Kinetics of Ligand Substitution Reaction of Some Aminopolyacetatonickel(II) Complexes with Reference to Activation Parameters

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The substitution reactions of some Ni(II)–L complexes (L: ethylenediamine-*N,N'*-diacetate, edda^{2-}; nitrilotriacetate, nta^{3-}; iminodiacetate, ida^{2-}) with 4-(2-pyridylazo)resorcinol (H_2par) have been studied spectrophotometrically at $I=0.10$. Rate constant k (mol dm^{-3}, s) at 25 °C, activation enthalpy $\Delta H^{\ne}$/kJ mol^{-1} and activation entropy $\Delta S^{\ne}$/J K^{-1} mol^{-1} are respectively: 1.7×10^3, 58.5 and 12.5 for k[Ni^{2+}][Hpar$^-$]; 4.0×10^2, 51.8 and -22 for k[Ni(nta)$^-$][Hpar$^-$]; 1.0×10^3, 41.8 and -46 for k[Ni(edda)][Hpar$^-$]; 2.7×10^{-4}, 109 and 30 for k[(par)-Ni(edda)$^{2-}$]; 5.1×10^{-3}, 88 and 17 for k[(par)Ni(Hedda)$^-$]; 1.7×10^3, 122 and 226 for k[Ni(ida)][Hpar$^-$]. In terms of activation parameters some discussions are made on the effect of coordinated ligands on the lability of leaving ligands and pre-equilibrium involving partial dissociation of leaving ligands.

Extensive investigations[1] have indicated that the ligand substitution reaction of metal chelates with multidentate ligands proceeds through an intermediate in which a central metal ion is bonded with both leaving and entering ligands and that the cleavage of the bond between the metal and leaving ligand is the rate-determining step. We have previously reported the kinetics and mechanism of ligand substitution reactions of Ni(II)–NTA and Ni(II)–EDDA complexes with PAR at 25 °C[2]**. We have pointed out on the basis of values of rate constants that the effect of ligands already present in a complex on the ease of replacement of the leaving ligand is closely related to the electron-donating properties of the ligands.[2,3] It seems worthwhile to consider the labilization of the leaving ligands by the bound ligand in terms of activation parameters.

Experimental

Preparation of all reagents except IDA, instrumentation and experimental procedure for measuring equilibria and reaction rates are the same as described previously.[2] Reagent grade IDA, obtained from Dojin-do Chemical Co., Japan, was recrystallized twice from distilled water.

Results

Ligand Substitution Reaction of the Ni(II)–EDDA Complex with PAR. The ligand substitution reaction of the ethylenediamine-*N,N'*-diacetatonickel(II) complex with 4-(2-pyridylazo)resorcinol at 17.1, 20.3, and 23.2 °C has been measured by the same method as described previously.[2] The mechanism proposed for the reaction is as follows:[2]

$$\text{Ni(edda)} + \text{Hpar}^- \xrightarrow{k_1} \text{(par)Ni(edda)}' + \text{H}^+ \qquad (1)$$

$$\begin{tikzcd}
\text{(par)Ni(edda)}^{2-} \arrow[rd, "k_2"] \arrow[dd, shift left, leftrightarrows, "+\text{H}^+"', "K^{\text{H}}_{\text{(par)Ni(Hedda)}}"] & \\
& \text{Ni(par)} + \text{edda}' \arrow[dd, "\text{fast}"', "+\text{Hpar}^-"] \\
\text{(par)Ni(Hedda)}^- \arrow[ru, "k_{2,\text{H}}"'] & \\
& \text{Ni(par)}_2{}^{2-}
\end{tikzcd} \qquad (2)$$

The rate constants and formation constants of the protonated complex at various temperatures, and the values of activation parameters are given in Table 1.

