CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

Kinetics of the Reaction between Cyanide Ion and the Nickel(II) Complexes of Iminodiacetate and N-Methyliminodiacetate

BY LEE C. COOMBS AND DALE W. MARGERUM[1]

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The reactions of NiL_2^{2-} and of NiL, where L^{2-} is iminodiacetate (IDA^{2-}) or N-methyliminodiacetate ($MIDA^{2-}$), with excess CN^- to give $Ni(CN)_4^{2-}$ are measured over a wide range of cyanide concentrations. The NiL_2^{2-} complexes are much slower to react than the NiL complexes. With the bis complexes the rate-determining steps involve the removal of one L^{2-} ligand by dissociation or by cyanide attack followed by the rapid conversion of the mono complex to $Ni(CN)_4^{2-}$: rate = $(k_d^{NiL_2} + k_{CN}^{NiL_2}[CN^-])[NiL_2^{2-}]$. Although the $k_d^{NiL_2}$ values are the same order of magnitude (4.5×10^{-3} sec^{-1} for IDA and 1.5×10^{-3} sec^{-1} for MIDA), the $k_{CN}^{NiL_2}$ rate constant is much larger for IDA (2.5×10^2 M^{-1} sec^{-1}) than for MIDA (5.3 M^{-1} sec^{-1}). The mono complexes rapidly add two cyanides and the observed kinetics are first order in cyanide and first order in $NiL(CN)_2^{2-}$. The fact that only three cyanides are involved in the rate-determining step is confirmed in the kinetics of the reverse reaction between $Ni(CN)_4^{2-}$ and L^{2-} which is first order in each reactant and inverse first order in cyanide. The mechanism is

$$NiL + 2CN^- \rightleftharpoons NiL(CN)_2^{2-} \quad \text{(rapid)}$$

$$NiL(CN)_2^{2-} + CN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ni(CN)_3L^{3-} \quad \text{(rate-determining)}$$

$$Ni(CN)_3L^{3-} + CN^- \rightleftharpoons Ni(CN)_4^{2-} + L^{2-} \quad \text{(rapid)}$$

where for IDA and MIDA, respectively, the stability constants for $NiL(CN)_2^{2-}$ are 1.6×10^{11} and 2.1×10^{10} M^{-2}, the k_3 values are 5.0×10^4 and 5.3×10^4 M^{-1} sec^{-1}, and the reverse rate constants are 4.7×10^{-7} and 1.9×10^{-7} sec^{-1}.

Introduction

The reactions of aquonickel ion[2] and of triethylenetetraminenickel(II)[3] with cyanide to form tetracyanonickelate(II) ion are both first order in the nickel complexes and fourth order in total cyanide. These reactions are very fast compared to the reaction of ethylenediaminetetraacetatonickelate(II) with cyanide and the rate-determining step with the EDTA complex involves only three cyanide ions followed by a rapid reaction with another cyanide to give $Ni(CN)_4^{2-}$.[4] A mixed complex of $Ni(EDTA)(CN)^{3-}$ forms rapidly[5] and the observed kinetics are first order in this complex and second order in cyanide.

In the present work the reactions of the nickel complexes of iminodiacetate (IDA^{2-}) and of N-methyliminodiacetate ($MIDA^{2-}$) with cyanide are studied and are fast compared to the EDTA complex. Unlike $NiEDTA^{2-}$ neither of the bis complexes of the iminodiacetates, NiL_2^{2-}, shows any evidence of forming a stable complex with CN^-. The bis complexes are not converted directly to $Ni(CN)_4^{2-}$ but must first lose one ligand and cyanide ion assists this loss. Therefore, the reactions observed with the bis complex are

$$NiL_2^{2-} \xrightarrow{k_d^{NiL_2}} NiL + L^{2-} \qquad (1)$$

$$NiL_2^{2-} + CN^- \xrightarrow{k_{CN}^{NiL_2}} NiLCN^- + L^{2-} \qquad (2)$$

followed by the more rapid conversion of the mono complex to $Ni(CN)_4^{2-}$. The mono complexes react very rapidly to give remarkably stable mixed cyanide complexes which contain two cyanide ions. The resulting $NiL(CN)_2^{2-}$ complex reacts with one more CN^- in a rate-determining step similar to the EDTA reaction in that a total of only three cyanides is involved

$$NiL + 2CN^- \overset{\text{rapid}}{\rightleftharpoons} NiL(CN)_2^{2-} \qquad K_1K_2 \qquad (3)$$

$$NiL(CN)_2^{2-} + CN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ni(CN)_3L^{3-} \qquad (4)$$

$$Ni(CN)_3L^{3-} + CN^- \overset{\text{rapid}}{\rightleftharpoons} Ni(CN)_4^{2-} + L^{2-} \qquad K_4 \qquad (5)$$

Experimental Section

The disodium salt of iminodiacetic acid was obtained as the practical grade from Eastman Organic Chemicals, and methyliminodiacetic acid was obtained from Aldrich Chemical Co. Both ligands were recrystallized twice from water–ethanol mixtures. Approximately 0.01 M solutions of $Ni(IDA)_2^{2-}$ and of $Ni(MIDA)_2^{2-}$ were prepared by adding a slight excess of nickel perchlorate to a weighed amount of ligand in solution, followed by precipitation of the excess nickel as the hydroxide (final pH 10–11). The solutions were filtered through a 0.22-μ Millipore filter and adjusted to pH 9 with $HClO_4$ for storage. These solutions were standardized by addition of 0.1 M NaCN and measurement of the absorbance of $Ni(CN)_4^{2-}$.

