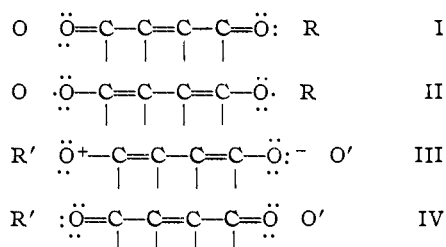


agent to the acceptor center. But in every case, the mechanism by remote attack competes against adjacent attack, so that ligands which have a small though definite capacity for electron conduction are not recognized and, in any case, the relative rates at which reaction by remote attack takes place, even when corrected for the different degrees of electrostatic repulsion in the activated complex, do not provide a measure of the relative conductances of the ligands in the usual sense (as for example when the conductances of metals are compared). The electron transport is presumably very rapid, and the different groups differ in the facility with which they adopt a configuration appropriate to the conduction process.

The mechanism of conduction by the conjugated systems is itself a matter of some general interest. It can be represented formally by the succession of changes



State III is arrived at when the conjugated system gains an electron from the reducing agent and loses one to the oxidizing agents. If state II is written

with opposed spins, all the states represented are resonance forms of the ground state. The representation presumably corresponds to the "double exchange" mechanism discussed by Halpern and Orgel.<sup>9</sup> These authors have outlined the features of the different mechanisms which can be considered, including in addition to that already mentioned, the super-exchange mechanism and the ordinary chemical mechanism involving net loss of an electron to the oxidizing center as the first step, or net gain of an electron from reducing agent as the first step. The second two may be distinguishable from the first two because of the chemical consequences of forming radical ions from the bridging ligand. But it is not clear how the first two can be distinguished from each other unless the conductance of the groups is actually measured and related to the properties of the bridging group, the properties of interest including the energy required to generate the excited states. If as we surmise a binuclear intermediate is in fact formed, none of the descriptions offered may be particularly apt, since then the important consideration is not how the electron gets from the donor to the acceptor center but, rather, the energy levels of the intermediate and how they are populated.

**Acknowledgment.**—This work was supported by the Atomic Energy Commission under Contract AT(11-1)-378.

(9) J. Halpern and L. E. Orgel, *Disc. Farada Soc.*, in press (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

## Kinetics of Nickel(II) Ligand Exchange Reactions: Cyanide Ion and (Ethylenedinitrilo)-tetraacetate Ion

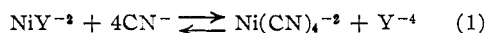
BY D. W. MARGERUM, T. J. BYDALEK AND JOHN J. BISHOP

RECEIVED NOVEMBER 9, 1960

Nickel(II) forms mixed complexes with cyanide and (ethylenedinitrilo)-tetraacetate ions. The transition between the octahedral, paramagnetic EDTA complex and the planar, diamagnetic cyanide complex is kinetically controlled by the presence of three cyanide ions around nickel. This study indicates that it is not necessary to postulate a direct bimolecular exchange between  $\text{Ni}(\text{CN})_4^{-2}$  and nickel complexes such as previously reported.

### Introduction

In this work the formation and dissociation kinetics of the tetracyanonickelate ion are studied in the presence of the EDTA anion ( $\text{Y}^{-4}$ ). The reaction



involves both the displacement of a multidentate ligand by monodentate ligands and the transition from an octahedral, paramagnetic complex to a planar, diamagnetic complex. This work indicates that this transition is kinetically controlled by the presence of cyanide ions about nickel.

As a result of radiocyanide exchange experiments the  $\text{Ni}(\text{CN})_4^{-2}$  complex has been considered labile.<sup>1,2</sup> However, there is a slow exchange of radionickel between  $\text{Ni}(\text{CN})_4^{-2}$  and the nickel

complexes of ethylenediamine, oxalate, tartrate<sup>3</sup> and several amino acids.<sup>4</sup> The sluggishness of these systems must be attributed in part to the cyanide complex since the other complexes are labile. Thus, rapid exchange is observed with  $\text{Ni}(\text{en})_3^{+2}$  and  $\text{Ni}^{+2}$  and with  $\text{Ni}(\text{en})_3^{+2}$  and  $\text{en}^{6,6}$ . In addition, the nickel(II) complexes of oxalate and tartrate are considered labile.<sup>7</sup> Although the exchange of radiocyanide with  $\text{Ni}(\text{CN})_4^{-2}$  has been too rapid to measure the exchange of radionickel with this complex is not appreciable within one minute at pH 4 to 8. The precipitation of  $\text{Ni}(\text{CN})_2$  prevents a more detailed study.<sup>8</sup> Since the formation rate of  $\text{Ni}(\text{CN})_4^{-2}$  from  $\text{Ni}^{+2}$  and  $\text{CN}^-$  is very rapid, some dissociation step of  $\text{CN}^-$  from a

(1) A. W. Adamson, J. P. Welker and M. Volpe, *J. Am. Chem. Soc.*, **72**, 4030 (1950).

