Kinetics of Ligand Substitution Reaction between Cyanide Ion and NiL_2 (L=4-(2-Pyridylazo)resorcinol, Diethylenetriamine, and Ethylenediamine)

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The kinetics of substitution reaction of cyanide ion with some bis complexes $[NiL_2]^{2-2n}$, where L^{n-} is 4-(2-pyridylazo)resorcinolate, diethylenetriamine, or ethylenediamine, to form the square planar complex $[Ni(CN)_4]^{2-}$ has been studied spectrophotometrically in aqueous solutions. The rate expression has the form:rate$=\{k_d^{NiL_2}+k'[CN^-]\}[NiL_2^{2-2n}]$, where k' is a composite rate constant in case of par and dien and is equal to $k_{CN}^{NiL_2}$ in case of en. These results indicate that these bis complexes are not directly converted into $[Ni(CN)_4]^{2-}$ but first lose one ligand molecule and cyanide assists this loss. The backward reaction between $[Ni(CN)_4]^{2-}$ and L is first order in each reactant and inverse first order in cyanide. Though the mechanism for the reactions appears to be same, there are kinetic differences in the behaviour of en and the other two chelates. The rate determining step for the three reactions have been identified. The activation parameters for the forward reaction have been evaluated to support the proposed mechanism. The temperature dependence of backward reaction has also been given.

The mechanism of formation and dissociation reactions of some complexes of polyamines with nickel(II) has been investigated previously.[1–5] Ligand exchange reactions involving complexes of polyamines and nickel (II) with amine-*N*-acetic acids,[6] 2,2′-bipyridyl, 1,10-phenanthroline, and 2,2″,6′,2″-terpyridyl[7] have been studied extensively. A considerable work has been reported on the formation of $[Ni(CN)_4]^{2-}$ from nickel complexes of amine-*N*-acetic acids,[8] polyamines,[9] 1, 10-phenanthroline,[10] and from $Ni^{2+}_{(aq)}$.[11,12] Crouse and Margerum[13] have studied the reactions of $[Ni(CN)_4]^{2-}$ with various ligands in the presence and the absence of iodine as a scavanger for cyanide ion.

Previously we reported the formation of $[Ni(CN)_4]^{2-}$ from binuclear complexes Ni_2L, where L is ttha[14,15] and dtpa.[15] In the present paper, the kinetics of reactions of $NiL_2{}^{2-2n}$ with CN^- is reported (Eq. 1).

$$NiL_2{}^{2-2n} + 4CN^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [Ni(CN)_4]^{2-} + 2L^{n-} \qquad (1)$$

where L^{n-} indicates 4-(2-pyridylazo)resorcinolate (par), diethylenetriamine (dien), or ethylenediamine (en), and k_f and k_b are the overall rate constants for forward and backward reactions.

Experimental

Diethylenetriamine, obtained from Eastman Kodak Co., (U.S.A.) and ethylenediamine (BDH) were purified by distillation at 45 °C under reduced pressure and stored in amber coloured bottles. The monosodium salt of par was obtained from Riedel (Germany) and was used after recrystallization. Sodium perchlorate (AR) was used to maintain ionic strength (*I*). All other chemicals used were of AR grade. Complex species $[Ni(dien)_2]^{2+}$, $[Ni(en)_2]^{2+}$, $[Ni(par)_2]^{2-2n}$, and $[Ni(CN)_4]^{2-}$ were prepared by mixing stoichiometric amounts of aqueous nickel(II) ion and ligand at appropriate pH. Sodium cyanide and nickel(II) perchlorate solutions were standardized as reported earlier.[8] A borate buffer was used wherever mentioned, otherwise sodium hydroxide and perchloric acid were used to maintain pH.

A stopped-flow spectrophotometer model SF-3A from Hitech, England and an ECIL storage oscilloscope model OS-7865 equipped with a Polaroid camera were used for measuring rates of rapid reactions. Details of apparatus used for the study of slow reactions and pH measurements were reported previously.[8]

Kinetic Measurements

The ligand exchange reactions of $[Ni(dien)_2]^{2+}$ and $[Ni(en)_2]^{2+}$ with cyanide ion were followed at 267 nm (λ_{max} of $[Ni(CN)_4]^{2-}$, $\varepsilon=1.16\times10^4$ $dm^3\,mol^{-1}\,cm^{-1}$) or 285 nm ($\varepsilon=4.63\times10^3$ $dm^3\,mol^{-1}\,cm^{-1}$) where the absorbances of the other species were negligible under the present conditions. The forward reactions were run in excess cyanide. The results gave pseudo first order plots, and the rate expression is given by

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

where $[NiL_m]_T$ indicates the total concentration of nickel(II) complexes with L^{n-}, which contains mixed cyanide complexes of the type $NiL(CN)_x$. The forward and backward reactions in case of $Ni(par)_2$ were followed at 494 nm (λ_{max} of NiL_2, $\varepsilon=8.2\times10^4$ $dm^3\,mol^{-1}\,cm^{-1}$) by monitoring disappearance or appearance of $Ni(par)_2$.