Ligand Substitution Reaction of the Ni(II)–NTA Complex with PAR. The ligand substitution reaction of the nitrilotriacetatonickel(II) complex with 4-(2-pyridylazo)resorcinol at 20.2 and 15.4 °C has been followed as described previously.[2] The reaction proceeds as follows:[2]

$$\text{Ni(nta)}^- + \text{Hpar}^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{(par)Ni(nta)}^{3-} + \text{H}^+ \qquad (3)$$

$$\text{(par)Ni(nta)}^{3-} \xrightarrow{k_2} \text{Ni(par)} + \text{nta}'$$
$$\xrightarrow[\text{fast}]{+\text{Hpar}} \text{Ni(par)}_2{}^{2-} \qquad (4)$$

Rate constants at various temperatures and activation

TABLE 1. RATE CONSTANTS FOR LIGAND SUBSTITUTION OF Ni(II)–EDDA WITH PAR, ACTIVATION PARAMETERS AND STABILITY CONSTANTS OF THE PROTONATED COMPLEX

Reaction temp/°C	$\frac{k_1}{\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}}$	k_2/s^{-1}	$k_{2,\text{H}}$/s^{-1}	$K^{\text{H}}_{\text{(par)Ni(Hedda)}}$/mol^{-1} dm^3	
17.1	6.1×10^2	8.0×10^{-5}	2.1×10^{-3}	$10^{8.06\pm0.10}$	
20.3	7.5×10^2	1.3×10^{-4}	2.6×10^{-3}	$10^{8.04\pm0.10}$	
23.2	9.0×10^2				
25.0[a]	1.0×10^3	2.7×10^{-4}	5.1×10^{-3}	$10^{8.02\pm0.10}$	
$\Delta H^{\ne}$/kJ mol^{-1}	41.8 ± 1.5	109 ± 10	88 ± 15	ΔH/kJ mol^{-1}	0 ± 10
$\Delta S^{\ne}$/J K^{-1} mol^{-1}	-46 ± 5	30 ± 30	17 ± 30	ΔS/J K^{-1} mol^{-1}	154 ± 30

a) Ref. 2.

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** Ligand abbreviations are: EDDA (H_2edda) for ethylenediamine-*N N'*-diacetic acid; NTA (H_3nta) for nitrilotriacetic acid; IDA (H_2ida) for iminodiacetic acid; PAR (H_2par) for 4-(2-pyridylazo)resorcinol.

TABLE 2. RATE CONSTANTS FOR LIGAND SUBSTITUTION OF Ni(II)-NTA WITH PAR AND ACTIVATION PARAMETERS

Reaction temp/°C	$\frac{k_1}{\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}}$	$\frac{k_1\ k_2}{k_{-1}}/\text{s}^{-1}$
15.4	1.94×10^2	2.56×10^{-6}
20.2	2.74×10^2	4.08×10^{-6}
25.0[a)]	4.00×10^2	5.26×10^{-6}
$\Delta H^{\ast}$/kJ mol^{-1}	51.8 ± 2.5	
$\Delta S^{\ast}$/J K^{-1} mol^{-1}	-22 ± 5	

a) Ref. 2.

parameters are summarized in Table 2.

Ligand Substitution Reaction of the Ni(II)-IDA Complex with PAR. We have studied the ligand substitution reaction of the bis(iminodiacetato)nickel(II) complex with PAR:

$$\text{Ni(II)-IDA} + \text{PAR} \rightleftharpoons \text{Ni(II)-PAR} + \text{IDA} \quad (5)$$

Under the present experimental conditions, the Ni(II)-IDA and Ni(II)-PAR complexes are the 1 : 2 complexes *i.e.* $\text{Ni(ida)}_2{}^{2-}$ and $\text{Ni(par)}_2{}^{2-}$, respectively. The dominant species of PAR is the monoionic species Hpar^-. Reaction (5) is so much favored to the right that the reaction of the Ni(II)-IDA complex with PAR goes to completion. The overall ligand substitution reaction is described as

$$\text{Ni(ida)}_2{}^{2-} + 2\text{Hpar}^- \longrightarrow \text{Ni(par)}_2{}^{2-} + 2\text{ida}' \quad (6)$$

where ida′ represents IDA not combined to nickel. The initial rates were analyzed. The reaction was found to be of first-order with respect to $\text{Ni(ida)}_2{}^{2-}$ and Hpar^-. Some conditional second-order rate constants are summarized in Table 3.