Nickel perchlorate, $Ni(ClO_4)_2 \cdot 6H_2O$, was prepared from reagent grade $NiCO_3$ and $HClO_4$ and was recrystallized twice from water. Sodium cyanide solutions were standardized by the argentimetric method just prior to use. Standard $Ni(CN)_4^{2-}$ solutions used in the reverse rate studies were prepared by stoichiometric addition. Ionic strength was adjusted with $NaClO_4$ (twice recrystallized) to 0.10 M except for the reverse reaction with IDA which was 0.33 M. The pH of all reactions was maintained at 10.8 ± 0.2 using dilute NaOH.

Solutions containing only the 1:1 complexes of Ni(IDA) and of

(1) Correspondence to be addressed to this author.
(2) G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, **7**, 2239 (1968).
(3) G. B. Kolski and D. W. Margerum, *ibid.*, **8**, 1125 (1969).
(4) D. W. Margerum, T. J. Bydalek, and J. J. Bishop, *J. Amer. Chem. Soc.*, **83**, 1791 (1961).
(5) D. W. Margerum and L. I. Simandi, "Proceedings of the 9th International Conference on Coordination Chemistry," W. Schneider, Ed., Verlag Helvetica Chimica Acta, Basel, Switzerland, 1966, p 371.

Ni(MIDA) cannot exist at pH 11 because of the disproportionation reaction

$$2NiL + 2OH^- \rightleftarrows NiL_2^{2-} + Ni(OH)_2(s) \qquad (6)$$

however dilute solutions can be prepared which contain mixtures of NiL and NiL_2^{2-} without any $Ni(OH)_2$ precipitate. In the reaction of these mixtures with CN^- the NiL complex is converted to $Ni(CN)_4^{2-}$ much faster than the NiL_2^{2-} complex and its kinetics was determined in this way.

The forward reaction rates were followed on a Durrum–Gibson stopped-flow apparatus with a 2.0-cm observation cell (Kel-F) by monitoring the formation of $Ni(CN)_4^{2-}$ at 267 mμ (ε 1.16×10^4 M^{-1} cm^{-1}). A Tektronix Model 564 storage oscilloscope equipped with a Polaroid camera was used to record the data. Oscilloscope time scans as fast as 20 msec/cm were used. A least-squares first-order program for the IBM 7094 computer was used to calculate the observed forward rate constants from the per cent transmittance–time data taken from the stopped-flow pictures. The reactions were first order because CN^- was in excess

$$\frac{d[Ni(CN)_4^{2-}]}{dt} = k_{obsd}[NiL_n]_T \qquad (7)$$

and $[NiL_n]_T$ includes any rapidly formed mixed cyanide complexes.

Reverse rates for the IDA and MIDA systems were followed with Cary Model 14 and Model 16 spectrophotometers, respectively, by monitoring the disappearance of $Ni(CN)_4^{2-}$ at 267 and 285 mμ (ε 4.63×10^3 M^{-1} cm^{-1}) using 10-cm cells.

Results

Kinetics of CN^- Reaction with NiL_2^{2-}.—Reactions first order in NiL_2^{2-} concentration are observed when cyanide is in excess in accord with eq 7. The values for the observed first-order rate constants depend on the concentration of cyanide (Tables I and II), but as Figure 1 shows, this dependence is first order in cyanide at higher concentrations and approaches zero order in cyanide at lower concentrations. The high molar absorptivity of $Ni(CN)_4^{2-}$ permitted an accurate determination of rate constants even at extremely low concentrations. With both IDA and MIDA the value for k_{obsd} can be expressed by

$$k_{obsd}\ (\text{for } NiL_2) = k_d^{NiL_2} + k_{CN}^{NiL_2}[CN^-] \qquad (8)$$

TABLE I

CYANIDE DEPENDENCE ON THE OBSERVED FORWARD RATE CONSTANTS—$Ni(IDA)_2^{2-}$ SYSTEM[a]

$[CN^-]_T$, M	$[CN^-]_T/4[Ni]_T$ [b]	k_{obsd},[c] sec^{-1}
1.00×10^{-5}	2	$(7.1 \pm 0.2) \times 10^{-3}$
1.78×10^{-5}	4	$(1.06 \pm 0.02) \times 10^{-2}$
3.16×10^{-5}	7	$(1.09 \pm 0.09) \times 10^{-2}$
5.62×10^{-5}	13	$(1.7 \pm 0.3) \times 10^{-2}$
1.00×10^{-4}	23	$(2.2 \pm 0.4) \times 10^{-2}$
1.11×10^{-4}	28	$(2.5 \pm 0.2) \times 10^{-2}$
1.11×10^{-4}	8	$(2.4 \pm 0.3) \times 10^{-2}$
5.55×10^{-4}	41	$(9 \pm 1) \times 10^{-2}$
1.11×10^{-3}	82	$(2.2 \pm 0.5) \times 10^{-1}$
1.66×10^{-3}	123	$(4.4 \pm 0.4) \times 10^{-1}$
2.22×10^{-3}	164	$(6.6 \pm 0.4) \times 10^{-1}$
2.22×10^{-3}	10	$(4.3 \pm 0.3) \times 10^{-1}$
1.11×10^{-2}	49	3.3 ± 0.3
2.22×10^{-2}	97	8.3 ± 0.7
3.33×10^{-2}	146	$(1.3 \pm 0.1) \times 10$
4.44×10^{-2}	195	$(1.5 \pm 0.2) \times 10$

[a] $[NiL_2^{2-}]_i = 5.9 \times 10^{-7}$–$4.7 \times 10^{-5}$ M, 25°, pH 10.8 ± 0.2, μ 0.10. [b] $[Ni]_T = [NiL] + [NiL_2^{2-}]$. [c] Average of three to six runs.

