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The Study of Kinetics and Mechanism of Ligand Substitution Reactions of $[PdPar(OH)]^-$ and $[Cd(Par)_2]^{2-}$ (Par = 4-(2-Pyridylazo)resorcinol) with Cyanide ^{1}Ions by Stopped Flow Technique

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Abstract

The reaction of $[PdPar(OH)]^-$ with cyanide ion has been followed at 510 nm (λ_{max} of $[PdPar(OH)]^-$) while the reaction of $[Cd(Par)_2]^{2-}$ with cyanide ions has been followed at 495 nm (λ_{max} of [Cd(Par)] or $[Cd(Par)_2]$) by the stopped flow technique at pH = 11.0 ± 0.02, $I = 0.1$ M ($NaClO_4$) and temperature = 25 ± 0.1 °C under pseudo-first-order conditions taking cyanide in large excess. The reaction between $[PdPar(OH)]^-$ and cyanide ion follows first-order kinetics in both $[CN^-]$ and $[PdPar(OH)]^-$. The reactions of [Cd(Par)] and $[Cd(Par)_2]$ with cyanide ions also follow first-order kinetics in each reactant at higher cyanide concentrations. The reactions of [PdPar(OH)] and $[Cd(Par)_2]$ with cyanide ions exhibit zero-order dependences in $[CN^-]$ at extremely low cyanide concentrations.

The reverse reaction between $[Pd(CN)_4]^{2-}$ and Par, and $[Cd(CN)_4]^{2-}$ and Par follow first-order kinetics in each reactant and an inverse first-order dependence in cyanide ion. It is inferred that the fourth step is the rate determining one in a proposed five step mechanistic scheme. Additional studies viz. effect of ionic strength, pH dependence and temperature dependence were also conducted and support the proposed mechanistic scheme.

Introduction

The kinetics of formation and dissociation reactions of mono and bis complexes of metal ions in aqueous solution have been widely studied since the development of techniques for the study of fast reactions [1]. Kinetic investigations of the reactions of bis complexes of Ni(II) have been done by many workers. The formation of $[Ni(CN)_4]^{2-}$ from the reactions of $Ni(en)_2$, $Ni(dien)_2$ and $Ni(Par)_2$ with cyanide ion has been studied by Nigam *et al.* [2]. Recently we have been investigating the kinetics and mechanism of reactions involving the exchange of polyaminocarboxylate ligands complexed to Ni(II) [3] and Fe(III) [4] by a monodentate ligand viz. cyanide ion. There have been many studies on the substitution reactions of bis and binuclear complexes of Ni(II) [2, 5] and Fe(III) [6, 7]. Very little, however, is known so far on the exchange reactions of bis complexes of Pd(II) and Cd(II).

In the present study, we report the kinetics of the reactions of $PdPar(OH)^-$ and $CdPar_2{}^{2-}$ with CN^- represented by eqns. (1) and (2). Par is further abbreviated to R in the following narration, k_f and

$$PdR(OH)^- + 4CN^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Pd(CN)_4]^{2-} + R^{2-} + OH^- \qquad (1)$$

$$CdR_2{}^{2-} + 4CN^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Cd(CN)_4]^{2-} + 2R^{2-} \qquad (2)$$

k_r are the overall rate constants for the forward and reverse reactions. The reaction of CdR with cyanide is also investigated independently to provide further support for the mechanism proposed for the bis complex reaction with cyanide.

Experimental

The reagents used were of AR(BDH) grade unless stated otherwise. The stock solution of $[PdCl_4]^{2-}$ was prepared by using a method given in the literature [8] and standardized gravimetrically using dimethylglyoxime as a precipitant [9]. Tetracyanopalladate(II) was prepared by using palladous chloride and potassium cyanide in stoichiometric amounts as the starting materials [10]. A solution of tetracyanocadmate(II) was prepared according to the method of Brauer [11]. The mono complexes $PdR(OH)^-$ and CdR and the bis complex $CdR_2{}^{2-}$ were prepared by mixing solutions containing stoichiometric amounts of $[PdCl_4]^{2-}$ or $CdSO_4$ with recrystallized sodium salt of Par (Reidel, F.R.G.), respectively. Sodium cyanide was standardized argentometrically [12]. A borate buffer was used to maintain desired pH wherever needed. $NaClO_4$ (E. Merck) was used to maintain the ionic strength.

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A stopped flow spectrophotometer model SF-3A from Hitech (U.K.) equipped with a storage oscilloscope model OS-768S (ECIL, India) was used for the study of both forward and reverse reactions. A polaroid camera was used to record the kinetic traces. All pH measurements were made on a digital pH meter model LI-120 from Elico (India) using B.D.H. buffers for standardization. A Shimadzu double beam spectrophotometer model UV-240, with a circulatory arrangement for thermostating the cell compartment, was used for the kinetic studies of slower reactions. An ultracryostat model 2 NBE (VEB Kombinat Medizin and Labortechnik Kombinatsbetrieb) was used to maintain the temperature of the reactants.