TABLE 3. CONDITIONAL RATE CONSTANTS FOR REACTION OF THE Ni(II)-IDA COMPLEX WITH PAR
I=0.10 (NaClO$_4$)

$\frac{C_{\text{IDA}}}{\text{mol dm}^{-3}}$	$\log\frac{[\text{H}^+]}{\text{mol dm}^{-3}}$	$\frac{k_0}{\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}}$	$\alpha_{\text{ida(H)}}/\{K^{\text{ida}}_{\text{Ni(ida)}_2}(C_{\text{IDA}}-2C_{\text{Ni}})\}$
		30.0±0.1 °C[a)]	
5.60×10^{-4}	8.631	36.0	7.94×10^{-3}
1.12×10^{-3}	8.407	28.4	6.03×10^{-3}
5.60×10^{-4}	8.908	23.5	5.01×10^{-3}
5.60×10^{-4}	9.15	18.0	3.55×10^{-3}
		25.0±0.1 °C[b)]	
1.12×10^{-3}	8.628	9.50	4.17×10^{-3}
1.12×10^{-3}	9.062	5.17	1.95×10^{-3}
1.12×10^{-3}	8.926	7.43	2.46×10^{-3}
1.12×10^{-3}	8.163	22.0	1.07×10^{-2}
5.60×10^{-4}	8.851	12.6	5.62×10^{-3}
		19.3±0.1 °C[a)]	
5.60×10^{-4}	8.203	13.0	2.29×10^{-2}
5.60×10^{-4}	8.656	6.50	8.91×10^{-3}
5.60×10^{-4}	8.909	5.60	5.62×10^{-3}
5.60×10^{-4}	9.148	4.05	3.72×10^{-3}
1.12×10^{-3}	7.736	16.9	3.16×10^{-2}
1.12×10^{-3}	8.988	2.92	2.34×10^{-3}
		14.1±0.2 °C[a)]	
5.60×10^{-4}	8.248	8.29	2.29×10^{-2}
5.60×10^{-4}	8.701	4.05	8.71×10^{-3}
5.60×10^{-4}	8.977	3.2	5.13×10^{-3}
5.60×10^{-4}	9.169	2.7	3.63×10^{-3}
5.60×10^{-4}	9.209	2.7	3.47×10^{-3}
5.60×10^{-4}	8.453	6.7	1.48×10^{-2}

a) $C_{\text{Ni}}=1.02\times10^{-5}$, $C_{\text{PAR}}=1.00\times10^{-4}$ mol dm^{-3}.
b) $C_{\text{Ni}}=5.09\times10^{-6}$, $C_{\text{PAR}}=5.00\times10^{-5}$ mol dm^{-3}.

The dependence of IDA concentration on the conditional rate constant points to predissociation of IDA in $\text{Ni(ida)}_2{}^{2-}$ because the values of the rate constant decrease with increasing concentration of IDA and $-\log\,[\text{H}^+]$. We assume the following reaction scheme:

$$\text{Ni(ida)}_2{}^{2-} \rightleftharpoons \text{Ni(ida)} + \text{ida}' \quad (7)$$

$$\text{Ni(ida)} + \text{Hpar}^- \xrightarrow{k_2} \text{Ni(par)} \xrightarrow[\text{fast}]{+\text{Hpar}^-} \text{Ni(par)}_2{}^{2-} \quad (8)$$