(2) A. G. MacDiarmid and N. F. Hall, *ibid.*, **76**, 4222 (1954).

(3) F. A. Long, *ibid.*, **73**, 537 (1951).

(4) R. C. Calkins and N. F. Hall, *ibid.*, **80**, 5028 (1958).

(5) J. E. Johnson and N. F. Hall, *ibid.*, **70**, 2344 (1948).

(6) D. S. Popplewell and R. G. Wilkins, *J. Chem. Soc.*, 4098 (1955).

(7) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

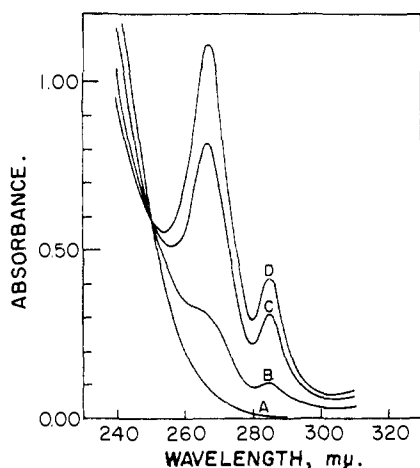
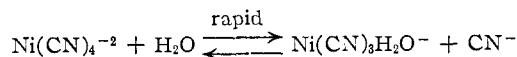


Fig. 1.—Ultraviolet spectra of the reaction of  $\text{NiY}^{-2}$  and  $\text{CN}^-$ ,  $[\text{NiY}_T] = 5.22 \times 10^{-5} M$ ,  $[\text{CN}^-] = 4.30 \times 10^{-3} M$  and  $[\text{OH}^-] = 1.10 \times 10^{-3} M$ . 10 cm. cell length and 1  $m\mu$ /sec. scanning speed: A, pure  $\text{NiY}^{-2}$ ; B, 2:0 min. after mixing; C, 26:0 min. after mixing; D, 42:0 min. after mixing. Times given are for start of scan at 310  $m\mu$ .

nickel cyanide complex must be slow. MacDiarmid and Hall<sup>2</sup> propose an aquation displacement mechanism rather than a cyanide addition mechanism in the radiocyanide exchange



If this is correct, then  $\text{Ni}(\text{CN})_3(\text{H}_2\text{O})^-$  or  $\text{Ni}(\text{CN})_2(\text{H}_2\text{O})_x$  must be sluggish in the release of cyanide ion.

The  $\text{NiY}^{-2}$  complex is very slow in its exchange with radionickel in neutral or slightly basic solutions.<sup>8</sup> The rate of dissociation of EDTA from nickel has been measured below pH 5 by exchange reactions<sup>9</sup> and by acid dissociation.<sup>10</sup> In addition the sluggish nature of  $\text{NiY}^{-2}$  is known at pH 10–11, where this is used to advantage in EDTA titrations.<sup>11</sup>

The somewhat labile nature of  $\text{Ni}(\text{CN})_4^{-2}$  and the definitely sluggish nature of  $\text{NiY}^{-2}$  might suggest that any slowness in (1) is entirely due to the EDTA coordination, but actually the cyanide coordination is equally important.

### Experimental

A Beckman Model DU spectrophotometer with a thermostated cell compartment ( $\pm 0.1^\circ$ ) was used for all rate data. Spectra were obtained with a Cary Model 14. The hydroxide ion concentration used in all calculations was corrected for cyanide hydrolysis.

Nickel chloride solutions were standardized with EDTA using  $\text{MgCl}_2$  back titrations. Reagent grade EDTA was recrystallized twice from water before use. Sodium cyanide solutions were standardized with nickel and EDTA. Sodium chloride was used to adjust the solutions to constant ionic strength. Stock solutions of  $\text{Ni}(\text{CN})_4^{-2}$  were prepared using a slight excess of NaCN and similarly  $\text{NiY}^{-2}$  solutions were used with a slight excess of EDTA. All solutions were kept  $\text{CO}_2$  free to prevent spectrophotometric interference from

(8) F. A. Long, S. S. Jones and M. Burke, *Brookhaven Conf. Rept.*, BNL-C-8, Chem. Conf. No. 2, 106 (1948).

(9) C. M. Cook, Jr. and F. A. Long, *J. Am. Chem. Soc.*, **80**, 33 (1958).

(10) D. W. Margerum, *J. Phys. Chem.*, **63**, 336 (1959).

(11) G. Schwarzenbach, "Complexometric Titrations," Interscience Publishers, Inc., New York, N. Y., 1957.

the carbonate ion. All rate constants reported are averages of two or more runs with a maximum deviation of 2%.