The absorbances of par and $[Ni(par)_2]$ remained constant for a pH range of 8—9.5. Considering the protonation constants $\log K_{H_3L}^{H_2L}=2.6$, $\log K_{H_2L}^{HL}=5.5$ and $\log K_{HL}^{H}=12.5$,[16] at higher pH the dominant species of par is the monoprotonated one. The absorption of par increases above pH 9.5 and hence all the reactions were studied at a pH of 9.0±0.1. The reaction of NiL complex with cyanide was also studied at 494 nm ($\varepsilon_{NiL}=3.63\times10^4$ $dm^3\,mol^{-1}\,cm^{-1}$) by monitoring its disappearance. At the working pH, percentage of NiL was calculated[17] to be 80%.

For the study of reaction of $[Ni(CN)_4]^{2-}$ with par, solutions of par higher than 1.0×10^{-4} $mol\,dm^{-3}$ could not be used because they do not obey Lambert-Beer law above this concentration. The reaction could not be followed at 267 or 285 nm (absorption maxima of $[Ni(CN)_4)^{2-}]$ because NiL_2 and par also absorb appreciably at these wave lengths ($\varepsilon_{NiL_2}=1.15\times10^4$ $dm^3\,mol^{-1}\,cm^{-1}$, $\varepsilon_{par}=2.75\times10^3$ $dm^3\,mol^{-1}\,cm^{-1}$ at 267 nm).

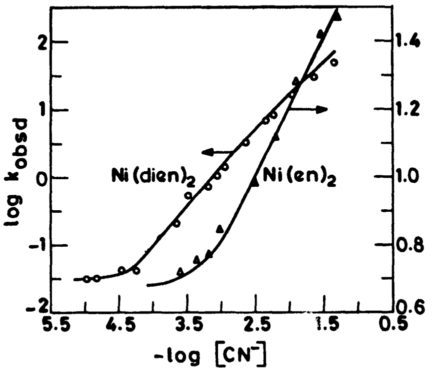

Fig. 1. Cyanide dependence of the observed forward rate constants in the reaction of $[Ni(dien)_2]^{2+}$ and $[Ni(en)_2]^{2+}$ with cyanide ion. pH 11.0, 25 °C and $I=0.1$ mol dm^{-3}.

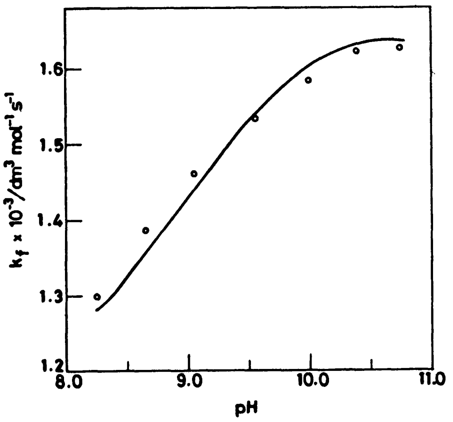

Fig. 2. Effect of pH on the reaction of $[Ni(dien)_2]^{2+}$ with cyanide at 25 °C and $I=0.1$ mol dm^{-3}.

Results

I. Reaction of Ni(dien)$_2$ with Cyanide. The rate of formation of $[Ni(CN)_4]^{2-}$ is first order each in $[Ni(dien)_2]^{2+}$ and CN^- at pH 11.0 where cyanide is present in large excess. The effect of cyanide can be seen in Fig. 1 where the slope of log k_{obsd} *vs.* log $[CN^-]$ plot gives the order of reaction in cyanide. The order in cyanide varies from zero at low cyanide concentration to one at higher cyanide concentration. A similar observation was also reported by Coombs and Margerum[18] while studying the reaction of cyanide ion with bis complexes of nickel(II) with imino-*N*-diacetate (ida) and methylimino-*N*-diacetate (mida). The observed zero order dependence in cyanide indicates a slow dissociation step according to Eq. 3 followed by further reaction of NiL with cyanide to give $[Ni(CN)_4]^{2-}$

$$NiL_2 \xrightarrow{k_d^{NiL_2}} NiL + L. \tag{3}$$

Thus k_{obsd} can be expressed by Eq. 4

$$k_{obsd} = k_d^{NiL_2} + k_3[CN^-]_T. \tag{4}$$

The values of $k_d^{NiL_2}=3.85\times10^{-2}$ s^{-1} and $k_3=1.34\times10^3$ dm^3 mol^{-1} s^{-1} at 25 °C and $I=0.1$ mol dm^{-3} ($NaClO_4$).

Dependence of k_f on pH: The pH was varied from 8.2 to 11.0 and it was found that the reaction rate increases with an increase of pH and then levels at pH higher than 9.5 (Fig. 2). The difference in reactivities of CN^- and HCN can be resolved using Eq. 5.

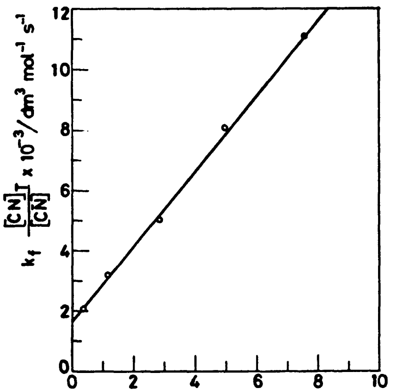

Fig. 3. Resolution of rate constants for the reaction of $[Ni(dien)_2]^{2+}$ with cyanide ion.