Kinetic Measurements

The ligand exchange reactions of $[PdR(OH)]^-$ with cyanide ions are followed at 510 nm (λ_{max} of $[PdR(OH)]^-$, $\epsilon = 3.34 \times 10^4$ M^{-1} cm^{-1}) by monitoring the disappearance of $[PdR(OH)]^-$ over a pH range of 8.5–11.25. The reactions of [CdR] and $[CdR_2]^{2-}$ with cyanide ions are followed at 495 nm (λ_{max} of $[CdR_2]^{2-}$, $\epsilon = 9.08 \times 10^4$ M^{-1} cm^{-1}) by monitoring the disappearance of CdR_2 over a pH range of 9.0–11.25. All forward reactions have been run in the presence of a large excess of CN^- and gave pseudo-first-order plots. At these wavelengths Par also absorbs appreciably, so suitable corrections were applied to the absorbances of $[PdR(OH)]^-$, $[CdR_2]^{2-}$ and [CdR] at this wavelength. A formula derived for calculation of the concentration C_A of CdR_2 species is given in eqn. (3).

$$C_A = (A_t - C_A^0 \epsilon_B)/(\epsilon_A - \epsilon_B) \tag{3}$$

A_t is the total absorbance at time t, ϵ_A and ϵ_B are the respective molar extinction coefficients of the complex and Par respectively at that wavelength and C_A^0 is the initial concentration of complex species. The reverse reactions, that is the formations of $[PdR(OH)^-]$ and $[CdR_2]^{2-}$ from tetracyanopalladate(II) and tetracyanocadmate(II) with Par have also been followed at 510 and 495 nm, respectively. The spectra of $[Pd(CN)_4]^{2-}$ and $[Cd(CN)_4]^{2-}$ are almost featureless in this region.

Results

Reaction of $[PdR(OH)^-]$ with Cyanide

The rate of formation of $[Pd(CN)_4]^{2-}$ is first order in $[PdR(OH)]^-$ in the presence of excess cyanide. The effect of the concentration of cyanide can be seen in Fig. 1, where the slope of a plot of log k_{obs} versus log$[CN^-]_T$ gives the order of reaction in cyanide. The various rate constants are given in Table 1a. The order in cyanide varies from zero at low cyanide concentration to one at higher cyanide concentration. This zero-order dependence indicates a slow release of hydroxyl ions from $[PdR(OH)]^-$ according to eqn. (4) followed by further reaction of [PdR] with cyanide to give $[Pd(CN)_4]^{2-}$.

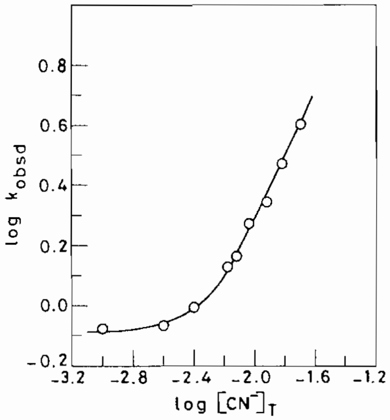

Fig. 1. Cyanide dependence of the observed forward rate constants on the reaction of $[PdR(OH)]^-$ with cyanide ion. Reaction conditions as given in Table 1a.

$$PdR(OH)^- \longrightarrow PdR + OH^- \tag{4}$$

Thus k_{obs} can be expressed by eqn. (5)

$$k_{obs} = k_d^{PdR(OH)} + k'[CN^-] \tag{5}$$

$k_d^{PdR(OH)} = 1.5 \times 10^{-1}$ s^{-1} and $k' = 1.88 \times 10^2$ M^{-1} s^{-1} at 25 °C and $I = 0.1$ M ($NaClO_4$).

Dependence of Reaction Rate of $[PdR(OH)]^-$ and CN^- on pH

The reaction has been studied in the pH range 8.5–11.25. An S-shaped curve is obtained in this pH range with a levelling off at pH ~11 (Fig. 2). This pH profile in the lower range can be explained on the basis of different reactivities of HCN and CN^-. Levelling of the rate at pH above 10.75 appears to be due to polymerization of $[PdR(OH)]^-$ species [13].

Reaction of $[CdR_2]^{2-}$ with Cyanide

The exchange reaction of CdR_2 with cyanide ions has been followed at 495 nm. The rate of decay of CdR_2 is first order in $[CdR_2]^{2-}$ over a wide range of cyanide concentrations (present in excess). The effect of variation of cyanide can be seen in Fig. 3, where the slope of a plot of log k_{obs} versus log $[CN^-]_T$ gives the order with respect to cyanide ion. A significant feature of this curve is that at low cyanide concentration the plot tends towards zero-order dependence in cyanide. This observation indicates the slow dissociation of the bis complex according to eqn. (6).

$$[CdR_2]^{2-} \longrightarrow CdR + R^{2-} \tag{6}$$

TABLE 1. Rate constants at excess cyanide concentration

(a) $[PdR(OH)]^-$–CN^- reaction: $[PdR(OH)^-] = (1.0–4.0) \times 10^{-5}$ M, pH = 11.0 ± 0.02, temperature = 25 ± 0.1 °C, $I = 0.1$ M ($NaClO_4$)