Figure 1 shows the  $\text{NiY}^{-2}$  spectrum and the changing spectra as  $\text{Ni}(\text{CN})_4^{-2}$  is formed in a typical rate. Reactions were followed at 285  $m\mu$  where  $\text{Y}^{-4}$  and  $\text{NiY}^{-2}$  exhibit a small absorbance compared to  $\text{Ni}(\text{CN})_4^{-2}$ . Under the conditions of the forward reaction in (1), the  $\text{NiY}^{-2}$ ,  $\text{CN}^-$ , and  $\text{Y}^{-4}$  absorbances are negligible, while for the reverse reaction the  $\text{Y}^{-4}$  must be present in a large excess and therefore has a constant absorbance. However, in both the forward and reverse reactions other absorbance terms occurred because of the formation of intermediate complexes which were in equilibrium with the reactants. Thus, for the forward reaction the observed absorbance  $A$  is the sum of the absorbance of the tetracyanonickelate,  $A_{\text{Ni}(\text{CN})_4}$ , and the absorbance of other species such as  $\text{NiYCN}^{-3}$ . The expression

$$[\text{Ni}(\text{CN})_4^{-2}] = \frac{A - A_i}{b(\epsilon_{\text{Ni}(\text{CN})_4} - \epsilon_i)} \quad (2)$$

can be derived where  $A_i (= \epsilon_i b \text{Ni}_T)$  is the initial absorbance of the reactants at zero time. Its value is dependent on the extent of  $\text{NiYCN}^{-3}$  and  $\text{NiY}(\text{CN})_2^{-4}$  formation. The molar absorptivity of  $\text{Ni}(\text{CN})_4^{-2}$ ,  $\epsilon_{\text{Ni}(\text{CN})_4}$ , is 4630, while the molar absorptivity of the reaction mixture,  $\epsilon_i$ , varies from 30 to 120. The cell length,  $b$ , was 10 cm. in most runs. Equation 2 is applicable because the intermediate complexes form instantly and are in a constant equilibrium ratio with the reactants. This is also evident in Fig. 1 where an isosbestic point verifies the transition from one set of reactants in equilibrium to a set of products in equilibrium. Equation 2 holds only when the cyanide ion concentration is constant during a run. This condition was met by using excess cyanide ion or by following only the first few per cent. of the reaction. The forward rates gave excellent linear plots of  $\log [\text{NiY}_T]$  versus time, where  $[\text{NiY}_T] = \text{Ni}_T - [\text{Ni}(\text{CN})_4^{-2}]$ , and  $\text{NiY}_T$  is the sum of all  $\text{NiY}^{-2}$ ,  $\text{NiYCN}^{-3}$ , etc. complexes prior to the rate step.

### Results

**Mixed Complexes of  $\text{NiY}^{-2}$  and  $\text{CN}^-$ .**—An instantaneous absorbance increase not due to  $\text{Ni}(\text{CN})_4^{-2}$  is observed when cyanide ion is added to  $\text{NiY}^{-2}$ , indicating the presence of a mixed complex. Kinetic and equilibrium data indicate a 1:1 complex between  $\text{NiY}^{-2}$  and  $\text{CN}^-$ , presumably  $\text{NiYCN}^{-3}$ . The stability of this complex was determined spectrophotometrically at 275  $m\mu$ , at  $\mu = 1.01$  and 0.11. The  $\epsilon_{\text{NiYCN}}$  was measured by differential methods immediately after mixing a large excess of  $\text{NiY}^{-2}$  with  $\text{CN}^-$  so that the formation of  $\text{Ni}(\text{CN})_4^{-2}$  was negligible. The concentration of  $\text{NiYCN}^{-3}$  was calculated from

$$[\text{NiYCN}^{-3}] = \frac{A - A_{\text{NiY}}}{b(\epsilon_{\text{NiYCN}} - \epsilon_{\text{NiY}})}$$

where  $A$  is the observed absorbance and  $A_{\text{NiY}}$  is the absorbance the  $\text{NiY}^{-2}$  would have if it did not react with  $\text{CN}^-$ . The molar absorptivities at 275  $m\mu$  are  $\epsilon_{\text{NiYCN}} = 108$  and  $\epsilon_{\text{NiY}} = 5.7$ . The concentrations of  $\text{NiY}^{-2}$  and  $\text{CN}^-$  were found by difference and the  $K_{\text{NiYCN}}$  values are given in Table I where

$$K_{\text{NiYCN}} = \frac{[\text{NiY}^{-2}][\text{CN}^-]}{[\text{NiYCN}^{-3}]}$$

At  $\mu = 1.0$  and high concentrations of cyanide ion a second complex forms with a much higher absorbance at 285  $m\mu$ . This complex is believed to be  $\text{NiY}(\text{CN})_2^{-4}$  which is also postulated as a kinetic intermediate at lower concentrations of cyanide ion.