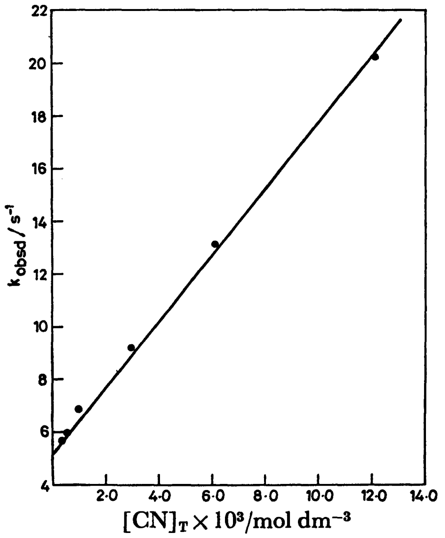

Fig. 4. Plot of k_{obsd} *vs.* $[CN]_T$ for the reaction of $[Ni(en)_2]^{2+}$ with cyanide ion.

$$k_f\frac{[CN]_T}{[CN^-]} = k_{CN} + k_{HCN}K_{HCN}[H^+], \tag{5}$$

where

$$\frac{[CN]_T}{[CN^-]} = 1 + K_{HCN}[H^+],$$

and K_{HCN} is the protonation constant of cyanide ion (log $K_{HCN}=9.0$ at 25 °C and $I=0.1$). Thus a plot of left hand side of Eq. 5 *vs.* $[H^+]$ gives a straight line (Fig. 3). The values of k_{HCN} and k_{CN} are 1.25×10^3 and 1.65×10^3 dm^3 mol^{-1} s^{-1}, respectively.

II. Reaction of $[Ni(en)_2]^{2+}$ with Cyanide Ion. The rate of reaction of $[Ni(en)_2]^{2+}$ with cyanide is first order in $[Ni(en)_2]^{2+}$ and the rate increases with an increase in cyanide ion concentration (Fig. 1). The nature of dependence on cyanide concentration shows that the bis complex dissociates and the monocomplex formed reacts rapidly with CN^- through the formation of mixed ligand complexes finally giving

TABLE 1. KINETICS OF THE DECOMPOSITION OF $Ni(CN)_4^{2-}$ IN ITS REACTION WITH dien, en, AND par

A. dien: $[Ni(CN)_4^{2-}]_i = 2.6\times10^{-5}$ mol dm^{-3}, pH 11.0, $I=0.1$ mol dm^{-3}, 25 °C.

$[dien]_T$/mol dm^{-3}	$10^9\times k'_{obsd}$/mol dm^{-3} s^{-1}	$10^6\times k_b$/s^{-1}
1.45×10^{-3}	6.90	4.76
1.09×10^{-3}	5.28	4.84
0.73×10^{-3}	3.61	4.95

B. en: $[Ni(CN)_4^{2-}]_i = 1.65\times10^{-5}$ mol dm^{-3}, pH 10.5, $I=0.5$ mol dm^{-3}, 25 °C.

$[en]_T$/mol dm^{-3}	$10^5\times k'_{obsd}$/mol dm^{-3} s^{-1}	$10^4\times k_b$/s^{-1}
0.18	5.8	3.2
0.20	7.4	3.7
0.25	8.5	3.4
0.30	9.6	3.2

C. par: $[Ni(CN)_4^{2-}]_i = 4.0\times10^{-6}$ mol dm^{-3}, pH 9.0, $I=0.15$, 30 °C.

$[par]_T$/mol dm^{-3}	$10^{10}\times k'_{obsd}$/mol dm^{-3} s^{-1}	$10^6\times k_b$/s^{-1}
4.0×10^{-5}	3.45	8.62
6.0×10^{-5}	4.75	7.92
8.0×10^{-5}	6.48	8.10
10.0×10^{-5}	8.24	8.24

$[Ni(CN)_4]^{2-}$. In this case, if first order dependence in cyanide is assumed,

$$k_{obsd} = k_d^{NiL_2} + k'[CN^-]. \tag{6}$$

So a plot of k_{obsd} *vs.* $[CN^-]$ should be a straight line, which is found to be the case for $[CN^-] > 10^{-3}$ mol dm^{-3} (Fig. 4). The values of $k_d^{NiL_2}$ and k' obtained from Fig. 4 are 5.1 s^{-1} and 1.3×10^3 dm^3 mol^{-1} s^{-1}, respectively. The value of $k_d^{NiL_2}$ for ethylenediamine is much larger than that for dien. This accounts for the slope being different from the expected value of one (Fig. 1).

Kinetics of Reactions of $[Ni(CN)_4]^{2-}$ with dien and en: The dissociation of $[Ni(CN)_4]^{2-}$ is greatly accelerated by the presence of polyamines in comparison to the much slower reaction of $[Ni(CN)_4]^{2-}$ with amine-*N*-acetic acids[8] or perchloric acid. The reaction is first order each in $[Ni(CN)_4]^{2-}$ and polyamine. A notable feature of these backward reactions is an inverse first order dependence in cyanide and the integrated rate expression has the form

$$(A_i - A_t) + A_i \ln\frac{A_t}{A_i} = -\frac{\varepsilon l}{4}k'_{obsd}t. \tag{7}$$

The terms used in Eq. 7 have their usual meaning as described earlier.[8] The values of k'_{obsd} and k_b are given in Table 1.