Then the rate equation of the formation of $\text{Ni(par)}_2{}^{2-}$ is given by

$$\begin{aligned}\text{Rate} &= k_2[\text{Ni(ida)}][\text{Hpar}^-]\\ &= k_2\frac{\alpha_{\text{ida(H)}}}{K^{\text{ida}}_{\text{Ni(ida)}_2}(C_{\text{IDA}}-2C_{\text{Ni}})}[\text{Ni(ida)}_2{}^{2-}][\text{Hpar}^-] \quad (9)\end{aligned}$$

where C_{IDA} and C_{Ni} are the total concentrations of IDA and nickel ion, respectively, and $\alpha_{\text{ida(H)}}=1+K^{\text{H}}_{\text{Hida}}[\text{H}^+]+K^{\text{H}}_{\text{Hida}}K^{\text{H}}_{\text{H}_2\text{ida}}[\text{H}^+]^2$.* The conditional rate constants are plotted against the values of $\alpha_{\text{ida(H)}}/\{K^{\text{ida}}_{\text{Ni(ida)}_2}(C_{\text{IDA}}-2C_{\text{Ni}})\}$ in Fig. 1. The non-zero intercept in the plot indicates another reaction path not involving predissociation of IDA in $\text{Ni(ida)}_2{}^{2-}$. The reaction, therefore, proceeds through two parallel reaction paths for which the following rate equation can be deduced:

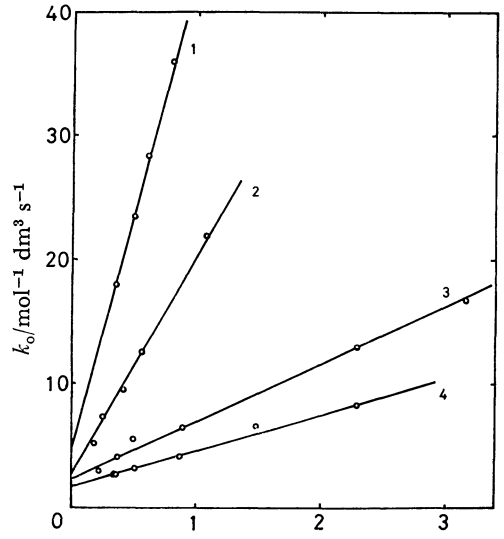

Fig. 1. Dependence of k_0 on the function $\alpha_{\text{ida(H)}}/\{K^{\text{ida}}_{\text{Ni(ida)}_2}(C_{\text{IDA}}-2C_{\text{Ni}})\}$.
Reaction temp/°C, 1: 30.0; 2: 25.0; 3: 19.3; 4: 14.1.

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* $K^{\text{ida}}_{\text{Ni(ida)}_2}=[\text{Ni(ida)}_2{}^{2-}]/\{[\text{Ni(ida)}][\text{ida}^{2-}]\}$, $K^{\text{H}}_{\text{Hida}}=[\text{Hida}^-]/\{[\text{ida}^{2-}][\text{H}^+]\}$, $K^{\text{H}}_{\text{H}_2\text{ida}}=[\text{H}_2\text{ida}]/\{[\text{Hida}^-][\text{H}^+]\}$. The values for these stability constants at a given temperature are available (G. Anderegg *Helv. Chim. Acta*, **47**, 1801 (1964)).

$$\frac{\mathrm{d}[\mathrm{Ni(par)_2}^{2-}]}{\mathrm{d}t} = k_1[\mathrm{Ni(ida)_2}^{2-}][\mathrm{Hpar}^-] + k_2[\mathrm{Ni(ida)}][\mathrm{Hpar}^-] = \left\{k_1 + \frac{k_2\alpha_{\mathrm{ida(H)}}}{K^{\mathrm{ida}}_{\mathrm{Ni(ida)_2}}(C_{\mathrm{IDA}}-2C_{\mathrm{Ni}})}\right\} \times [\mathrm{Ni(ida)_2}^{2-}][\mathrm{Hpar}^-] \tag{10}$$

Thus the observed second-order rate constant k_0 is equal to $k_1+k_2\alpha_{\mathrm{ida(H)}}/\{K^{\mathrm{ida}}_{\mathrm{Ni(ida)_2}}(C_{\mathrm{IDA}}-2C_{\mathrm{Ni}})\}$. Rate constants at various temperatures are tabulated in Table 4.