**Kinetics of the Forward Reaction.**—Because of the stability of the mixed complex, the actual reaction observed following the addition of excess

TABLE I

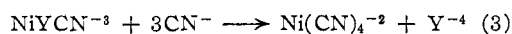
DETERMINATION OF  $K_{\text{NiYCN}}$   
 $\text{NiY}_T = 6.79 \times 10^{-4}$ , 10 cm. cell, 25.0°  
 $\mu = 0.11$ ,  $[\text{OH}^-] = 1.10 \times 10^{-3}$

[CN <sup>-</sup> ]	[NiYCN]	$K_{\text{NiYCN}}$
$1.11 \times 10^{-4}$	$0.822 \times 10^{-4}$	$2.65 \times 10^{-4}$
$2.79 \times 10^{-4}$	$2.04 \times 10^{-4}$	$2.70 \times 10^{-4}$
$3.35 \times 10^{-4}$	$2.44 \times 10^{-4}$	$2.59 \times 10^{-4}$
$4.46 \times 10^{-4}$	$3.16 \times 10^{-4}$	$2.60 \times 10^{-4}$
$5.58 \times 10^{-4}$	$3.89 \times 10^{-4}$	$2.41 \times 10^{-4}$
$6.14 \times 10^{-4}$	$4.05 \times 10^{-4}$	$2.79 \times 10^{-4}$
$6.70 \times 10^{-4}$	$4.34 \times 10^{-4}$	$2.77 \times 10^{-4}$
Av. = $2.6(\pm 0.2) \times 10^{-4}$		

$\mu = 1.01$ ,  $[\text{OH}^-] = 2.90 \times 10^{-3}$

[CN <sup>-</sup> ]	[NiYCN]	$K_{\text{NiYCN}}$
$1.71 \times 10^{-4}$	$1.36 \times 10^{-4}$	$1.40 \times 10^{-4}$
$2.57 \times 10^{-4}$	$1.97 \times 10^{-4}$	$1.47 \times 10^{-4}$
$4.28 \times 10^{-4}$	$2.92 \times 10^{-4}$	$1.80 \times 10^{-4}$
$5.14 \times 10^{-4}$	$3.47 \times 10^{-4}$	$1.60 \times 10^{-4}$
$8.56 \times 10^{-4}$	$4.55 \times 10^{-4}$	$1.95 \times 10^{-4}$
Av. = $1.7(\pm 0.3) \times 10^{-4}$		

cyanide is



Reaction 3 is first order in the concentration of  $\text{NiYCN}^{-3}$ . Plots of  $\log [\text{NiY}_T]$  against time are linear over at least 70% completion. At a constant excess cyanide ion concentration, different initial concentrations of  $\text{NiY}^{-2}$  give the same slope. Reaction 3 is also second order in cyanide ion concentration (corrected for hydrolysis and for the formation of  $\text{NiYCN}^{-3}$ ) over a range of cyanide concentration from  $5 \times 10^{-4}$  to  $2 \times 10^{-2}$  molar. The value used for the ionization constant of hydrocyanic acid was  $4.5 \times 10^{-10}$  which is in agreement with reported values.<sup>12,13</sup> Since this is a concentration constant, the calculation of the cyanide ion concentration is based on the measured quantity of sodium hydroxide used.

$$\frac{d[\text{Ni}(\text{CN})_4^{-2}]}{dt} = k_0[\text{NiY}_T] = k_f[\text{NiYCN}^{-3}][\text{CN}^-]^2 \quad (4)$$

Table II indicates this dependence at two different ionic strengths. The slight but steady decrease in the value of  $k_f$  at  $\mu = 1.01$  is associated

TABLE II

FORMATION RATE CONSTANT  
 $\mu = 0.11$   $[\text{Ni}_T] = 5.22 \times 10^{-5}$   $[\text{OH}^-] = 1.10 \times 10^{-3}$

[CN <sup>-</sup> ]	[CN <sup>-</sup> ]corr.	$k_0$ (min. <sup>-1</sup> )	$k_f = \frac{k_0}{[\text{CN}^-]^2_{\text{corr}}}$ (min. <sup>-1</sup> l. <sup>2</sup> moles <sup>-2</sup> )
$2.14 \times 10^{-3}$	$2.06 \times 10^{-3}$	$0.995 \times 10^{-3}$	$2.35 \times 10^{+2}$
$4.28 \times 10^{-3}$	$4.14 \times 10^{-3}$	$4.10 \times 10^{-3}$	$2.39 \times 10^{+2}$
$4.30 \times 10^{-3}$	$4.16 \times 10^{-3}$	$4.45 \times 10^{-3}$	$2.56 \times 10^{+2}$
$21.5 \times 10^{-3}$	$21.1 \times 10^{-3}$	$108 \times 10^{-3}$	$2.42 \times 10^{+2}$

$\mu = 0.11$   $[\text{Ni}_T] = 9.77 \times 10^{-5}$   $[\text{OH}^-] = 1.00 \times 10^{-3}$