III. Reaction of Ni(par)$_2$ and Ni(par) with Cyanide. The stability constant of Ni(par)$_2$ is fairly large (log $\beta_2=22.2$)[19] and a slow exchange reaction was observed for this system. As in the case of $[Ni(dien)_2]^{2+}$ and $[Ni(en)_2]^{2+}$, a cyanide free path was also observed at $[CN^-]$ less than 10^{-3} mol dm^{-3} (Fig. 5) which indicates the dissociation of bis complex in addition to the cyanide assisted dissociation of Ni(par)$_2$ and formation of mixed ligand complexes of type Ni(par)(CN)$_x$ and finally $[Ni(CN)_4]^{2-}$.

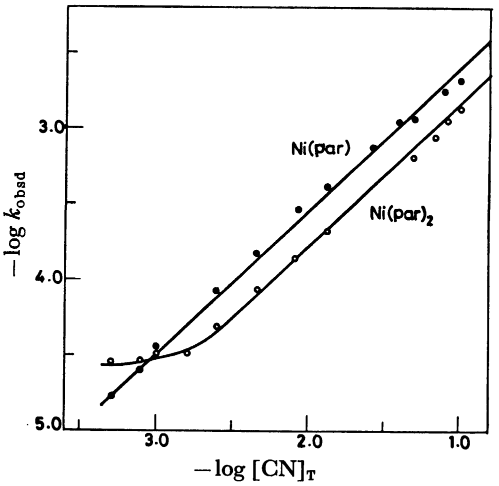

Fig. 5. Effect of cyanide ion concentration on the reaction of $[Ni(par)_2]^{2-}$ and [Ni(par)]. pH 9.0, 30 °C and $I=0.15$ mol dm^{-3}.

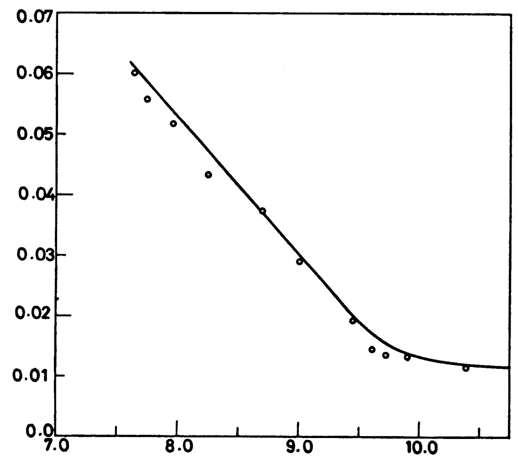

Fig. 6. Effect of hydrogen ion concentration on the reaction of [Ni(par)] with cyanide ion at 30 °C, and $I=0.1$ mol dm^{-3}.

The rate of the substitution reaction of monocomplex, [Ni(par)] was found to be first order with respect to cyanide over a wide range of cyanide concentration (Fig. 5). The rate constants are comparable with those of substitution reaction of the biscomplex (Fig. 5). This leads to a conclusion that the rate-determining step is the same in both reactions of Ni(par) and (Ni(par)$_2$ with cyanide ion.

Effect of pH on k_f: The rate of the forward reaction decreased with increase of pH (Fig. 6). This observation can be explained on the basis of labilities and structures[19] of the protonated forms of Ni(par)$_2$. It is also observed that reactions of Ni(par) and Ni(par)$_2$ with cyanide give similar rate constants on variation of pH.

A rate expression consistent with these observations is written below (Eq. 8).

$$\begin{aligned} k_{obsd} = k_f[CN]_T = \{&k_{CN} + k_{HCN}K_{HCN}[H^+] + k'_{CN}K_{NiHL}^{NiL}[H^+] \\ &+ k'_{HCN}K_{HCN}K_{NiHL}^{NiL}[H^+]^2\}[CN^-], \end{aligned} \tag{8}$$

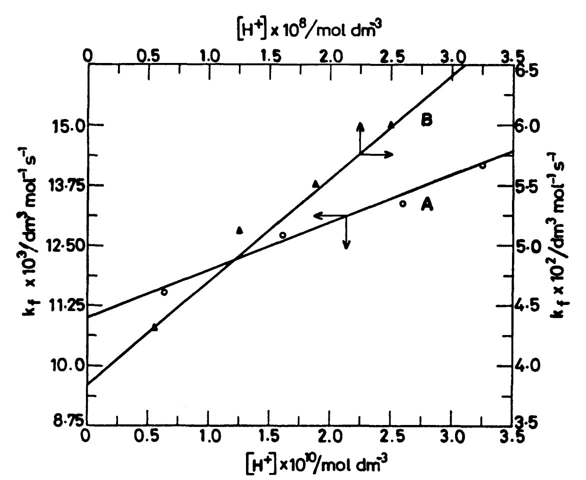

Fig. 7. Resolution of rate constants for the forward reaction of [Ni(par)] with cyanide ion.

where k_{CN} and k_{HCN} are the rate constants for the reaction of Ni(par) with CN$^-$ and HCN while k'_{CN} and k'_{HCN} are rate constants for the reaction of Ni (Hpar) with CN$^-$ and HCN respectively. K^{NiL}_{NiHL} is the protonation constant of Ni(par).