TABLE II

CYANIDE DEPENDENCE ON THE OBSERVED FORWARD RATE CONSTANTS—$Ni(MIDA)_2^{2-}$ SYSTEM[a]

$[CN^-]_T$, M	$[CN^-]_T/4[Ni]_T$ [b]	k_{obsd},[c] sec^{-1}
3.16×10^{-5}	3	$(1.7 \pm 0.1) \times 10^{-3}$
1.00×10^{-4}	9	$(2.1 \pm 0.2) \times 10^{-3}$
3.16×10^{-4}	29	$(3.2 \pm 0.2) \times 10^{-3}$
5.36×10^{-4}	49	$(3.9 \pm 0.2) \times 10^{-3}$
1.00×10^{-3}	91	$(6.1 \pm 0.2) \times 10^{-3}$
1.07×10^{-3}	98	$(6.6 \pm 0.1) \times 10^{-3}$
1.61×10^{-3}	47	$(9.4 \pm 0.2) \times 10^{-3}$
2.14×10^{-3}	195	$(1.3 \pm 0.1) \times 10^{-2}$
2.14×10^{-3}	11	$(1.24 \pm 0.08) \times 10^{-2}$
3.16×10^{-3}	286	$(1.94 \pm 0.03) \times 10^{-2}$
3.16×10^{-3}	7	$(1.95 \pm 0.02) \times 10^{-2}$
5.00×10^{-3}	11	$(2.95 \pm 0.04) \times 10^{-2}$
1.00×10^{-2}	23	$(5.46 \pm 0.08) \times 10^{-2}$
1.07×10^{-2}	55	$(5.7 \pm 0.1) \times 10^{-2}$
1.78×10^{-2}	41	$(9.87 \pm 0.02) \times 10^{-2}$
2.14×10^{-2}	110	$(1.14 \pm 0.05) \times 10^{-1}$
3.22×10^{-2}	166	$(1.7 \pm 0.1) \times 10^{-1}$
4.29×10^{-2}	221	$(2.2 \pm 0.2) \times 10^{-1}$

[a] $[NiL_2^{2-}]_i = 2.4 \times 10^{-6}$–$1.1 \times 10^{-4}$ M, 25°, pH 10.8 ± 0.2, μ 0.10. [b] $[Ni]_T = [NiL] + [NiL_2^{2-}]$. [c] Average of three to five runs.

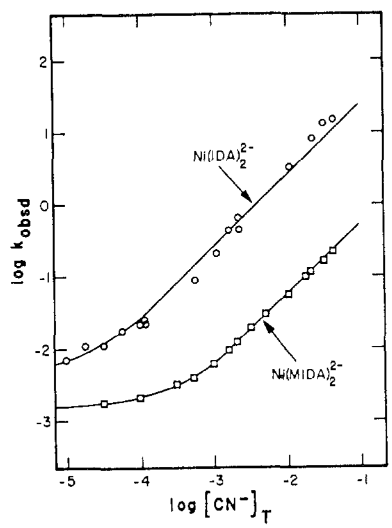

Figure 1.—Cyanide dependence on the observed forward rate constants for the $Ni(IDA)_2^{2-}$ and $Ni(MIDA)_2^{2-}$ systems. (Solid line calculated from experimentally measured rate constants.)

with $k_d^{NiL_2}$ equal to 4.5×10^{-3} sec^{-1} (IDA) and 1.5×10^{-3} sec^{-1} (MIDA) and $k_{CN}^{NiL_2}$ equal to 2.5×10^2 M^{-1} sec^{-1} (IDA) and 5.3 M^{-1} sec^{-1} (MIDA). This corresponds to the mechanism given in eq 1 and 2 where NiL or $NiLCN^-$ react rapidly with additional CN^- to give $Ni(CN)_4^{2-}$.

No evidence could be found for an $NiL_2(CN)^{3-}$ complex similar to the $Ni(EDTA)(CN)^{3-}$ complex which has a stability constant of 4×10^3 M^{-1} and was readily detected kinetically and spectrophotometrically.[4,5] If a $NiL_2(CN)^{3-}$ complex exists for either IDA or MIDA, it must have a stability constant less than 10 M^{-1}. The fact that the mixed cyanide complex exists with nickel–EDTA but not with NiL_2^{2-} is in accord with the