[CN <sup>-</sup> ]	[CN <sup>-</sup> ]corr.	$k_0$ (min. <sup>-1</sup> )	$k_f$ (min. <sup>-1</sup> l. <sup>2</sup> moles <sup>-2</sup> )
$0.59 \times 10^{-3}$	$0.52 \times 10^{-3}$	$0.066 \times 10^{-3}$	$2.44 \times 10^{+2}$
$1.48 \times 10^{-3}$	$1.37 \times 10^{-3}$	$0.489 \times 10^{-3}$	$2.58 \times 10^{+2}$
$7.40 \times 10^{-3}$	$7.16 \times 10^{-3}$	$12.1 \times 10^{-3}$	$2.36 \times 10^{+2}$
$14.8 \times 10^{-3}$	$14.3 \times 10^{-3}$	$46.9 \times 10^{-3}$	$2.30 \times 10^{+2}$

$\mu = 1.01$   $[\text{Ni}_T] = 5.22 \times 10^{-5}$   $[\text{OH}^-] = 2.90 \times 10^{-3}$

[CN <sup>-</sup> ]	[CN <sup>-</sup> ]corr.	$k_0$ (min. <sup>-1</sup> )	$k_f$ (min. <sup>-1</sup> l. <sup>2</sup> moles <sup>-2</sup> )
$1.72 \times 10^{-3}$	$1.66 \times 10^{-3}$	$5.27 \times 10^{-3}$	$1.91 \times 10^{+3}$
$2.58 \times 10^{-3}$	$2.51 \times 10^{-3}$	$11.6 \times 10^{-3}$	$1.82 \times 10^{+3}$
$4.30 \times 10^{-3}$	$4.22 \times 10^{-3}$	$31.8 \times 10^{-3}$	$1.79 \times 10^{+3}$
$8.60 \times 10^{-3}$	$8.48 \times 10^{-3}$	$123 \times 10^{-3}$	$1.72 \times 10^{+3}$

(12) H. T. Britton and R. A. Robinson, *J. Chem. Soc.*, 458 (1931).

(13) H. T. Britton and R. A. Robinson, *ibid.*, 2332 (1931).

with the observation of an increased  $\epsilon_f$  and can be attributed to the fact that a small part of the reaction is proceeding by a first order dependence on cyanide ion concentration due to the formation of  $\text{NiY}(\text{CN})_2^{-4}$ .

Table III indicates the expected effect of decreased hydroxide ion concentration causing the value of  $k_0$  to decrease because of cyanide ion hydrolysis. With the correction for hydrolysis the value of  $k_f$  varies only slightly with the hydroxide ion concentration. The concentration of hydroxide ion is again calculated from the sodium hydroxide added with corrections made for hydrolysis of cyanide.

TABLE III

EFFECT OF HYDROXIDE ION  
 $[\text{Ni}_T] = 5.22 \times 10^{-5}$ ,  $[\text{CN}_T] = 4.30 \times 10^{-3}$ , 25.0°

$[\text{OH}^-]$	$[\text{CN}^-]_{\text{corr.}}$	$k_0$	$k_f$
$\mu = 0.11$			
$2.96 \times 10^{-4}$	$3.95 \times 10^{-3}$	$3.98 \times 10^{-3}$	$2.55 \times 10^2$
$4.32 \times 10^{-4}$	$4.04 \times 10^{-3}$	$4.24 \times 10^{-3}$	$2.59 \times 10^2$
$1.06 \times 10^{-3}$	$4.16 \times 10^{-3}$	$4.45 \times 10^{-3}$	$2.56 \times 10^2$
$1.12 \times 10^{-2}$	$4.25 \times 10^{-3}$	$4.74 \times 10^{-3}$	$2.62 \times 10^2$
$\mu = 1.01$			
$2.96 \times 10^{-4}$	$3.95 \times 10^{-3}$	$2.67 \times 10^{-2}$	$1.71 \times 10^3$
$5.12 \times 10^{-4}$	$4.07 \times 10^{-3}$	$2.90 \times 10^{-2}$	$1.75 \times 10^3$
$1.20 \times 10^{-3}$	$4.17 \times 10^{-3}$	$3.03 \times 10^{-2}$	$1.70 \times 10^3$
$2.85 \times 10^{-3}$	$4.22 \times 10^{-3}$	$3.18 \times 10^{-2}$	$1.78 \times 10^3$
$1.12 \times 10^{-2}$	$4.24 \times 10^{-3}$	$3.22 \times 10^{-2}$	$1.79 \times 10^3$
$2.24 \times 10^{-2}$	$4.25 \times 10^{-3}$	$3.29 \times 10^{-2}$	$1.82 \times 10^3$
$4.48 \times 10^{-2}$	$4.25 \times 10^{-3}$	$3.21 \times 10^{-2}$	$1.73 \times 10^3$
$5.60 \times 10^{-2}$	$4.25 \times 10^{-3}$	$3.02 \times 10^{-2}$	$1.67 \times 10^3$
$1.19 \times 10^{-1}$	$4.25 \times 10^{-3}$	$2.91 \times 10^{-2}$	$1.61 \times 10^3$

The reaction rate increases greatly with increased ionic strength as seen in Table IV.