In high pH range, the terms containing protonated form of the complex can be neglected ($K^{NiPar}_{NiHPar}=10^{7.7}$ [20] in 50% dioxane, the value in aqueous solution is not known). Considering $1 \gg K_{HCN}[H^+]$ at pH>9.5, Eq. 8 under assumption of $[CN]_T \approx [CN^-]$ is transformed to

$$k_f = k_{CN} + k_{HCN}K_{HCN}[H^+]. \tag{9}$$

The value of k_{CN} and k_{HCN} can be evaluated by plotting k_f *vs.* [H$^+$] (Fig. 7), and are 1.11×10^{-2} and 1.01×10^{-2} dm^3 mol^{-1} s^{-1} respectively.

On the other hand, in lower pH range, the rate expression can be rearranged, assuming that $K_{HCN}[H^+] \gg 1$ and $[CN]_T \approx [HCN]$, to

$$k_f = k'_{CN}\frac{K^{NiL}_{NiHL}}{K_{HCN}} + k'_{HCN}K^{NiL}_{NiHL}[H^+]. \tag{10}$$

A plot of k_f *vs.* [H$^+$] gave a straight line (Fig. 7). The slope and intercept of this line give the values of product of k'_{HCN} and k'_{CN} with K^{NiL}_{NiHL}, and these are 8.36×10^5 and 3.90×10^7 dm^3 mol^{-1} s^{-1} respectively. The solid line in Fig. 6 shows the curve calculated from the various resolved rate constants.

IV. Kinetics of Reaction of $[Ni(CN)_4]^{2-}$ *with par.* The stability constant of tetracyanonickelate(II) is much greater than those of Ni(par) and Ni(par)$_2$ ($\log \beta_4=30.5$[12], $\log K_{Ni(par)}=17.8$, and $\log \beta_2=22.2$).[19] By using very dilute solution of $[Ni(CN)_4]^{2-}$ ($\approx 10^{-6}$ mol dm^{-3}) and a moderately high concentration of par ($\approx 10^{-4}$ mol dm^{-3}), it is possible to force the backward reaction. An excellent fit to the data was obtained by assuming a first order dependence in $[Ni(CN)_4]^{2-}$ and par and an inverse first order dependence in cyanide. The rate equation is formulated as given in Eq. 11, assuming that the change in absorbance of par during the course of reaction is negligible due to its high concentration compared to $[Ni(CN)_4]^{2-}$.

$$(A_t-A_0) + (A_\infty-A_0)\ln\frac{A_\infty-A_t}{A_\infty-A_0} = -\frac{\varepsilon l}{4}k'_{obsd}t, \tag{11}$$

where A_0 is the initial absorbance due to par, (A_t and A_∞ are the absorbances at time t and after completion of reaction, ε is the molar absorption coefficient of Ni(par)$_2$ and l is the light path length. Plots of left hand side of Eq. 11 *vs.* t, were linear (Fig. 8). From the plots, k'_{obsd} can be calculated and hence k_b($k_b=k'_{obsd}/[par]_T$). The values are given in Table 1.

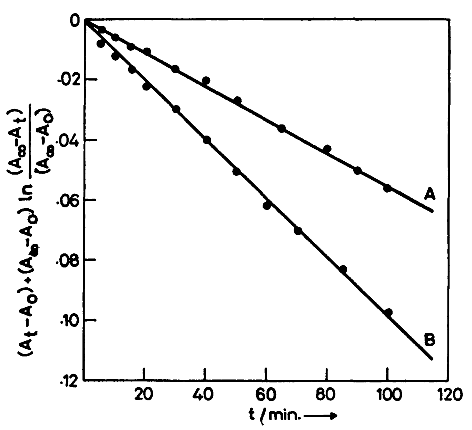

Fig. 8. Inverse first order plots for reaction of $[Ni(CN)_4]^{2-}$ with par at 30 °C, pH 9.0 and $I=0.15$ mol dm^{-3}, using Eq. 11. $[Ni(CN)_4]^{2-}=4\times10^{-6}$ mol dm^{-3}; (A) [par]$=6\times10^{-5}$ mol dm^{-3}, (B) [par]$=1\times10^{-4}$ mol dm^{-3}.

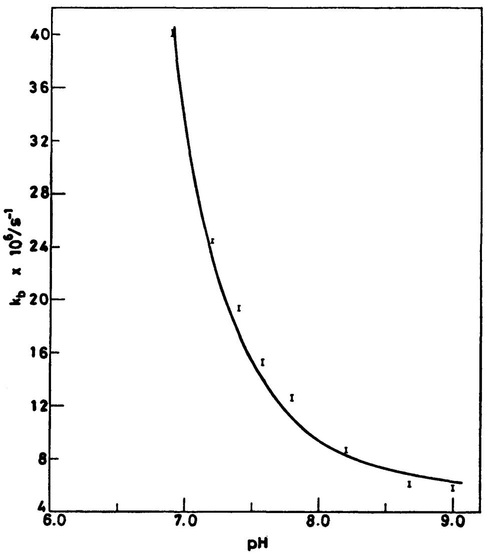

Fig. 9. Effect of pH on the backward reaction between $[Ni(CN)_4]^{2-}$ and par at 30 °C and $I=0.15$ mol dm^{-3}.