TABLE III

LIGAND DEPENDENCE ON THE OBSERVED FORWARD RATE CONSTANTS AT 25°, pH 10.9 ± 0.1, AND μ 0.10

$[L^{2-}]/[NiL_2^{2-}]_i$	k_{obsd}, sec^{-1}
	$Ni(IDA)_2^{2-}$ System[a]
	$[NiL]_T$[b] = 1.11 × 10^{-5} M
	$[CN^-]_T$ = 1.78 × 10^{-5} M
0	(10.6 ± 0.2) × 10^{-3}
1.7	(9.7 ± 0.2) × 10^{-3}
8.6	(9.0 ± 0.8) × 10^{-3}
	$[CN^-]_T$ = 3.16 × 10^{-5} M
0	(1.09 ± 0.09) × 10^{-2}
1.7	(1.25 ± 0.03) × 10^{-2}
8.6	(1.24 ± 0.08) × 10^{-2}
	$Ni(MIDA)_2^{2-}$ System[c]
	$[NiL_2^{2-}]_i$ = 5.71 × 10^{-5} M
	$[CN^-]_T$ = 5.00 × 10^{-3} M
0	(2.78 ± 0.05) × 10^{-2}
35	(2.83 ± 0.07) × 10^{-2}
61	(2.84 ± 0.03) × 10^{-2}
123	(2.77 ± 0.09) × 10^{-2}
	$[CN^-]_T$ = 1.00 × 10^{-2} M
0	(5.6 ± 0.1) × 10^{-2}
35	(5.6 ± 0.1) × 10^{-2}
61	(5.5 ± 0.1) × 10^{-2}
123	(5.5 ± 0.1) × 10^{-2}

[a] Average of three runs followed at 267 mμ. [b] $[NiL]_T$ = [NiL] + $[NiL_2^{2-}]$. [c] Average of three runs followed at 285 mμ.

observations[6,7] that one carboxylate group is free in the EDTA complex, $Ni(EDTA)(H_2O)^{2-}$, while this would not be so with NiL_2^{2-}.

As seen in Table III, there is no significant effect caused by variation of the free L^{2-} concentration as would be required if the kinetic step involved a dissociation of an L^{2-} ligand prior to the first-order CN^- reaction. Therefore, CN^- must react directly with NiL_2^{2-}. Accordingly, the same rate constant for $k_{CN}^{NiL_2}$ should hold with equal or excess concentrations of NiL_2^{2-} rather than excess CN^-. The reaction was measured with $Ni(MIDA)_2^{2-}$ in excess and was followed by its disappearance at 610 mμ as well as by the appearance of $Ni(CN)_4^{2-}$ at 285 and 310 mμ. The results are given in Table IV. There are no reaction intermediates of appreciable concentration and the rate of disappearance of $Ni(MIDA)_2^{2-}$ is the same within experimental error as the rate of appearance of $Ni(CN)_4^{2-}$.

At low concentrations of CN^- the aqueous dissociation of NiL_2^{2-} contributes to the rate, and, as will be shown in the next section, once NiL forms, it reacts very rapidly to give $Ni(CN)_4^{2-}$. The direct CN^- reaction with $Ni(MIDA)_2^{2-}$ is much slower than with $Ni(IDA)_2^{2-}$ while the k_d values are closer together. As a result the reaction of $Ni(MIDA)_2^{2-}$ is nearly zero order in $[CN^-]$ below 10^{-4} M cyanide.

Kinetics of CN^- Reaction with NiL.—The reaction of the mono complex also was studied at pH 10.8 in order to avoid possible contributions of HCN to the reaction rate which is known to be important in the reactions of the aquonickel, nickel–trien, and nickel–EDTA complexes.[2,3,5] This necessitated working with a mixture of NiL and NiL_2^{2-} but the reaction of NiL_2^{2-} is much slower and corrections are made for its contributions. With excess cyanide ion the observed kinetics were first order in the 1:1 complex as given in Table V.

(6) D. W. Margerum, *J. Phys. Chem.*, **63**, 336 (1959).
(7) G. S. Smith and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 556 (1959).

TABLE IV

FORWARD RATE CONSTANTS UNDER EXCESS $Ni(MIDA)_2^{2-}$ CONDITIONS AT 25°, pH 10.9 ± 0.1, AND μ 0.10

$[CN^-]_T$, M	$[CN^-]_T/[NiL_2^{2-}]_i$	$k_{CN}^{NiL_2}$,[a] M^{-1} sec^{-1}
	$[NiL_2^{2-}]_i$ = 1.407 × 10^{-2} M, λ 310 mμ	
1.00 × 10^{-2}	0.71	5.8 ± 0.1
5.00 × 10^{-3}	0.36	6.5 ± 0.1
3.16 × 10^{-3}	0.22	6.8 ± 0.2
	Av	6.4 ± 0.5
	$[NiL]_T$[b] = 1.09 × 10^{-4} M, λ 285 mμ	
1.78 × 10^{-2}	164	5.46 ± 0.01
1.00 × 10^{-2}	92	5.34 ± 0.04
5.00 × 10^{-3}	44	5.63 ± 0.04
3.16 × 10^{-3}	28	5.69 ± 0.07
	Av	5.6 ± 0.1
	$[NiL_2^{2-}]_i$ = 1.407 × 10^{-2} M, λ 610 mμ	
1.78 × 10^{-2}	1.21	5.7 ± 0.1
1.00 × 10^{-2}	0.71	6.1 ± 0.1
5.00 × 10^{-3}	0.36	6.4 ± 0.2
3.16 × 10^{-3}	0.22	6.4 ± 0.2
	Av	6.2 ± 0.3

[a] Average of four runs; corrected for $k_d^{NiL_2}$. [b] $[NiL]_T$ = [NiL] + $[NiL_2^{2-}]$.