TABLE 4. RATE CONSTANTS FOR LIGAND SUBSTITUTION OF Ni(II)-IDA WITH PAR AND ACTIVATION PARAMETERS

Reaction temp/°C	k_1 / mol^{-1} dm^3 s^{-1}	k_2 / mol^{-1} dm^3 s^{-1}
14.1	≈1.6	2.9×10^2
19.3	≈2.1	4.8×10^2
25.0	≈3.0	1.7×10^3
30.0	≈4.5	3.8×10^3
$\Delta H^{\neq}$/kJ mol^{-1}		122±15
$\Delta S^{\neq}$/J K^{-1} mol^{-1}		226±50

Activation parameters for k_2 are 121±15 kJ mol^{-1} for the activation enthalpy and 226±50 J K^{-1} mol^{-1} for the activation entropy. Activation parameters for k_1 are not evaluated because of uncertainty.

TABLE 5. THERMODYNAMIC PARAMETERS FOR NICKEL COMPLEXES

Ligand	N_xO_y	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	log K (25 °C)	Ref.
NH_3	N_1	−17	−2	2.83	c
Acetate	O_1	0	8	0.41	d
en	N_2	−38.7	14	7.49	e
Oxalate	O_2	1.3	1.0×10^2	5.16	f
Glycinate	N_1O_1	−18.3	56	6.13	g
IDA	N_1O_2	−21.1	84	8.07	h
MIDA[a]	N_1O_2	−20	1.0×10^2	8.67	i
NTA	N_1O_3	−10.6	1.8×10^2	11.49	j
EDDA	N_2O_2	−41.8	1.2×10^2	13.65	k
HEDTA[b]	N_2O_3	−43.1	1.9×10^2	17.1	l
EDTA	N_2O_4	−36	2.4×10^2	18.7	l

a) Methyliminodiacetic acid. b) *N*′-(2-Hydroxyethyl)-ethylenediamine-*N*,*N*,*N*′-triacetic acid. c) K.B. Yatsimirskii and P.M. Milyukov, *Zh. Fiz. Khim.*, **31**, 843 (1957). d) Calculated from the data (N. Tanaka and K. Kato, *Bull. Chem. Soc. Jpn.*, **32**, 516 (1959)). e) F. Holmes and D. R. Williams, *J. Chem. Soc., A*, **1967**, 1702. f) A. McAuley and G. H. Nancollas, *J. Chem. Soc.*, **1961**, 2215. g) R.M. Izatt, H.D. Johnson, and J. J. Christensen, *J. Chem. Soc., Dalton Trans.*, **1972**, 1152. h) G. Anderegg, *Helv. Chim. Acta*, **47**, 1801 (1964). i) G. Anderegg, *Helv. Chim. Acta*, **48**, 1718 (1965). j) J.A. Hull, R.H. Davies, and L. A. K. Staveley, *J. Chem. Soc.*, **1964**, 5422. k) G. Degischer and G. H. Nancollas, *Inorg. Chem.*, **9**, 1259 (1970). l) D.L. Wright, J.H. Holloway, and C.N. Reilley, *Anal. Chem.*, **37**, 884 (1965).

Discussion

In order to estimate thermodynamic parameters for pre-equilibrium of partial dissociation preceding the rate-determining steps in substitution, we need to consider thermodynamic parameters for some nickel complexes.