Effect of pH on the Reaction of $[Ni(CN)_4]^{2-}$ *with par*: The reaction was studied in the pH range 6.5—9.5 and the rate increased with decrease of pH (Fig. 9). $[Ni(CN)_4]^{2-}$ is known to be protonated only at pH below 5.0.[12] Therefore, the above behaviour can be explained on the basis of reactivities of the protonated forms of par *viz.* H$_2$par and Hpar. A rate law expressing the behaviour over the whole pH range investigated can be written as Eq. 12,

$$k_b\frac{[par]_T}{[par^{2-}]}\cdot\frac{1}{[H^+]} = k_{Hpar}K_{Hpar} + k_{H_2par}K_{H_2par}K_{Hpar}[H^+], \tag{12}$$

where

Table 2. Temperature dependence of forward reaction

A: Cyanide independent path, $k_{\mathrm{d}}^{\mathrm{NiL_2}}$. A′: Cyanide dependent path, k_3 or $k_{\mathrm{CN}}^{\mathrm{NiL_2}}$.

Temp/°C	Ni(par)$_2$-CN$^{\mathrm{a,a'}}$)		Ni(dien)$_2$-CN$^{\mathrm{b,b'}}$)		Ni(en)$_2$-CN$^{\mathrm{c'}}$)
	A $10^5\times k_{\mathrm{d}}^{\mathrm{NiL_2}}/\mathrm{s^{-1}}$	A′ $10^2\times k_3/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$	A $10^2\times k_{\mathrm{d}}^{\mathrm{NiL_2}}/\mathrm{s^{-1}}$	A′ $10^{-3}\times k_3/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$	A′ $10^{-3}\times k_{\mathrm{CN}}^{\mathrm{NiL_2}}/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
25	—	—	3.57±0.07	1.30±0.03	1.52±0.05
30	3.02±0.07	1.30±0.03	6.96±0.10	2.10±0.04	2.10±0.04
35	4.78±0.03	1.78±0.06	9.67±0.06	2.70±0.05	2.65±0.03
40	7.48±0.05	2.41±0.04	17.62±0.12	3.40±0.05	3.55±0.05
45	11.50±0.06	3.25±0.05	—	—	—
$E_{\mathrm{a}}/\mathrm{kJ\ mol^{-1}}$	71.1	49	77.4	39.7	44.7
$\Delta S^{*}/\mathrm{K^{-1}\ J\ mol^{-1}}$	−106	−162	−25	−60.7	−79.4

a) $[\mathrm{CN^-}]=8\times10^{-4}$ mol dm^{-3}; pH 10.0; $I=0.15$ mol dm^{-3}, a′) $[\mathrm{CN^-}]=5\times10^{-2}$ mol dm^{-3}; pH, I same as in a. b) $[\mathrm{CN^-}]=6\times10^{-5}$ mol dm^{-3}; pH 11.0; $I=0.1$ mol dm^{-3}, b′) $[\mathrm{CN^-}]=2.2\times10^{-3}$ mol dm^{-3}; pH, I same as in b. c′) $[\mathrm{CN^-}]=1.22\times10^{-2}$ mol dm^{-3}; pH 11.0, $I=0.1$ mol dm^{-3}.

Table 3. Temperature dependence of backward reaction ($k_{\mathrm{b}}=K_4{}^{-1}k_{-3}$)

Temp/°C	$[\mathrm{Ni(CN)_4}]^{2-}$–par$^{\mathrm{a)}}$ $10^5\times k_{\mathrm{b}}/\mathrm{s^{-1}}$	$[\mathrm{Ni(CN)_4}]^{2-}$–dien$^{\mathrm{b)}}$ $10^6\times k_{\mathrm{b}}/\mathrm{s^{-1}}$	$[\mathrm{Ni(CN)_4}]^{2-}$–en$^{\mathrm{c)}}$ $10^4\times k_{\mathrm{b}}/\mathrm{s^{-1}}$
25	—	4.76±0.05	3.20±0.03
30	0.83±0.01	8.05±0.07	5.03±0.04
35	1.32±0.02	13.1 ±0.04	7.96±0.07
40	2.06±0.04	21.6 ±0.06	12.29±0.05
45	3.18±0.03	—	—

a) $[\mathrm{Ni(CN)_4}]^{2-}=4.6\times10^{-6}$ mol dm^{-3}; [par] = 1×10^{-4} mol dm^{-3}; pH 9.0, $I=0.15$ mol dm^{-3}. b) $[\mathrm{Ni(CN)_4}]^{2-}=2.6\times10^{-5}$ mol dm^{-3}; [dien] = 1.45×10^{-3} mol dm^{-3}; pH 11.0; $I=0.1$ mol dm^{-3}. c) $[\mathrm{Ni(CN)_4}]^{2-}=1.65\times10^{-5}$ mol dm^{-3}; [en] = 0.18 mol dm^{-3}; pH 11.0; $I=0.1$ mol dm^{-3}.

$$\frac{[\mathrm{par}]_{\mathrm{T}}}{[\mathrm{par}]^{2-}}=1+K_{\mathrm{Hpar}}[\mathrm{H^+}]+K_{\mathrm{H_2par}}K_{\mathrm{Hpar}}[\mathrm{H^+}]^2+K_{\mathrm{H_3par}}K_{\mathrm{H_2par}}K_{\mathrm{Hpar}}[\mathrm{H^+}]^3.$$

From plots of left-hand side of Eq. 12 *vs.* [H$^+$], k_{HL} and $k_{\mathrm{H_2L}}$ were calculated to be 6.35×10^{-10} s^{-1} and 3.98×10^{-8} s^{-1}, respectively. Using these values, k_{b} was calculated for the whole range of pH. A good agreement between the calculated curve and the experimental points (Fig. 9) justifies the assumptions made in deriving the above rate equation.