TABLE V

CYANIDE DEPENDENCE ON THE OBSERVED FORWARD RATE CONSTANTS AT 25°, pH 10.8 ± 0.2, AND μ 0.10

$[CN^-]_T$, M	$[CN^-]_T/4[NiL]_i$	k_{obsd},[a] sec^{-1}
	NiIDA System	
	$[NiL]_i$ = (5.0–5.4) × 10^{-7} M, $[NiL_2]_i$ = (5.7–6.1) × 10^{-7} M	
1.00 × 10^{-5}	5	(3.7 ± 0.1) × 10^{-1}
1.78 × 10^{-5}	8	(7 ± 1) × 10^{-1}
3.16 × 10^{-5}	16	1.4[b]
	NiMIDA System	
	$[NiL]_i$ = (4.1–5.0) × 10^{-7} M, $[NiL_2]_i$ = (2.3–2.4) × 10^{-6} M	
3.16 × 10^{-5}	16	(8 ± 1) × 10^{-1}
1.00 × 10^{-4}	61	4.6 ± 0.3
3.16 × 10^{-4}	193	16.0 ± 0.7

[a] Average of three to five runs. [b] Single determination.

Figure 2 shows that the observed cyanide dependence also is first order; the values for the rate constants which are first order in total NiL and first order in CN^- are 5.0 × 10^4 M^{-1} sec^{-1} for IDA and 5.3 × 10^4 M^{-1} sec^{-1} for MIDA.

The experimental conditions require low concentrations of NiL, and therefore direct evidence of any mixed cyanide complexes is not available. However, experience with other nickel–aminocarboxylate complexes and with nickel–trien gives every reason to expect such complexes. The reverse kinetics show that a mixed complex of $NiL(CN)_2^{2-}$ must form very rapidly and completely and that it is attacked by CN^- to give the second-order reactions found.

Kinetics of the Reverse Reactions.—The $Ni(CN)_4^{2-}$ complex is very stable ($\log \beta_4$ = 30.5[2]) compared to the

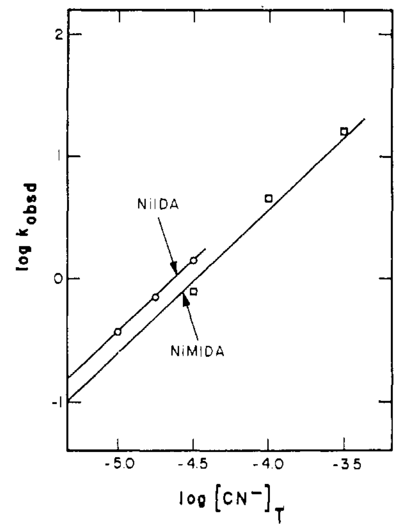

Figure 2.—Cyanide dependence on the observed forward rate constants for the NiIDA and NiMIDA systems. (Solid line calculated from experimentally measured rate constants.)

NiL and NiL_2^{2-} complexes (for IDA[8] log K_1 = 8.26, log β_2 = 14.61 at 30°, μ 0.10; for MIDA[9] log K_1 = 8.73, log β_2 = 15.95 at 20°, μ 0.10). Nevertheless, using very dilute $Ni(CN)_4^{2-}$ solutions and moderately high concentrations of free L^-, it is possible to measure the reverse reaction. The rate of disappearance of $Ni(CN)_4^{2-}$ under these conditions is not a simple kinetic expression although it is obvious from the experiments that the rate depends on $Ni(CN)_4^{2-}$ and on L^{2-} and that it is suppressed by CN^-. An excellent fit to the data is obtained by assuming the rate dependence

$$\frac{-d[Ni(CN)_4^{2-}]}{dt} = \frac{k_r[Ni(CN)_4^{2-}][L^{2-}]}{[CN^-]} \tag{9}$$

The integrated rate expression in terms of the absorbance of $Ni(CN)_4^{2-}$ is given in eq 10 where A_i is the initial absorbance, A is the absorbance at any time, ϵ is the molar absorptivity (at 267 or 285 mμ), l is the cell path (10 cm), and $k'_{obsd} = k_r[L^{2-}]$. Values for k'_{obsd} at

$$(A_i - A) + A_i \ln (A/A_i) = -\frac{\epsilon l}{4}k'_{obsd}t \tag{10}$$

different $[L^{2-}]$ concentrations and for k_r are given in Table VI. The reactions are not fast and were followed for 30–95% completion in time intervals of 10–15 min. The k_r values are 4.7 × 10^{-7} sec^{-1} for IDA and 1.9 × 10^{-7} for MIDA.

Extrapolation of the absorbance to zero time indicates that an intermediate exists in equilibrium with $Ni(CN)_4^{2-}$ prior to the rate-determining step. The intermediate absorbance is small and it is believed to be caused by small concentrations of $Ni(CN)_3L^{3-}$. The proposed reaction mechanism is given in the reverse reactions in eq 4 and 5.

The large excess of L^{2-} used in the reverse reactions rapidly converts any NiL to NiL_2^{2-} and at equilibrium eq 11 should hold. The absorbance at equilibrium,

$$Ni(CN)_4^{2-} + 2L^{2-} \rightleftarrows NiL_2^{2-} + 4CN^- \tag{11}$$

(8) S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, **74**, 5052 (1952).
(9) G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).