$[CN^-]_T$ (M)	k_{obs} (s^{-1})	$10^{-2} \times k_f = k_{obs}/[CN^-]_T$ ($M^{-1} s^{-1}$)
2.0×10^{-2}	3.98	1.99
1.5×10^{-2}	2.95	1.97
1.2×10^{-2}	2.19	1.83
9.12×10^{-3}	1.86	2.04
7.59×10^{-3}	1.45	1.91
6.61×10^{-3}	1.35	2.04
3.98×10^{-3}	0.99[a]	
2.51×10^{-3}	0.74[a]	
1.0×10^{-3}	0.76[a]	k_f(av) = $(1.96 \pm 0.07) \times 10^2$

(b) $[CdR_2]^{2-}$–CN^- and [CdR]–CN^- reaction: pH = 11.0 ± 0.02, temperature = 25 ± 0.1 °C, $I = 0.1$ M ($NaClO_4$)

$[CN^-]_T$ (M)	$Cd(Par)_2$		Cd(Par)	
	$10^1 \times k_{obs}$ (s^{-1})	$10^{-2} \times k_f$ ($M^{-1} s^{-1}$)	$10^1 \times k_{obs}$ (s^{-1})	$10^{-2} \times k_f$ ($M^{-1} s^{-1}$)
1.5×10^{-2}	25	1.7	16	1.0
1.12×10^{-2}	19	1.7		
9.0×10^{-3}	16	1.8	9.9	1.1
7.5×10^{-3}	14	1.9	8.0	1.1
5.0×10^{-3}	8.9	1.8	5.1	1.0
4.0×10^{-3}	7.4	1.9		
2.5×10^{-3}			2.7	1.1
2.0×10^{-3}	4.8			
8.0×10^{-4}	4.0[a]			
5.0×10^{-4}	4.0[a]			
2.0×10^{-4}	3.8[a]	k_f(av) = $(1.8 \pm 0.1) \times 10^2$		k_f(av) = $(1.08 \pm 0.04) \times 10^2$

[a] Zero order dependence in $[CN^-]$.

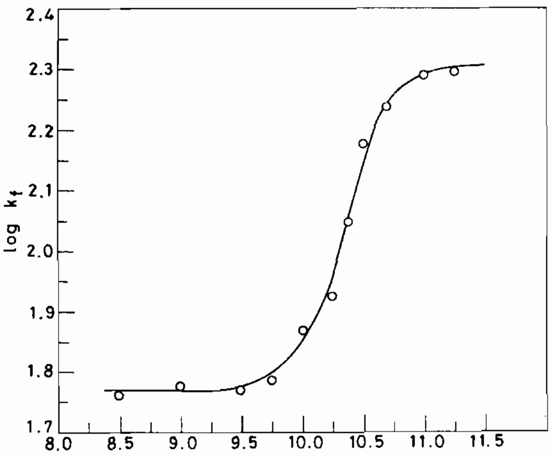

Fig. 2. Effect of pH on the reaction of $[PdR(OH)]^-$ with cyanide. $[PdR(OH)]^- = 4.0 \times 10^{-5}$ M, $[CN^-] = 1.5 \times 10^{-2}$ M, temperature 25 ± 0.1 °C and $I = 0.1$ M ($NaClO_4$).

The observed rate constant, k_{obs}, for the reaction under study can be expressed as

$$k_{obs} = k_d^{CdR_2} + k'[CN^-] \tag{7}$$

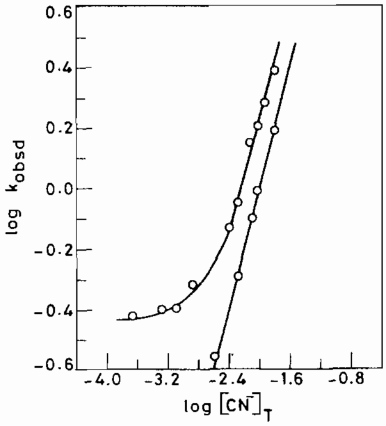

Fig. 3. Effect of cyanide ion concentration on the reaction of $[Cd(Par)_2]^{2-}$ and [Cd(Par)] with cyanide ions. Reactions conditions as given in Table 1b.

The monocomplex [CdR] also reacts with excess cyanide following first-order kinetics with respect to cyanide. The rate constants are comparable with those of substitution reactions of the bis complex (Fig. 3) at the same concentration of cyanide. This

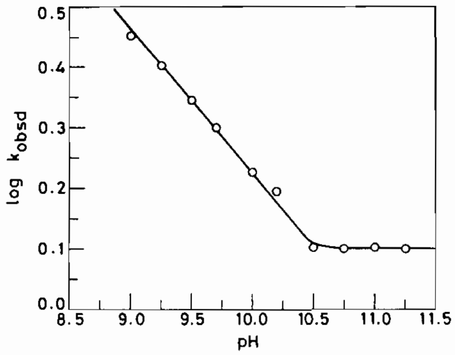

Fig. 4. Dependence of pH on the $[CdR_2]^{2-}$–CN^- reaction. Reaction conditions as given in Table 2.

leads to the conclusion that the rate determining step is the same in reactions of [CdR] and $[CdR_2]^{2-}$. The observed rate constants are given in Table 1b.