TABLE IV

IONIC STRENGTH EFFECT  
 $[\text{Ni}_T] = 5.22 \times 10^{-5}$ ,  $[\text{CN}_T] = 4.30 \times 10^{-3}$ , pH 11.0, 25.0°

$\mu$	Av. $k_f$
0.003	$2.47 \times 10^1$
0.11	$2.56 \times 10^2$
1.01	$1.79 \times 10^3$

The temperature dependence given in Table V follows the Arrhenius expression and gives an  $E_a$  value of 5.94 kcal./mole at  $\mu = 0.11$ . The values for  $\Delta H^*$  and  $\Delta S^*$  are 5.35 kcal./mole and -37.8 e.u., respectively.

TABLE V

TEMPERATURE DEPENDENCE  
 $[\text{Ni}_T] = 5.22 \times 10^{-5}$ ,  $[\text{CN}_T] = 2.15 \times 10^{-2}$ , pH 11.0,  $\mu = 0.11$

Temp., °C.	$k_f$
10.3	$1.38 \times 10^2$
25.0	$2.42 \times 10^2$
40.0	$3.79 \times 10^2$

*Kinetics of Reverse Reaction.*—The dissociation of  $\text{Ni}(\text{CN})_4^{-2}$  in the presence of a large excess of  $\text{Y}^{-4}$  was run under conditions where the amount of  $\text{NiYCN}^{-3}$  formation was negligible, so that the reverse of reaction 1 was observed. Once again the absorbance of the reactants extrapolated to zero time indicates an intermediate in equilibrium with  $\text{Ni}(\text{CN})_4^{-2}$  prior to the rate determining step.

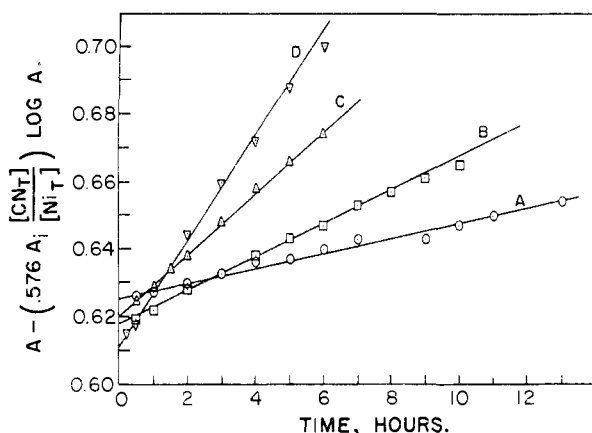


Fig. 2.—Plot of  $A - \left[0.576 A_i \times \frac{[\text{CN}_T]}{[\text{Ni}_T]}\right] \log A$  vs. time;  $[\text{Ni}_T] = 4.93 \times 10^{-6}$ ,  $[\text{CN}_T] = 2.03 \times 10^{-6}$  and  $\mu = 1.01$ ,  $25.0^\circ$ .

$[\text{Y}^{-4}]/[\text{CN}_T]$	
A—	500
B—	1000
C—	2000
D—	3000

This is found only at relatively high  $[\text{Y}^{-4}]$  and can be attributed to a small concentration of another mixed complex such as  $\text{Ni}(\text{CN})_3\text{Y}^{-5}$ . This is apparently not a very stable complex. Figure 2 indicates the fit of an unusual kinetic expression

$$A - \left(0.576 A_i \times \frac{[\text{CN}_T]}{[\text{Ni}_T]}\right) \log A = \left(\frac{A_i k K_4 [\text{Y}]}{4 [\text{Ni}_T]}\right) t + A_i - \left(0.576 A_i \times \frac{[\text{CN}_T]}{[\text{Ni}_T]}\right) \log A_i \quad (5)$$

which can be derived from a first order dependence on the concentration of  $\text{Ni}(\text{CN})_4^{-2}$  and  $\text{Y}^{-4}$  and inverse first order dependence on the concentration of  $\text{CN}^-$  assuming negligible amounts of the mixed complex. The term  $K_4$  is the instability constant for the loss of one cyanide from  $\text{Ni}(\text{CN})_4^{-2}$ . The average value of  $kK_4$  was  $1.3 \times 10^{-6} \text{ min.}^{-1}$ .

**Stability of  $\text{Ni}(\text{CN})_4^{-2}$ .**—The instability constant of  $\text{Ni}(\text{CN})_4^{-2}$  calculated from the kinetics and the equilibrium constants of  $\text{NiY}^{-2}$  and  $\text{NiYCN}^{-3}$  gives a value of  $3.0 \times 10^{-32}$  at an ionic strength of 1.01 which is in agreement with the recently reported stability of this complex.<sup>14</sup>