TABLE VI
RATE CONSTANTS FOR THE REACTIONS OF IDA AND MIDA WITH $Ni(CN)_4^{2-}$

$[Ni(CN)_4^{2-}]_i$ = 4.72 × 10^{-6} M, 25°, pH 10.9 ± 0.1, μ 0.33		$[Ni(CN)_4^{2-}]_i$ = 9.50 × 10^{-6} M, 25°, pH 10.7 ± 0.1, μ 0.10	
$10^8k'_{obsd}$, M sec^{-1}	10^7k_r, sec^{-1}	$10^{10}k'_{obsd}$, M sec^{-1}	10^7k_r, sec^{-1}
5.46[a]	4.96	18.3[d]	1.75
4.94[a]	4.49	12.8[d]	1.23
5.53[a]	5.03	14.8[d]	1.42
2.52[b]	4.58	4.39[e]	2.10
2.59[b]	4.71	3.70[e]	1.77
2.21[b]	4.02	4.25[e]	2.03
1.29[c]	4.69	2.39[f]	2.28
1.31[c]	4.76	2.45[f]	2.34
1.34[c]	4.88	2.26[f]	2.16
Av	4.7 ± 0.3	Av	1.9 ± 0.4

[a] $[IDA^{2-}]$ = 1.10 × 10^{-1} M. [b] $[IDA^{2-}]$ = 5.50 × 10^{-2} M. [c] $[IDA^{2-}]$ = 2.75 × 10^{-2} M. [d] $[MIDA^{2-}]$ = 1.04 × 10^{-2} M. [e] $[MIDA^{2-}]$ = 2.09 × 10^{-3} M. [f] $[MIDA^{2-}]$ = 1.04 × 10^{-3} M.

A_∞, can be used to calculate the β_2 value for NiL_2^{2-} according to eq 12 which holds when L^{2-} is in large excess (β_4 refers to the $Ni(CN)_4^{2-}$ constant). The

$$\beta_2 = \frac{256(A_i - A_\infty)^5\beta_4}{\epsilon^4l^4A_\infty[L^{2-}]^2} \tag{12}$$

results are log β_2 = 14.9 ± 0.3 for IDA (25°, μ 0.33) and log β_2 = 16.1 ± 0.1 for MIDA (25°, μ 0.10) which are in excellent agreement with the corresponding literature values[8,9] of 14.61 (30°, μ 0.10) and 15.95 (20°, μ 0.10). Therefore, the assumption that any other species must be present in very small concentrations in the reverse reaction is justified.

Discussion

A combination of the reverse reaction and the forward reaction of NiL gives the reaction mechanism in eq 3–5 where $k_r = K_4^{-1}k_{-3}$ and k_{obsd} for the forward reaction is $k_3[CN^-]$. The mass action law requires the observed reactant in the forward reaction to be $NiL(CN)_2^{2-}$ in order to account for all four cyanides. For this to be the case the stability constants for $NiL(CN)_2^{2-}$ must be very large; otherwise at the low cyanide concentrations used NiL could not have been completely converted to $NiL(CN)_2^{2-}$. The equilibrium constants and the ratio of the rate constants give eq 13, where β_4 is the

$$K_1K_2 = \frac{K_4^{-1}k_{-3}\beta_4}{k_3K_{NiL}} \tag{13}$$

constant for $Ni(CN)_4^{2-}$ and K_1K_2 is for $NiL(CN)_2^{2-}$. The K_1K_2 value for $Ni(IDA)(CN)_2^{2-}$ is 1.6 × 10^{11} M^{-2} and for $Ni(MIDA)(CN)_2^{2-}$ it is 2.1 × 10^{10} M^{-2}. These values meet the requirement of essentially complete conversion of any NiL to $NiL(CN)_2^{2-}$ in the forward reaction. The K_1K_2 values are the same order of magnitude as the maximum possible value estimated[2] for $Ni(CN)_2(H_2O)_4$, where K_1K_2 has to be less than 3 × 10^{11} M^{-2}. A negative tridentate ligand normally would greatly reduce the ability of nickel to add negative ligands but this is not the case here and it suggests that there is a change in the nature of the bonding. The presence of IDA^{2-} or $MIDA^{2-}$ around nickel may place the mixed complex in a more stable configuration

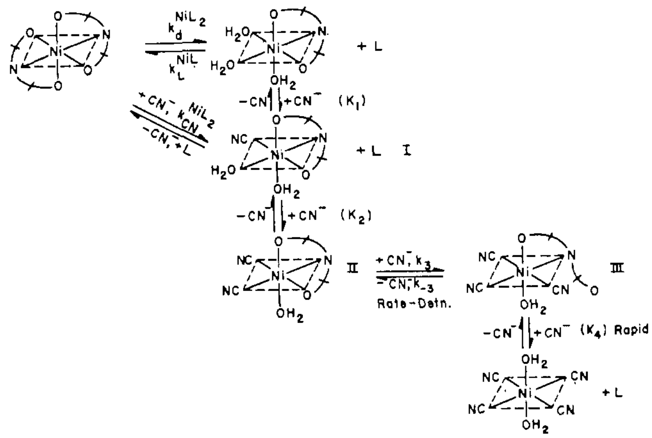

Figure 3.—Proposed mechanism for the reaction of nickel iminodiacetate complexes with cyanide ion.

with greater tetragonal distortion than is the case for octahedral complexes. A tendency for the mixed complex to be of a square-planar nature could explain both the large K_1K_2 stability constants and the relatively large value for k_3 ($= k_{CN}^{NiL(CN)_2}$) for MIDA which is 10,000 times greater than the value of $k_{CN}^{NiL_2}$. Square-planar substitution reactions of $Ni(CN)_4^{2-}$ with a strong nucleophile such as en or even trien are very fast compared to octahedral substitution reactions of strong nucleophiles coordinated to nickel.