Dependence of Reaction Rate on pH

The reaction rate of $[CdR_2]^{2-}$ with CN^- ion is found to decrease with increase of pH from 9.0 to 10.5 and then remain almost constant (Fig. 4). This behaviour is due to different reactivities of unprotonated and protonated forms of the reactant species. The results indicate that the protonated form of CdR complex is more labile than the unprotonated one. It is also observed that reactions of [CdR] and $[CdR_2]^{2-}$ with cyanide ions give similar rate constants at comparable pH (Table 2).

Kinetics of Reverse Reaction

The stability constants of $[Pd(CN)_4]^{2-}$ and $[Cd(CN)_4]^{2-}$ are much greater than those of $[PdR(OH)]^-$, [CdR] and $[CdR_2]^{2-}$ complexes ($\log\beta_4$ $[Pd(CN)_4]^{2-}$ = 42 [14], and $\log\beta_4$ $[Cd(CN)_4]^{2-}$ = 19 [15], $\log K_{PdR(OH)}$ = 4.9 [16] and $\log\beta_2$ $[Cd(Par)_2]$ = 17.5 [17]). It becomes possible to force the reverse reactions only by using very dilute solutions of $[Pd(CN)_4]^{2-}$ or $[Cd(CN)_4]^{2-}$ and a moderately high concentration of Par. Also a higher temperature has to be used for the rate to be conveniently measurable. As Par does not obey the Lambert–Beer Law at a concentration higher than 10^{-4} M, low concentrations of $[Pd(CN)_4]^{2-}$ and $[Cd(CN)_4]^{2-}$ (2×10^{-6} M) were taken in order to maintain pseudo-first-order conditions.

The formation of PdR(OH) or CdR_2 or decay of $[Pd(CN)_4]^{2-}$ and $[Cd(CN)_4]^{2-}$ were used to obtain the rate law given in eqn. (8).

$$-d[Cd(CN)_4{}^{2-}]/dt = k_r[Cd(CN)_4{}^{2-}][Par]_T/[CN^-] \tag{8a}$$

$$-d[Pd(CN)_4{}^{2-}]/dt = k_r[Pd(CN)_4{}^{2-}][Par]_T/[CN^-] \tag{8b}$$

TABLE 2. Effect of pH on the rate constants of $[CdR_2]^{2-}$–CN^- and $[CdR]$–CN^- reactions; temperature = 25 ± 0.1 °C, I = 0.1 M ($NaClO_4$)

pH	CdR_2		CdR	
	k_{obs} (s^{-1})	$10^{-2} \times k_f$ (M^{-1} s^{-1})	k_{obs} (s^{-1})	$10^{-2} \times k_f$ (M^{-1} s^{-1})
8.5			1.4	1.9
9.0	2.8	3.8	1.2	1.6
9.25	2.5	3.4	1.1	1.4
9.5	2.2	3.0		
9.7	2.0	2.7		
10.0	1.7	2.2	9.7×10^{-1}	1.3
10.2	1.6	2.1		
10.5	1.3	1.7	8.7×10^{-1}	1.2
10.75	1.3	1.7	8.4×10^{-1}	1.1
11.0	1.3	1.7	8.3×10^{-1}	1.1
11.25	1.3	1.7		

The integrated form of eqn. (8) can be written as

$$(A_t - A_0) + (A_\infty - A_0)\ln\frac{A_\infty - A_t}{A_\infty - A_0} = -\frac{\epsilon \times l}{4}k'_{obs}t \tag{9}$$

A_0 is the initial absorbance due to Par. A_t and A_∞ are the absorbances at time t and after completion of reaction respectively, ϵ is the molar extinction coefficient of PdR(OH) or $Cd(Par)_2{}^{2-}$ and l is the path length. By plotting the left hand side of eqn. (9) versus t, we get a straight line, from which we can calculate k'_{obs} and hence k_r ($k_r = k'_{obs}/[Par]_T$). These are included in Table 3.

Dependence of Forward Rate on Ionic Strength

The rate of forward reaction between CdR_2 and CN^- increases with increase in ionic strength (Fig. 5). The value of Z_AZ_B obtained from the slope of the straight line is close to two (Bronsted–Bjerrum plot).

Activation Parameters of the Forward and Reverse Reaction Rates

The forward and reverse reactions were studied over a temperature range of 25–45 °C. The Arrhenius equation was obeyed by both forward and reverse reactions. The activation parameters for forward reactions have been calculated for both the situations where order dependence on cyanide is zero or/and one. These data are given in Table 4. The activation parameters for the reverse reaction are also included in Table 4.