#### Discussion

Cyanide ion converts  $\text{NiY}^{-2}$  to  $\text{Ni}(\text{CN})_4^{-2}$  at a much greater rate than the aqueous dissociation rate of the EDTA complex. This would be the anticipated result of cyanide ion additions to  $\text{NiY}^{-2}$  causing an increase in the concentration of the partially bonded EDTA complexes. However, if cyanide ion only caused the acceleration of the EDTA dissociation, then rate terms similar to those observed in the acid dissociation would be expected (i.e.  $k[\text{HNiY}^{-1}] + k'[\text{H}^+][\text{HNiY}^{-1}] + k''[\text{H}^+]^2[\text{HNiY}^{-1}] + k'''[\text{H}^+]^3[\text{HNiY}^{-1}]$ ). Instead, over a wide range of cyanide ion concentration the only rate term involves three cyanide ions (i.e.  $k_f[\text{NiYCN}^{-3}][\text{CN}^-]^2$ ). Furthermore, the

(14) H. Freund and C. R. Schneider, *J. Am. Chem. Soc.*, **81**, 4780 (1959).

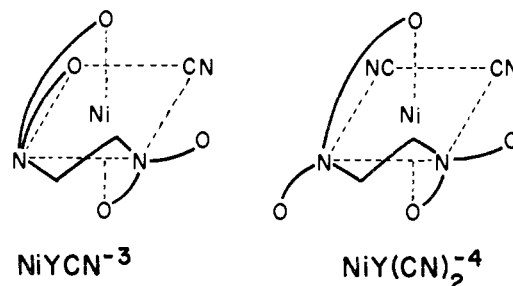
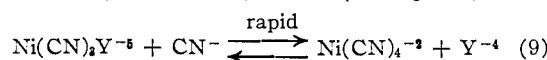
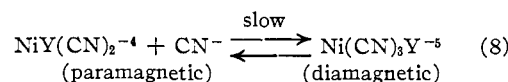
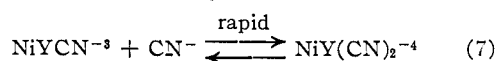
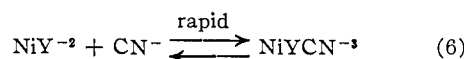


Fig. 3.—Proposed structures of cyanide intermediates.

absorbance jump at zero time in the reverse reaction indicates that  $\text{Y}^{-4}$  can establish a rapid equilibrium with  $\text{Ni}(\text{CN})_4^{-2}$  prior to the rate determining step where the complex changes from the diamagnetic cyanide type to the paramagnetic EDTA type. Therefore, the positioning of three cyanide ions around nickel(II) appears to be the true rate controlling factor and not just the unfolding of the EDTA chelate. The proposed mechanism is



The rate expression used for the reverse reaction in equation 5 was derived from this mechanism assuming the concentration of  $\text{Ni}(\text{CN})_3\text{Y}^{-5}$  to be small compared to the concentration of  $\text{Ni}(\text{CN})_4^{-2}$ . The evidence for the mixed complexes shown in equations 6 to 9 has already been discussed. The magnetic character of the intermediates has not been measured but the assignment agrees with their general spectral character. The assignment of  $-3$ ,  $-4$  and  $-5$  charges to these complexes is an arbitrary one and the possibility does exist that such highly charged complexes could add protons. However, there is no appreciable kinetic pH effect.

The X-ray study of  $\text{NiY}^{-2}$  by Smith and Hoard<sup>15</sup> makes it possible to suggest the step by step intermediates in this reaction by substituting a cyanide ion first for the  $\text{H}_2\text{O}$  bound to  $\text{Ni}^{+2}$  and then for the weakest  $\text{Y}^{-4}$  bond to  $\text{Ni}^{+2}$  as seen in Fig. 3. The reaction mechanism could be expanded in equation 8 to give another intermediate  $\text{NiY}(\text{CN})_3^{-5}$  (paramagnetic) undergoing a first order transition to  $\text{Ni}(\text{CN})_3\text{Y}^{-5}$  (diamagnetic). The reaction rate seems to parallel the planar alignment of nickel and the three cyanide ions. Thus, the more sterically hindered 1,2-cyclohexanediaminetetraacetic acid reacts several orders of magnitude slower with cyanide ion. The entropy of activation is quite negative considering the separation of charges in the mixed complex. This fact and the pronounced ionic strength effect lend support to the proposed mechanism. The lack of a

(15) G. S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959).

hydroxide ion effect also supports the argument that the rate is primarily controlled by the positioning of the cyanide ions around the nickel rather than just the unfolding of  $Y^{-4}$ .

Previous exchange studies<sup>3,4</sup> of radionickel complexes with  $Ni(CN)_4^{-2}$  have proposed a direct bimolecular exchange of the nickel complexes. How the ligands rearranged themselves was not clear. The inert character of  $Ni(CN)_3$  type intermediates postulated in this study offers a more plausible explanation for the observed kinetics and also explains salt effects. Thus, the true behavior of  $Ni(CN)_4^{-2}$  and  $Ni(gly)_2$  was obscured by the fact that the experiments<sup>4</sup> were performed

in an excess of glycine (proportional to  $Ni(gly)_2$ ) which could react with  $Ni(CN)_4^{-2}$ . Similarly, the dissociation mechanism with  $Ni(en)_3^{+2}$  was ruled out because the reaction was still very fast in excess en<sup>3</sup>. In fact, excess en speeds up the reaction. This is to be expected if en attacks  $Ni(CN)_4^{-2}$  in a manner similar to the EDTA mechanism. Direct bimolecular exchange of nickel complexes is not disproved but an alternate mechanism involving inert nickel cyanide complexes seems more likely.