The entire reaction mechanism is pictured in Figure 3 where, for the sake of clarity, possible structures are shown. The actual structures are not known for the reaction intermediates or even for $Ni(IDA)_2^{2-}$ where a *trans* (facial) configuration is assumed. This structure has been assigned to the bis-MIDA complexes of Co(III),[10] Ru(III),[11] and Cr(III)[12] and is the predominant species for the bis-IDA complexes of Co(III) and Ru(III) but not for Cr(III). With Pd(II) the *trans* isomer predominates in both cases.[13]

The series of steps diagrammed in Figure 3 agree with the suggested mechanism in which square-planar substitutions permit rapid reactions between structure III and $Ni(CN)_4^{2-}$ and where structure II may react in a similar manner.

TABLE VII

RATE AND EQUILIBRIUM CONSTANTS FOR THE NICKEL IMINODIACETATE SYSTEMS AT 25°

Constant	IDA	MIDA
$k_{CN}^{NiL_2}$, M^{-1} sec^{-1}	$(2.5 \pm 0.7) \times 10^2$	5.3 ± 0.2
k_3, M^{-1} sec^{-1}	$(5.0 \pm 0.2) \times 10^4$	$(5.3 \pm 0.1) \times 10^4$
$K_1K_2k_3$, M^{-3} sec^{-1}	8.13×10^{15}	1.12×10^{15}
$k_d^{NiL_2}$, sec^{-1}	$(4.5 \pm 0.5) \times 10^{-3}$	$(1.5 \pm 0.1) \times 10^{-3}$
k_L^{NiL}, M^{-1} sec^{-1} [a]	1.0×10^4	2.6×10^4
$K_4^{-1}k_{-3}$, sec^{-1}	$(4.7 \pm 0.3) \times 10^{-7}$	$(1.9 \pm 0.4) \times 10^{-7}$
K_1K_2, M^{-2}	1.6×10^{11}	2.1×10^{10}
Log K_{NiL}	8.26 (30°)[b]	8.73 (20°)[c]
Log $\beta_2^{NiL_2}$	14.61 (30°)[b]	15.95 (20°)[c]

[a] Calculated from $k_d^{NiL_2}$ and $K_2^{NiL_2}$. [b] Reference 8. [c] Reference 9.

IDA complex in all cases with one important exception. In the CN^- attack on NiL_2^{2-} the N-methyl group slows the reaction by a factor of 47 while the k_d values are slower by a factor of only 3. The methyl group somehow hinders the cyanide substitution of the tridentate ligand in a manner different from the H_2O substitution reaction.

The steps presented in Figure 3 show how a reaction mechanism could proceed with three cyanides in the rate-determining step but it does not indicate why four cyanides are used with aquonickel ion and nickel–trien and only three in this case. Seven other aminocarboxylate complexes of nickel have the same dependence on three cyanide ions[14] and this dependence also is found for $CoEDTA^{2-}$ and $CoCyDTA^{2-}$.[15,16] Therefore, this is not an isolated phenomenon. Several reasons for the different behavior in regard to the number of cyanides needed in the rate-determining step can be suggested. First, charge repulsion between intermediates such as $NiL(CN)_3^{3-}$ and another CN^- may prevent the fourth cyanide from being effective. Second, the presence of a strong nitrogen donor group can assist in converting nickel to a square-planar configuration. Therefore, the amine group in IDA and MIDA may serve in place of a fourth cyanide in the critical kinetic step. This would account for the behavior compared to aquonickel but not for polyamines. However, third, the behavior of trien and en with $Ni(CN)_4^{2-}$ suggests that chelation

TABLE VIII

FORMATION AND DISSOCIATION RATE CONSTANTS FOR NICKEL(II) COMPLEXES AT 25°

L	k_L^{Ni}	k_d^{NiL}	k_L^{NiL}	$k_d^{NiL_2}$	$k_{NH_3}^{NiL}$
NH_3	4.0×10^3 [a]	4.0,[a] 5.8[c]	2.6×10^4 [a,d]	3.3×10^2	2.6×10^4 [a,d]
gly^-	1.5×10^4 [e]	2.4×10^{-2} [e]	6.0×10^4 [e]	0.95[e]	1.4×10^4 [b]
IDA^{2-}	4.5×10^4 [f]	2.8×10^{-4} [f]	1.0×10^4 [g]	4.5×10^{-3} [g]	2.5×10^3 [b]
NTA^{3-}	4.8×10^5 [h,i]	3.5×10^{-6} [h,i]	...	...	4.6×10^3 [b]

[a] D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966); μ 0.10. [b] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1088 (1967); μ 0.25. [c] G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 4208 (1962); μ 0.20. [d] S. Marks, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **7**, 836 (1968); μ 0.20. [e] G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962); μ 0.15. [f] T. J. Bydalek and A. H. Constant, *Inorg. Chem.*, **4**, 833 (1965); μ 1.25 (k_L^{Ni}); μ 0.10 (k_d^{NiL}). [g] This work; μ 0.10. [h] T. J. Bydalek and M. L. Blomster, *ibid.*, **3**, 667 (1964); μ 1.25. [i] N. Tanaka and M. Kimura, *Bull. Chem. Soc. Jap.*, **40**, 2100 (1967); μ 1.25.