Thermodynamic parameters for some nickel complexes are given in Table 5 where the data are presented in the order of numbers of available coordination sites; N_xO_y represents a ligand having x nitrogen atoms and y oxygen atoms for coordination. The data in Table 5 illustrate a striking difference between ΔH and ΔS values for nitrogen and oxygen donors. The Ni(edda) complex is formed with exothermic enthalpy similar to that of the $\mathrm{Ni(en)^{2+}}$ complex and the stability constant of the former is larger than that of the latter due to the contribution of positive entropy for chelation of carboxylates. The ΔH values for nitrogen coordination are appreciably more exothermic and constitute the major portion of ΔH. The contribution of nickel–carboxylate bonds to the total ΔH values is very small (see values for acetate and oxalate in Table 5). Interactions with carboxylate groups, being of a more electrostatic character, would be expected to have only a small and probably endothermic effect. It is possible to estimate approximate values for the contribution made by each nickel–nitrogen bond and each nickel–oxygen bond by assuming additivity. We can deduce the ΔH and ΔS values per coordinated nitrogen atom to be about 20 kJ mol^{-1} and about 0 J K^{-1} mol^{-1}, respectively, and per coordinated oxygen atom which forms a chelate ring, about 0 kJ mol^{-1} and 40—60 J K^{-1} mol^{-1}, respectively.

Results in the present study are summarized in Table 6. The rate-determining step of reactions A, B, and C (Table 6) is the dissociation of a water molecule coordinated to nickel(II). We have previously pointed

TABLE 6. ACTIVATION PARAMETERS FOR REACTIONS OF SOME NICKEL(II) COMPLEXES

Reaction (Equation number in the text)	Rate equation	Reaction product	Rate constant at 25 °C k(mol dm^{-3}, s)	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}
A[a]	$k[\mathrm{Ni^{2+}}][\mathrm{Hpar^-}]$	$\mathrm{Ni(par)_2}^{2-}$	1.7×10^3	58.5± 2.5	12.5± 5
B (Eq. 3)	$k[\mathrm{Ni(nta)^-}][\mathrm{Hpar^-}]$	(par)Ni(nta)	4.0×10^2	51.8± 2.5	−22 ± 5
C (Eq. 1)	$k[\mathrm{Ni(edda)}][\mathrm{Hpar^-}]$	(par)Ni(edda)′	1.0×10^3	41.8± 1.5	−46 ± 5
D (Eq. 2)	$k[\mathrm{(par)Ni(edda)^{2-}}]$	$\mathrm{Ni(par)_2}^{2-}$	2.7×10^{-4}	109 ±10	30 ±30
E (Eq. 2)	$k[\mathrm{(par)Ni(Hedda)^-}]$	$\mathrm{Ni(par)_2}^{2-}$	5.1×10^{-3}	88 ±15	17 ±30
F (Eq. 8)	$k[\mathrm{Ni(ida)}][\mathrm{Hpar^-}]$	$\mathrm{Ni(par)_2}^{2-}$	1.7×10^3	122 ±15	226 ±50

a) Ref. 3. (The values of k at 20.0 and 15.4 °C are 1.25×10^3 and 8.43×10^2 mol^{-1} dm^3 s^{-1}, respectively.)

out that there should be the dissociation of one donor oxygen atom of the coordinated ligand in the Ni–NTA and Ni–EDDA complexes before the incoming ligand (PAR) can gain a coordination foothold.[2] The $\Delta S^{\neq}$ value for reactions B and C which is more negative than that for reaction A is attributable to the dissociation of a carboxylate at the pre-equilibrium step. On the other hand, as the contribution of such dissociation of carboxylate to $\Delta H^{\neq}$ may be regarded as about 0 kJ mol^{-1} (*vide supra*), the decrease in $\Delta H^{\neq}$ in going from reaction A to B and C supports the view that the labilization of the remaining water molecules by the bound ligands is closely related to the electron-donating properties of the latter ligands: when a ligand coordinated to the central metal ion donates electrons to the central metal to a greater extent, the bond of the central metal with the remaining coordinated water molecules will be weakened and more easily broken.