TABLE 3. Kinetics of reverse reaction

$10^5 \times [\mathrm{Par}]_T$ (M)	$10^{10} \times k'_{\mathrm{obs}}$ (M s^{-1})	$10^6 \times k_r$ (s^{-1}) ($k'_{\mathrm{obs}}/[\mathrm{Par}]$)
(a) $[\mathrm{Pd(CN)_4}]^{2-}$–Par reaction: $[\mathrm{Pd(CN)_4}^{2-}] = 1.33 \times 10^{-6}$ M, pH = 9.0 ± 0.02, temperature = 40 ± 0.1 °C, I = 0.1 M $\mathrm{NaClO_4}$)		
3.0	1.13	3.78
5.0	1.85	3.71
7.5	2.99	3.99
9.0	3.41	3.79
		k_r(av) = (3.82 ± 0.1) × 10^{-6}
(b) $[\mathrm{Cd(CN)_4}]^{2-}$–Par reaction: $[\mathrm{Cd(CN)_4}^{2-}] = 2.0 \times 10^{-6}$ M, pH = 9.0 ± 0.02, temperature = 30 ± 0.1 °C, I = 0.1 M ($\mathrm{NaClO_4}$)		
4.0	0.76	1.90
6.66	1.07	1.61
7.5	1.24	1.66
9.0	1.64	1.83
		k_r(av) = (1.75 ± 0.12) × 10^{-6}

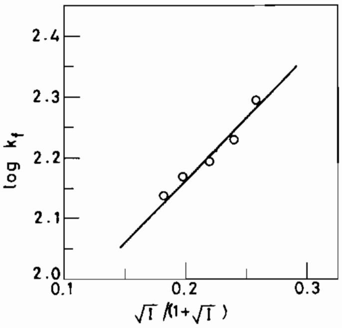

Fig. 5. Dependence on ionic strength of the $[\mathrm{CdR_2}]^{2-}$–$\mathrm{CN^-}$ reaction. $[\mathrm{CdR_2}]^{2-} = 5.0 \times 10^{-6}$ M, $[\mathrm{CN^-}] = 7.5 \times 10^{-3}$ M, pH = 11.0 ± 0.02, temperature = 25 ± 0.1 °C.

Discussion

A detailed study of forward and reverse reaction of $[\mathrm{CdR_2}]^{2-}$ with cyanide ions reveals a mechanism given in eqns. (10)–(14).

$$[\mathrm{CdR_2}]^{2-} \xrightarrow{k_d^{\mathrm{CdR_2}}} \mathrm{CdR} + \mathrm{R}^{2-} \quad \text{v. slow} \qquad (10)$$

$$-\mathrm{CN^-} \ \Big\uparrow\!\Big\downarrow \ {+\mathrm{CN^-}} \ \ K_1\ (\text{fast})$$

$$[\mathrm{CdR_2}]^{2-} + \mathrm{CN^-} \overset{K'_1}{\rightleftharpoons} [\mathrm{CdR(CN)}]^- + \mathrm{R}^{2-} \quad \text{fast} \qquad (11)$$

$$[\mathrm{CdR(CN)}]^- + \mathrm{CN^-} \overset{K_2}{\rightleftharpoons} [\mathrm{CdR(CN)_2}]^{2-} \quad \text{fast} \qquad (12)$$

$$[\mathrm{CdR(CN)_2}]^{2-} + \mathrm{CN^-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{CdR(CN)_3}]^{3-} \quad \text{r.d.s.} \qquad (13)$$

$$[\mathrm{CdR(CN)_3}]^{3-} + \mathrm{CN^-} \overset{K_4}{\rightleftharpoons} [\mathrm{Cd(CN)_4}]^{2-} + \mathrm{R}^{2-} \quad \text{fast} \qquad (14)$$

In the reaction of $[\mathrm{CdR_2}]^{2-}$ with cyanide, a zero-order dependence in $[\mathrm{CN^-}]$ at low and a first-order dependence in $[\mathrm{CN^-}]$ at higher cyanide concentration is found, while in the case of [CdR] reaction only first-order dependence in $[\mathrm{CN^-}]$ was observed. This is consistent with earlier observations on $\mathrm{NiL_2}$–$\mathrm{CN^-}$ [2, 18] reaction systems (where L = ethylenediamine, diethylenetriamine, 4-(2-pyridylazo)resorcinol, iminodiacetic acid and *N*-methyliminodiacetic acid).

However, in the case of the reaction of $[\mathrm{PdR(OH)}]^-$ with cyanide a zero-order and a first-order dependence was seen at low and high cyanide concentrations respectively. This points to a slow loss of the hydroxyl group in the first step and also a cyanide assisted rapid displacement of $\mathrm{OH^-}$ according to eqns. (15) and (16). This is followed by three steps similar to eqns. (12)–(14) postulated for the reaction of $[\mathrm{CdR_2}]^{2-}$ with cyanide.