V. Effect of Temperature on All Three Reactions. The forward reactions were studied in temperature range 25—45 °C at two different cyanide concentrations *i.e.* where order with respect to cyanide is zero and one respectively. The rate constants obeyed the Arrhenius equation. The activation parameters were calculated and are given in Table 2. The high energy of activation at low [CN$^-$] (cyanide independent path) indicates rupture of metal–ligand bond accompanied by a less negative entropy change as compared to cyanide dependent path of high [CN$^-$]. The backward reaction rates ($k_{\mathrm{b}}=K_4{}^{-1}$ k_{-3}) for all the three reactions in this temperature range are given in Table 3. Although these are composite rate constants, they also obeyed the Arrhenius equation.

Discussion

A detailed study of forward and backward reaction (Eq. 1) reveals that the substitution of polydentate ligands in octahedral bis complexes of Ni(II) proceeds by an associative mechanism. A mechanism consistent with experimental observation can now be written (Eqs. 13—17).

$$\begin{tikzcd}
\mathrm{NiL_2} \arrow[r, "k_{\mathrm{d}}^{\mathrm{NiL_2}}"] & \mathrm{NiL}+\mathrm{L}, \arrow[d, shift right, "+\mathrm{CN^-}\ K_1"'] & \text{(13)} \\
\mathrm{NiL_2}+\mathrm{CN^-} \arrow[r, shift left, "k_1'"] & \mathrm{NiL(CN)}+\mathrm{L} \arrow[l, shift left] \arrow[u, shift right, "-\mathrm{CN^-}\ \text{fast}"'] & \text{fast, (14)}
\end{tikzcd}$$

$$\mathrm{NiL(CN)}+\mathrm{CN^-} \overset{K_2}{\rightleftharpoons} \mathrm{NiL(CN)_2} \qquad \text{fast,} \tag{15}$$

$$\mathrm{NiL(CN)_2}+\mathrm{CN^-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{NiL(CN)_3} \qquad \text{rds,} \tag{16}$$

$$\mathrm{NiL(CN)_3}+\mathrm{CN^-} \overset{K_4}{\rightleftharpoons} \mathrm{Ni(CN)_4}^{2-}+\mathrm{L} \qquad \text{fast.} \tag{17}$$

The bis complexes do not convert directly to [Ni(CN)$_4$]$^{2-}$ but lose one of the ligands before the rate determining step (Eqs. 13 and 14), and mixed ligand complexes of type NiL(CN)$_x$ ($x=1$ or 2) are formed rapidly. Addition of third cyanide (Eq. 16) is rate determining.

The observed first order dependence in cyanide leads to a conclusion that either $k_{\mathrm{CN}}^{\mathrm{NiL_2}}$ or k_3 may be the slowest step. The average value of $k_{\mathrm{CN}}^{\mathrm{NiL_2}}$ ($=6.8\times10^4$ dm^3 mol^{-1} s^{-1}) obtained under the condition [Ni(dien)$_2^{2+}$]>[CN$^-$] is higher than the observed value of k_3 ($=1.34\times10^3$ dm^3 mol^{-1} s^{-1}) at higher cyanide concentration (Tables 4 and 6) indicating that $k_{\mathrm{CN}}^{\mathrm{NiL_2}}$ is not the rate determing step for [Ni(dien)$_2$]$^{2+}$–CN$^-$ reaction system.

However, mono and bis complexes of nickel(II)

TABLE 4. FORWARD RATE CONSTANTS IN PRESENCE OF EXCESS OR COMPARABLE

$[Ni(dien)_2]^{2+}$ AT 25 °C, pH 11.0 AND $I=0.1$ mol dm^{-3}
$[Ni(dien)_2{}^{2+}]=3.6\times10^{-3}$ mol dm^{-3}

$[CN]_T$/mol dm^{-3}	$k_{CN}^{NiL_2}$/dm^3 mol^{-1} s^{-1}
3.55×10^{-3}	$(6.6\pm0.6)\times10^4$
3.33×10^{-3}	$(7.1\pm0.7)\times10^4$
1.06×10^{-4}	$(6.9\pm1.0)\times10^4$

TABLE 5. EFFECT OF IONIC STRENGTH ON THE OBSERVED PSEUDO FIRST ORDER RATE CONSTANT FOR THE REACTION OF $[Ni(en)_2]^{2+}$ WITH CYANIDE ION

$[Ni(en)_2]_T=9.2\times10^{-5}$ mol dm^{-3}, $[CN]_T=4.0\times10^{-3}$ mol dm^{-3}, pH 11.0, 25 °C.