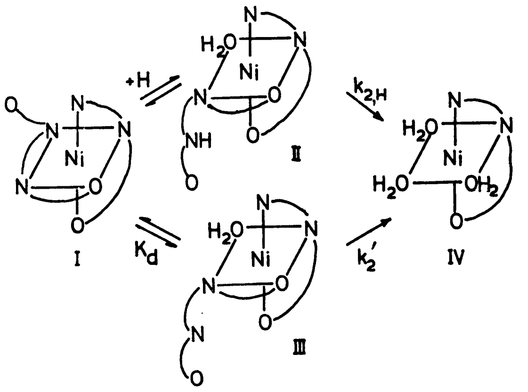

Fig. 2. Proposed reaction mechanism for the dissociation of the intermediate. EDDA and PAR are symbolized as O–N–N–O and N–N–O, respectively. Charges are omitted.

In our previous paper,[2] it was pointed out that judging from the stability constants of EDDA[4]: [Hedda$^-$]/{[edda^{2-}][H$^+$]}$=10^{9.57}$ and [H$_2$edda]/{[Hedda$^-$][H$^+$]}$=10^{6.48}$, the proton in the protonated complex (II in Fig. 2) should be attached to a nitrogen atom in the EDDA which is the most basic. In this work, we determined the values of the stability constants of the protonated complex at 17.1 and 20.3 °C which are the same as the value at 25.0 °C within an experimental error (Table 1). This indicates that the enthalpy for reaction I→II in Fig. 2 is zero kJ mol^{-1}. All the enthalpies for the protonation of nitrogen atoms in MIDA, NTA, and EDDA are approximately -30 kJ mol^{-1}.[5] Taking into account the fact that the contribution of nickel–carboxylate bonds to the total enthalpy values is rather small, the enthalpy for detaching a nitrogen atom in the (par)Ni(edda)$^{2-}$ complex seems to be about 30 kJ mol^{-1}. In reaction I→II in Fig. 2, the endothermic enthalpy for detaching a nitrogen–nickel bond is compensated by the exothermic enthalpy for binding a proton to a nitrogen atom, and so the net enthalpy change for reaction I→II may be nearly zero kJ mol^{-1}.

It may be of interest to examine the difference in rates between reactions D and E from kinetic and mechanistic point of view. The difference in activation parameters for k_2 (reaction D in Table 6) and $k_{2,\mathrm{H}}$ (reaction E in Table 6) is explained on the basis of the equilibria preceding rate-determining steps. If we accept a possible mechanism given in Fig. 2, k_2 is given as follows

$$k_2 = K_\mathrm{d}k_2'$$

where K_d is the equilibrium constant between I and III and k_2' is a rate constant for the rate-determining step (III→IV). The first Ni–N bond rupture (I→III) would require an energy corresponding to $\Delta H \approx 20$ kJ mol^{-1} and $\Delta S \approx 0$ J K^{-1} mol^{-1}. This is consistent with our experimental data of the activation parameters for $k_{2,\mathrm{H}}$ (II→IV) and k_2' (III→IV) within error limits.

In the substitution of the Ni(II)–IDA complex with PAR, the formation of a mixed-ligand intermediate involving both IDA and PAR could not be observed. However, by analogy with the EDDA and NTA systems, it seems reasonable to speculate that the reaction for the IDA system also proceeds through an intermediate with both leaving and entering ligands. Then the k_2 process in Eq. 10 corresponds to an overall reaction involving formation of the mixed-ligand intermediate and dissociation of the leaving ligand IDA from the intermediate. The large activation enthalpy for reaction F in Table 6 is close to the sum of the activation enthalpies for reactions B (or C) and E: the intermediate is not so stable. The large enthaly of activation for reaction F is largely offset by an exceptionally large entropy of activation. But sufficient information is not available to explain such a remarkably positive entropy of activation.

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