TABLE 4. Activation parameters for the forward and reverse reactions

	Forward reaction		Reverse reaction
	Zero-order dependence	First-order dependence	
(a) $[\mathrm{PdR(OH)}]^-$–$\mathrm{CN^-}$ system			
$\Delta H^{\circ\neq}$ (kJ $\mathrm{mol^{-1}}$)	67.1 ± 1.3	16.6 ± 1.0	37.7 ± 1.1
$\Delta S^{\circ\neq}$ (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)	−21.7 ± 4.5	−146 ± 3.4	−224 ± 4.0
(b) $[\mathrm{CdR_2}]^{2-}$–$\mathrm{CN^-}$ system			
	39.7 ± 1.0	14.6 ± 0.3	13.1 ± 1.0
	−120.1 ± 3.3	−153.3 ± 0.9	−305.1 ± 1.8

$$\begin{tikzcd}
{[\mathrm{PdR(OH)}]^-} \arrow[r, "k_d^{\mathrm{PDR(OH)}}"] & {[\mathrm{PdR}] + \mathrm{OH}^- \quad \text{v. slow} \quad (15)} \arrow[d, shift left, "+\mathrm{CN}^-"', "K_1\ \text{(fast)}"] \\
{[\mathrm{PdR(OH)}]^- + \mathrm{CN}^-} \arrow[r, shift left, "K'_1"] & {[\mathrm{PdR(CN)}]^- + \mathrm{OH}^- \quad \text{fast} \quad (16)} \arrow[l, shift left] \arrow[u, shift left, "-\mathrm{CN}^-"]
\end{tikzcd}$$

A similar dissociation of hydroxyl ion has been demonstrated in the case of the $[\mathrm{FeTTHA(OH)_2}]^{5-}$–cyanide reaction investigated by us earlier [6].

In the reverse reaction, first-order dependence in both $[\mathrm{Cd(CN)_4}]^{2-}$ and Par while an inverse first-order dependence in $[\mathrm{CN^-}]$ is observed. The results on forward and reverse rates are interpreted to mean that these reactions take place in five steps (*vide infra*) in which the third step (eqn. (13)) is the rate determining one and that three cyanides were required around the central metal ion to bring about the rate determining step.

A steady state treatment on the intermediate species $[\mathrm{CdR(CN)_3}]^{3-}$, $[\mathrm{CdR(CN)_2}]^{2-}$, $[\mathrm{CdR(CN)}]^{1-}$ and [CdR] and a consideration of dissociation of $[\mathrm{CdR_2}]^{2-}$ gives a rate expression (17).

$$\text{Rate} = k_d^{\mathrm{CdR_2}}[\mathrm{CdR_2}^{2-}] + \frac{K'_1K_2k_3[\mathrm{CN^-}]^3[\mathrm{CdR_2}^{2-}]}{1 + K'_1[\mathrm{CN^-}] + K'_1K_2[\mathrm{CN^-}]^2} \qquad (17)$$

This expression reduces to a third; second- and first-order dependence in cyanide concentrations at low, medium and high cyanide concentrations respectively. The first term in eqn. (17) corresponds to dissociation of the bis complex $\mathrm{CdR_2}$ to CdR and R.

One can proceed now to derive the experimental rate law for the reverse reaction by applying steady state treatment to the intermediate produced in the rate determining step. viz. $[\mathrm{CdR(CN)_3}]^{3-}$. Thus,

$$[\mathrm{CdR(CN)_3}^{3-}] = \frac{k_3[\mathrm{CdR(CN)_2}^{2-}][\mathrm{CN^-}] + k_{-4}[\mathrm{Cd(CN)_4}^{2-}][\mathrm{R}^{2-}]}{k_4[\mathrm{CN^-}] + k_{-3}} \qquad (18)$$

$$-\mathrm{d}[\mathrm{Cd(CN)_4}^{2-}]/\mathrm{d}t = k_{-3}[\mathrm{CdR(CN)_3}^{3-}] = \frac{k_{-3}\{k_3[\mathrm{CdR(CN)_2}^{2-}][\mathrm{CN^-}] + k_{-4}[\mathrm{Cd(CN)_4}^{2-}][\mathrm{R}^{2-}]\}}{k_4[\mathrm{CN^-}] + k_{-3}} \qquad (19)$$

In the presence of excess Par, the first term in the numerator can be ignored. Our results on forward and reverse rate study show that the fifth step is fast compared to the fourth one and values of k_4 (also k_{-4}) must be quite large. Thus even though $[\mathrm{CN^-}]$ may be small, $k_4[\mathrm{CN^-}]$ may still be quite large compared to k_{-3} which may be omitted in the denominator. With these assumptions eqn. (19) reduces to eqn. (20)

$$\text{Rate} = -\mathrm{d}[\mathrm{Cd(CN)_4}^{2-}]/\mathrm{d}t = \frac{k_{-3}K_4^{-1}[\mathrm{Cd(CN)_4}^{2-}][\mathrm{R}^{2-}]}{[\mathrm{CN^-}]} = \frac{k_r[\mathrm{Cd(CN)_4}^{2-}][\mathrm{R}^{2-}]}{[\mathrm{CN^-}]} \qquad (20)$$

where $K_4^{-1} = k_{-4}/k_4$, and $k_r = k_{-3}K_4^{-1}$.
This rate expression is in agreement with the observed rate law for reverse reaction given in eqn. (8). Similarly one can also derive the rate expression for the $[\mathrm{PdR(OH)}]^-$ and cyanide reaction.