$I(NaClO_4)$/mol dm^{-3}	k_{obsd}/s^{-1}
0.1	12.5
0.2	8.8
0.3	7.7
0.3	7.7
0.45	7.0

and par react with cyanide at similar rates (Fig. 6) under similar conditions. This fact suggests that the rate determining step may be same for both reactions. Based on our earlier studies on reactions of mono complexes[8)] of nickel(II) with amine-*N*-acetic acids, this would in all probability be the addition of third cyanide. The observed inverse first order dependence in cyanide for the backward reaction further supports the supposition that the step shown in Eq. 16 is rate determining.

For quantitative conversion to $NiL(CN)_2$ which is the reactive species for forward reaction in presence of moderate or high concentration of cyanide, the stability of the same must be quite high. Values of K_1K_2 (or β_2) can be calculated from an expression derived by us earlier and given in Eq. 18.

$$K_1K_2 = \frac{K_4{}^{-1}k_{-3}\beta_4}{k_3K_{NiL}}, \tag{18}$$

where the symbols used have their usual meanings.[8)] These values, given in Table 6, suggest that rapid conversion of NiL_2 to $NiL(CN)_2$ can be expected. For $[Ni(en)_2]^{2+}$ reaction with cyanide, the value of K_1K_2 ($=1.6\times10^{16}$) is many orders of magnitude higher than the maximum possible value ($=3\times10^{11}$)[12)] estimated for $Ni(CN)_2\cdot4H_2O$.[12)] The magnitude of stability constant of the ternary complex will be equal to or less than that of $Ni(en)_2\cdot4H_2O$.[12)] The large difference in stabilities calculated for $Ni(en)(CN)_2$ shows that Eq. 18, which has been derived on the supposition that addition of third cyanide is rate determining, is not applicable in the case of ethylenediamine complex though it is applicable to $[Ni(dien)_2]^{2+}$ and $[Ni(par)_2]^{2-}$ reaction. It seems that $k_{CN}^{NiL_2}$ for $[Ni(en)_2]^{2+}$ system is smaller than k_3 and the addition of first cyanide is slower than the addition of third cyanide. The observation of a negative salt effect (Table 5) further supports this proposition. A similar conclusion was made earlier by Coombs and Margerum[18)] for reactions of $[Ni(ida)_2]$ and $[Ni(mida)_2]$ with cyanide.

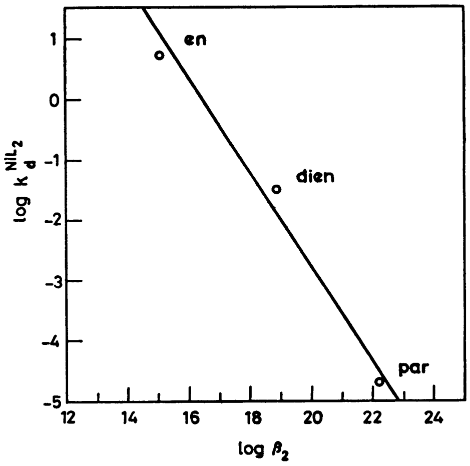

Fig. 10. A Linear Free Energy Relationship (LFER); a plot of log $k_d^{NiL_2}$ *vs.* log β_2.

The different kinetic behaviour of $[Ni(en)_2]^{2+}$ may be due to bidentate nature of ethylenediamine and presence of water molecules in cis positions.[21)] Water molecules in cis position are known to be less labile than the ones in trans location.[22)] The substitution of cis water by first cyanide is expected to be slower than the substitution, possibly of trans water, during the addition of third cyanide. In case of $[Ni(dien)_2]$ and $[Ni(par)_2]$, on the other hand, no water molecules are present due to tridentate ligands. The order of reactivity of bis complexes is reverse of the order of their stabilities. The dissociation rate constants $k_{CN}^{NiL_2}$ are also directly related to their overall stability constants β_2's. This free energy relationship is shown in

TABLE 6. SUMMARY OF THE RATE AND EQUILIBRIUM CONSTANTS OBTAINED AT 25 °C AND $I=0.1$ mol dm^{-3} ($NaClO_4$)

Constant	dien	en	par
K_{NiL}^{Ni}	5.0×10^{10}	4.0×10^{7}	6.3×10^{17}
$\beta_{NiL_2}^{Ni}$	7.94×10^{18}	1.26×10^{15}	1.58×10^{22}
$k_d^{NiL_2}$/s^{-1}	3.85×10^{-2}	5.1	1.86×10^{-5}
K_1K_2/dm^6 mol^{-2}	9.5×10^{10}	—	1.0×10^{11}
k_3/dm^3 mol^{-1} s^{-1}	$(1.34\pm0.2)\times10^3$	—	1.4×10^{-2}
k_{CN}/dm^3 mol^{-1} s^{-1}	1.65×10^3	–	1.11×10^{-2}
k_{HCN}/dm^3 mol^{-1} s^{-1}	1.25×10^3	—	1.01×10^{-2}
$k_{CN}^{NiL_2}$/dm^3 mol^{-1} s^{-1}	$(6.8\pm0.7)\times10^4$	$(1.3\pm0.2)\times10^3$	—
$K_4{}^{-1}k_{-3}$/s^{-1}	4.85×10^{-6}	3.38×10^{-4}	4.4×10^{-6}

Fig. 10. Table 6 summarises the various equilibrium and rate constant data obtained in this investigation.

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