**Acknowledgment.**—Work supported by U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

## Some Mixed Ligand Complexes with the Cyanide Complexes of Mercury<sup>1</sup>

BY LEONARD NEWMAN AND DAVID N. HUME

RECEIVED SEPTEMBER 28, 1960

Equilibria of the type  $Hg(CN)_3^- + X^- = Hg(CN)_3X^-$  have been studied polarographically at a temperature of 30° and an ionic strength of 2.0. When the ligand  $X^-$  is chloride, bromide and thiocyanate, the values of the formation constants are 0.4, 2.3 and 2.9, respectively. From a spectrophotometric study at an ionic strength of 4.0 the formation constant for the addition of one chloride ion to mercuric cyanide was found to be  $0.56 \pm 0.05$ .

### Introduction

In previous investigations the formation constants of  $Hg(CN)_2$ ,  $Hg(CN)_3^-$  and  $Hg(CN)_4^{2-}$  were measured polarographically<sup>2</sup> and the formation constant of  $HgOHCN$  was measured by both polarographic and solubility methods.<sup>3</sup> The knowledge that was obtained about the polarography of mercuric cyanide is utilized in the present paper for a polarographic investigation of mixed ligand complexes of the type  $Hg(CN)_3X^-$ . Equations previously developed for a spectrophotometric approach<sup>4</sup> are utilized to demonstrate that an anion, other than cyanide, can be added on to mercuric cyanide.

**Polarographic Study of Complexes of the Type  $Hg(CN)_3X^-$ .**—It was demonstrated previously that, in basic solutions, the cyanide liberated by the reduction of mercuric cyanide can complex with more mercuric cyanide diffusing toward the surface of the drop.<sup>2</sup> It was thought that this might, in part, be prevented if a ligand ( $X^-$ ) were added that could complex the mercuric cyanide. If the ligand were in large excess, the possible mixed anion complexes that could be formed directly are  $Hg(CN)_2X^-$  and  $Hg(CN)_2X_2^-$ . The species  $Hg(CN)_3X^-$  could also be formed as a consequence of the electrode reaction.

Utilizing the same apparatus, technique, conditions and reagents as previously described,<sup>2</sup> polarograms were obtained of solutions containing

$10^{-3} M$  mercuric cyanide with  $1 M$  chloride, bromide, thiocyanate or iodide. The ionic strength was maintained at 2.0 with sodium nitrate, the pH at  $11.0 \pm 0.1$ , the temperature at 30 and gelatin at 0.004%. The drop time was 4.3 seconds at the limiting current. In all cases except that of iodide a discrete cathodic wave was observed. The anodic wave for mercurous iodide is so close to the cathodic wave that the residual current cannot be measured, making it impossible to analyze the wave.

If a complex were not formed with the ligand, or if the cyanide liberated at the surface of the drop displaced all other ligands from the complex, then the analysis of the wave would not be dependent upon the concentration of the ligands. On examination of the results in Table I it can be seen that the analyses of the waves are dependent upon the presence of the added ligands. If  $Hg(CN)_2X_2^-$  or  $Hg(CN)_2X^-$  were the predominating species being reduced, a plot of  $E_{d.e.}$  vs.  $\log [(i_d - i)/i^2]$  would have a slope of 30 mv.,<sup>2</sup> the added ligands being in large excess. However, if  $Hg(CN)_3X^-$  were the predominating species, a plot of  $E_{d.e.}$  vs.  $\log [(i_d - i)/i^3]$  would have a slope of 30 mv. The data in Table I show the latter to be true. There are two possibilities through which  $Hg(CN)_3X^-$  can become the predominating species. The first is that  $Hg(CN)_2X^-$  is formed by the addition of one ligand to mercuric cyanide with the cyanide liberated at the surface of the drop complexing this species further. The second is that  $Hg(CN)_2X_2^-$  is first formed, from which the liberated cyanide displaces one  $X^-$ . No differentiation between these mechanisms can be made.

The stepwise formation constant for  $Hg(CN)_3X^-$  can be calculated from the observed concentration-

(1) Taken in part from the Ph.D. Thesis of Leonard Newman, Massachusetts Institute of Technology, June, 1956. This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(30-1)905.

(2) L. Newman, J. de O. Cabral and D. N. Hume, *THIS JOURNAL*, **80**, 1814 (1958).

(3) L. Newman and D. N. Hume, *ibid.*, **81**, 5901 (1959).

(4) L. Newman and D. N. Hume, *ibid.*, **79**, 4571 (1957).