A combination of the forward and reverse reactions of $[\mathrm{PdR(OH)}]^-$ with cyanide gives the value of K_1K_2 (or β_2) for $[\mathrm{PdR(CN)_2}]^{2-}$ which is the reactive species for the forward reaction in the presence of a moderate or high concentration of cyanide. The stability of this mixed ligand complex must be quite high. The value can be calculated by an expression similar to one given by Kolski and Margerum [19] for $\mathrm{Ni(CN)_4}^{2-}$ formation reactions. For the [PdR(OH)] reaction with cyanide, the expression takes the form

$$K_1K_2 = \frac{K_4^{-1}k_{-3}\beta_4}{k_3K_{\mathrm{PdR}}} \qquad (21)$$

β_4 is the overall formation constant of $[\mathrm{Pd(CN)_4}]^{2-}$, $k_r = K_4^{-1}k_{-3}$ and K_{PdR} is the stability constant of the mono complex. The value of K_1K_2 thus calculated for $\mathrm{PdR(CN)_2}$ is 1.14 × 10^{29}. It is difficult to calculate the value of product K_1K_2 for $[\mathrm{CdR(CN)_2}]$, because of lack of knowledge about the stability constant of the [CdR] complex.

The observed positive salt effect giving $Z_AZ_B \simeq 2$ and the observed first-order dependence may indicate that either eqn. (11) or eqn. (13) could be the rate determining step in the case of the $\mathrm{CdR_2}$–CN system. The step involving $k_{\mathrm{CN}}^{\mathrm{CdR_2}}$ (eqn. (11)) has been shown by Coombs and Margerum [18] to be the slow step while studying the reaction of $\mathrm{Ni(MIDA)_2}$ and $\mathrm{Ni(IDA)_2}$ with cyanide ion (MIDA = methyliminodiacetic acid, IDA = iminodiacetic acid). Nigam *et al.* [2] have also arrived at a similar conclusion in the case of the reaction of $\mathrm{Ni(en)_2}$ with the cyanide ion. On the other hand, addition of the third cyanide has been reported to be rate determining in the case of exchange in polyamino and aminocarboxylato chelates of Ni(II) by cyanide [3, 19]. In the case of the $\mathrm{Ni(dien)_2}$–$\mathrm{CN^-}$ reaction, the value of $k_{\mathrm{CN}}^{\mathrm{NiL_2}}$ is higher than the value of k_3 at a higher cyanide concentration which indicates that $k_{\mathrm{CN}}^{\mathrm{NiL_2}}$ is not the rate determining step [2].

It has been stated in the section on effect of pH (*vide infra*) that in the case of the $[\mathrm{PdR(OH)}]^-$–$\mathrm{CN^-}$ reaction a levelling off occurs in the lower and higher

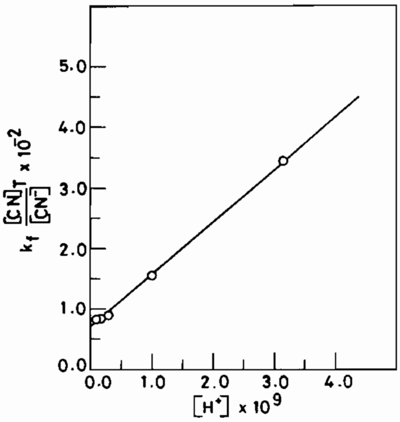

Fig. 6. Resolution of rate constants for the forward reaction of $[PdR(OH)]^-$ with cyanide ion at temperature = 25 °C and I = 0.1 M ($NaClO_4$).

pH region. The difference in reactivities of CN^- and HCN can be resolved using eqn. (22).

$$k_f[CN\}_T/[CN^-] = k_{CN} + k_{HCN}K_{HCN}[H^+] \quad (22)$$

where $[CN]_T/[CN^-] = \{1 + K_{HCN}[H^+]\}$ and K_{HCN} is the protonation constant of cyanide ion (log K_{HCN} = 9.2 at 25 °C and I = 0.1 M [21]). By plotting the left hand side of eqn. (22) versus $[H^+]$ (Fig. 6), we get a straight line. We can calculate k_{CN} and k_{HCN} from the intercept and the slope respectively (Table 5). Levelling of the rate above pH 10.75 appears to be due to hydrolytic polymerization of the $[PdR(OH)]^-$ species to give an inert polymeric species caused by the bridge forming property of the hydroxo ligand in the complex.

Similarly we can resolve the rate constants for the CdR–CN^- reaction between pH 9 and 10. In this pH range CdR exist as CdHR (pK_a = 10.5). A suitable plot for this is given in Fig. 7. The rate data above pH 10 is analysed in the following manner. At pH > 10 cyanide is present mainly as CN^- (pK_a = 9.2) while the cadmium complex is present as CdHR and CdR (pK_a = 10.5).