Table VII summarizes the equilibrium and rate constants. The MIDA complex acts very much like the of two amine nitrogens may help to keep four cyanides present around nickel in the rate-determining step. This has been discussed previously.[3]

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Table VIII compares the formation and dissociation rate constants of ammonia and some aminocarboxylates with nickel(II). A second glycine coordinates faster than the first but a second IDA is slower to coordinate than the first. The difference in electrostatic attraction accounts in part for this behavior but there also is a difference in lability of some of the coordinated water. Thus, the ammonia substitution for water is faster with $NiNH_3(H_2O)_5^{2+}$ than it is for $Ni(gly)(H_2O)_4^+$ than it is for $NiIDA(H_2O)_3^0$. The increased value of $k_d^{NiL_2}$ compared to k_d^{NiL} may also be largely an electrostatic effect.

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CONTRIBUTION FROM THE COLORADO STATE UNIVERSITY, FORT COLLINS, COLORADO 80521

The Kinetics of the Oxidation of Tin(II) by Vanadium(V) in Aqueous Perchlorate Solutions

BY B. SCHIEFELBEIN AND N. A. DAUGHERTY[1]

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In perchlorate solutions Sn(II) and V(V) react to produce Sn(IV) and V(IV). The rate of the reaction is given by: $-d[V(V)]/dt = k_3'[Sn(II)][V(V)]^2 + k_2'[Sn(III)][V(V)]$ where $k_2' = k_{21}[H^+]$ and $k_3' = k_{30} + k_{31}[H^+]$ or $k_{30}e^{\beta[H^+]}$. The activation parameters associated with k_{21} and k_{30} are: $\Delta H^* = 6.0 \pm 0.2$ kcal/mol, $\Delta S^* = 39.2 \pm 0.8$ cal/mol deg, $\Delta H^* = 3.9 \pm 0.3$ kcal/mol, $\Delta S^* = -29.5 \pm 1.1$ cal/mol deg. Some plausible mechanisms for the reaction are considered.

Introduction

Because the oxidation of Sn(II) may involve either a single, two-electron step or successive one-electron steps, the oxidation of Sn(II) is of mechanistic interest. In order to prevent the formation of colloidal stannic oxide, hydrochloric and sulfuric acids have been used[2-5] as solvents in previous studies. The use of these complexing solvents makes difficult unambiguous interpretation of the results. The problem of complex formation can be avoided by the use of perchlorate solutions. We have found[6] that the formation of stannic oxide is slow compared to the rate of oxidation of Sn(II) and that rate studies can be carried out in perchloric acid.

In hydrochloric acid the reaction between excess Sn(II) and V(V) produces both V(III) and V(IV) and the rate is reported[7] to be too fast to measure by conventional techniques. In contrast, the reaction in perchloric acid is slow and V(IV) is the only vanadium product.

Experimental Section

Materials.—Tin(II) perchlorate was prepared by the reaction of excess tin metal with copper(II) perchlorate dissolved in perchloric acid under conditions which allowed the isolation and recrystallization of the Sn(II) compound. In a typical preparation 12 g of tin was allowed to react overnight with *ca.* 14 g of the hydrated copper salt dissolved in 32 ml of 9 *M* $HClO_4$. The reaction mixture was then filtered through a glass frit and 50 ml of concentrated $HClO_4$ was added to the filtrate. Cooling the acid solution in an ice–salt bath yielded *ca.* 8 g of crystalline product. The crystals were recrystallized from 25 ml of warm, 65°, concentrated $HClO_4$. Apparently the reaction conditions are critical. Shortly after combining the reactants, in a preparation in which the quantities of reactants were doubled, the reaction mixture began to evolve fumes and became sufficiently hot to char the laboratory bench. All preparations of tin(II) perchlorate should be carried out with adequate safety precautions.

Stock solutions of tin(II) perchlorate were prepared by dissolving the solid in concentrated $HClO_4$ and diluting to an appropriate volume with water. All operations involving Sn(II) were carried out in an argon atmosphere.

Vanadium(V) perchlorate solutions were prepared by dissolving vanadium pentoxide in perchloric acid. The oxide was prepared by ignition of ammonium metavanadate at 400°.

Potassium trioxalatocobalt(III) was prepared according to published[8] methods.

Lithium and sodium perchlorates were prepared by neutralizing the metal carbonate with perchloric acid. The salt was recrystallized twice from water.

Analyses.—The Sn(II) content of the tin(II) perchlorate solutions was determined by treating an aliquot of the solution with a known excess of cerium(IV) sulfate and back-titration of the excess Ce(IV) with Fe(II) after the Sn(II)–Ce(IV) reaction was complete. The acid concentration of the Sn(II) solutions was calculated from a knowledge of the Sn(II) concentration and the total perchlorate concentration determined by passage of an aliquot through a cation-exchange resin and titration of the hydrogen ion in the eluent.

Vanadium(V) was determined by titration with Fe(II) in 6 *M* sulfuric acid.[9] The acid concentration of the vanadium(V) solutions was taken as the difference between the amount of acid initially added and the amount consumed by the reaction of vanadium pentoxide and perchloric acid.

(1) To whom correspondence should be addressed.

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