pH 5 the rate constants for both the forward and the reverse reactions in eq 5 were determined. The ratio of  $k_i/k_d$  is  $2 \times 10^{12} M^{-2}$  which is in good



agreement with an equilibrium constant of  $3 \times 10^{12} M^{-2}$  calculated from  $\log \beta_4 = 30.5$  and  $\text{p}K_a = 9.0$ .

Table V lists all of the rate constants and equilibrium constants determined in this work. The formation rate constants with HCN as a reactant are almost as large as the  $k_4$  value with only  $\text{CN}^-$  as a reactant. The dissociation rate constants increase with the degree of protonation of  $\text{Ni}(\text{CN})_4^{2-}$ .

TABLE V

CONSTANTS AT  $\mu = 0.1 M$  ( $\text{NaClO}_4$ ) AND 25.0°Formation Rate Constants,  $k_{ij}$ ,  $M^{-4} \text{sec}^{-1}$  ( $i = \text{CN}^-$ ,  $j = \text{HCN}$ )

$$k_{2,2} = 1.6 \times 10^{18}$$

$$k_{3,1} \simeq 4 \times 10^{19}$$

$$k_4 \simeq 6 \times 10^{19}$$

Dissociation Rate Constants of  $\text{H}_n\text{Ni}(\text{CN})_4^{n-2}$ 

$$k_{2\text{H}} = 9.2 \times 10^{-5} \text{sec}^{-1}$$

$$k_{3\text{H}} = 5.2 \times 10^{-4} \text{sec}^{-1}$$

$$k_{4\text{H}}K_{4\text{H}} = 3.3 \times 10^{-8} M^{-1} \text{sec}^{-1}$$

Stability Constant for  $\text{Ni}(\text{CN})_4^{2-}$  and Protonation Constants for  $\text{H}_n\text{Ni}(\text{CN})_4^{n-2}$ 

$$\log \beta_4 = 30.5 \pm 0.3$$

$$\log K_{\text{H}} = 5.4 \pm 0.2$$

$$\log K_{2\text{H}} = 4.5 \pm 0.2$$

$$\log K_{3\text{H}} = 2.6 \pm 0.4$$

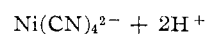
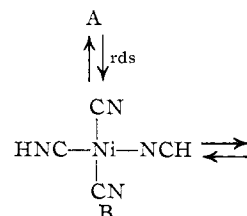
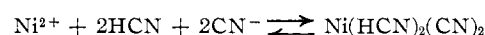
The equilibrium and kinetic studies show that  $\text{H}_3\text{Ni}(\text{CN})_4^+$ ,  $\text{H}_2\text{Ni}(\text{CN})_4$ , and  $\text{HNi}(\text{CN})_4^-$  are weak acids. This is consistent with the behavior of the first three protonation constants of  $\text{Fe}(\text{CN})_6^{4-}$  with  $\text{p}K_a$  values of 4.2, 2.2, and less than unity.<sup>17</sup>

Under the dilute conditions used there was no evidence for nickel-cyanide complexes with fewer than four cyanides. This sets limiting values for the stability constants of the 1:1, 1:2, and 1:3 complexes. At the highest cyanide ion concentration used where the fourth-order cyanide dependence was established, it can be assumed that no more than 10% of the nickel is present in the lower cyanide complexes. This requires  $K_1 < 10^5$ ,  $\beta_2 < 3 \times 10^{11}$ , and  $\beta_3 < 2 \times 10^{16}$ . This means that  $K_4 = [\text{Ni}(\text{CN})_4^{2-}]/[\text{Ni}(\text{CN})_3^-][\text{CN}^-]$  must be greater than  $10^{14}$ . This is a very large value and probably can be attributed to the transformation from a weak octahedral to a strong square-planar complex.

The over-all rate for the formation of  $\text{Ni}(\text{CN})_4^{2-}$  is extremely fast when compared to the rate at which  $\text{CN}^-$  would be expected to replace  $\text{H}_2\text{O}$  from the aquo-

nickel ion. Thus, at pH 6.8 the velocity equaled  $1.2 \times 10^{-5} M \text{sec}^{-1}$ , which is much greater than would be calculated from the Eigen outer-sphere association mechanism.<sup>18</sup> The rate from this mechanism would be  $K_{os}k^{\text{Ni-H}_2\text{O}}[\text{Ni}^{2+}(\text{aq})][\text{CN}^-] = 5.3 \times 10^{-7} M \text{sec}^{-1}$ , where  $K_{os} \simeq 1$  is the outer-sphere association constant for +2 and -1 ions, and  $k^{\text{Ni-H}_2\text{O}} = 3 \times 10^4 \text{sec}^{-1}$  is the rate of water loss from nickel. However, if HCN is assumed to react, the rate calculated from the outer-sphere association mechanism would be  $K_{os}k^{\text{Ni-H}_2\text{O}}[\text{Ni}^{2+}(\text{aq})][\text{HCN}] = 1.3 \times 10^{-5} M \text{sec}^{-1}$ , where  $K_{os} = 0.15$  for a +2 ion and a neutral species.<sup>19</sup> We must therefore conclude that aquonickel reacts first with HCN rather than with  $\text{CN}^-$  at pH 6.8. Proton transfer from the HCN complexes of nickel-aminocarboxylate complexes<sup>10</sup> was found to be rate limiting but in the present case the proton-transfer reactions should be faster than the velocities observed. No evidence was found for a proton-transfer limiting step.

A mechanism for the reaction in eq 5 must proceed through a series of complexes among  $\text{Ni}^{2+}$ , HCN, and  $\text{CN}^-$  before the rate-determining step (rds) where two HCN molecules and two  $\text{CN}^-$  ions surround the nickel ion. Species A may be a reaction intermediate or a transition state where the HCN molecules either are  $\pi$  complexes or else are in a different geometrical con-



figuration than in species B. In the forward reaction the rate-determining step is assigned to the formation of species B which then transfers its protons rapidly. Species B is believed to be the structure for the stable acid,  $\text{H}_2\text{Ni}(\text{CN})_4$ , because of the lack of spectral shifts due to protonation. This type of structure is similar to those proposed in the  $\text{BF}_3$  adducts of metal-cyanide complexes which also showed no visible-ultraviolet spectral shifts.<sup>20</sup>

The fifth-order kinetics observed in this work does not imply this order of molecularity. Intermediate nickel-cyanide complexes must precede the grouping of four cyanides around the nickel ion needed for the rate-determining step. Under the conditions in these experiments their concentrations were not sufficiently high to be observed either spectrally or kinetically.

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