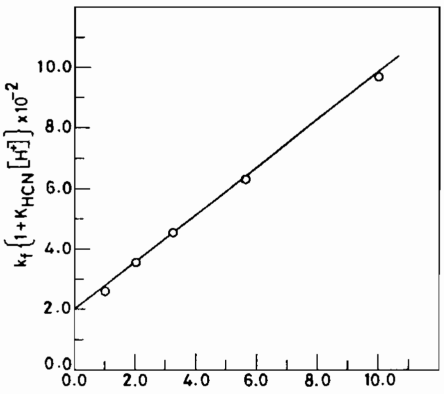

Fig. 7. Resolution of rate constants viz. k_{CN}^{CdHR} and k_{HCN}^{CdHR}.

$$\text{Rate} = k_f[CdR]_T[CN^-]$$
$$= \{[k_{CdR}[CdR] + k_{CdHR}[CdHR]\}[CN^-] \quad (23)$$

where

$$[CdR]_T = [CdR] + [CdHR]$$
$$= [CdR]\{1 + K_{CdHR}[H^+]\}$$

Therefore, $[CdR]_T/[CdR] = \{1 + K_{CdHR}[H^+]$. Thus eqn. (23) is transformed to eqn. (24)

$$k_f[CdR]_T/[CdR] = \{k^{CdR} + k^{CdHR}K_{CdHR}[H^+]\} \quad (24)$$

Transposing and dividing throughout by $[H^+]$, one obtains

$$k_f\{1 + K_{CdHR}[H^+]\}\frac{1}{[H^+]} - k_{CN}^{CdHR}K_{CdHR} = k_{CN}^{CdR}\frac{1}{[H^+]} \quad (25)$$

By plotting the left hand side of eqn. (25) versus $1/[H^+]$, we get a straight line passing through the origin (Fig. 8). A slope of this line gives the value of k_{CN}^{CdR} as 1.6 × 10^2 M^{-1} s^{-1}. All the rate constants are included in Table 5.

It is interesting to note that the reactivity of HCN is greater than CN^- towards Par complexes of Cd(II)

TABLE 5. Summary of the rate and equilibrium constant

Constant		Pd(II)	Cd(II)
K		$10^{4.9}$	
β_2			3.16 × 10^{17}
k_d	(M^{-1})	1.5 × 10^{-1}	2.0 × 10^{-1}
K_1K_2	(M^{-2})	1.14 × 10^{29}	
k_3	(M^{-1} s^{-1})	(1.96 ± 0.07) × 10^2	(1.8 ± 0.04) × 10^2
k_{CN}	(M^{-1} s^{-1})	7.0 × 10^1	2.0 × 10^2
k_{HCN}	(M^{-1} s^{-1})	5.5 × 10^1	4.9 × 10^2
$K_4^{-1}k_{-3}$	(s^{-1})	(3.82 ± 0.1) × 10^{-6}[a]	(1.75 ± 0.12) × 10^{-6}[b]

[a] At 40 ± 0.1 °C. [b] At 30 ± 0.1 °C.

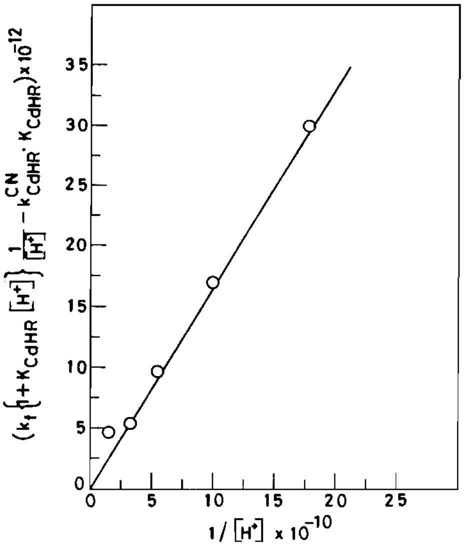

Fig. 8. Evaluation of rate constant k_{CN}^{CdR}.

as in the case of the $NiPar_2-CN^-$ [2] reaction while in case of NiL_2-CN^- reactions (L = polyaminocarboxylates) the reactivity order is reversed. It may also be mentioned that the reactivities of CdHPar are slightly higher than that of the CdPar complex.

The high activation enthalpy at low cyanide concentration (i.e. cyanide independent path) compared to high cyanide concentration (i.e. cyanide dependent path) in the $[PdR(OH)]^--CN^-$ reaction indicates the rupture of a metal–OH bond in the former process. The much less negative entropy of activation provides further support for cyanide independent dissociation in the first step (eqn. (15)) in the reaction mechanism. The large and negative entropy change for the forward reaction at high cyanide concentration and also for reverse reaction indicates the formation of a highly ordered activated complex in these cases.

In the case of the CdR_2-CN^- system, the activation parameters for the forward reaction (Table 4) indicate that the cyanide dependent dissociation (octahedral–tetrahedral transformation) is associated with low activation enthalpy but a highly negative entropy change. For reverse reaction involving a tetrahedral to octahedral conversion $\Delta H^{\neq}$ was found to be low and comparable to those reported by other workers [20] for some ligands.

In brief, the bis complex $[CdR_2]^{2-}$ and mono complex $[PdR(OH)]^-$ do not convert directly to cyano complexes of Cd(II) and Pd(II) respectively but lose one of the ligands, viz. Par in the case of Cd(II) and the hydroxy group in the case of Pd(II) before the rate determining step (eqns. (10), (11) and (15), (16)) and mixed ligand complexes of type $MR(CN)_x$ (where M = Pd(II) or Cd(II) and $x = 1$ or 2) are formed rapidly. Addition of the third cyanide constitutes the rate determining step. The fourth cyanide adds rapidly forming the tetracyano complexes of Cd(II) and Pd(II) finally.

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