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Kinetics of the Ligand Substitution Reactions of Tetrahedral Complexes $[Co(NN)(hmpa)_2]^{2+}$ ($NN=2,2'$-Bipyridine, 4,4′-Dimethyl-2,2′-bipyridine, or 1,10-Phenanthroline) in Hexamethylphosphoric Triamide, Nitrobenzene, Acetone, 1,2-Dichloroethane, and Nitromethane

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The substitution reaction rates of hexamethylphosphoric triamide (HMPA) for NN (NN=2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dmbpy), or 1,10-phenanthroline (phen)) on tetrahedral complexes $[Co(NN)(hmpa)_2]^{2+}$ were determined spectrophotometrically in pure HMPA or in nitrobenzene, acetone, 1,2-dichloroethane, and nitromethane at various concentrations of HMPA, for the purpose of clarifying the reaction mechanism and the effect of the bulkiness of HMPA. The ligand substitution reaction on bpy and dmbpy complexes proceeds simply *via* a dissociative mechanism in nitrobenzene. In inert solvents other than nitrobenzene, it proceeds in parallel *via* two simultaneous paths of both dissociative and associative mechanisms. In the case of the phen complex, the reaction proceeds only by a dissociative mechanism in pure HMPA and in all the inert solvents used. The activation enthalpies and the activation entropies of the dissociative mechanism of bpy and dmbpy complexes were (80—90) $kJ\ mol^{-1}$ and approximately zero $J\ K^{-1}\ mol^{-1}$, respectively, in all the solvents used. Those for the phen complex were (86—101) $kJ\ mol^{-1}$ and (−16—+36) $J\ K^{-1}\ mol^{-1}$, respectively, while those of the associative mechanism for bpy and dmbpy complexes in all the solvents used except nitrobenzene were (50—65) $kJ\ mol^{-1}$ and large negative values, respectively. Whether the substitution proceeds by the dissociative mechanism or by the associative one, both the steric and the solvent effects appear seriously, because HMPA is a bulky ligand and had a large dipole moment.

There are few accumulated kinetic data for reactions involving ligand substitution in tetrahedral complexes,[1] although those in octahedral ones[2] have been profoundly investigated. This is probably due to their fast reaction rates in the former complexes caused by the small crystal field stabilization. The measurements were made by NMR,[3–5] temperature jump,[6] *etc.*, and the thermodynamic requirements have severely restricted their studies.

We recently reported that hexamethylphosphoric triamide (HMPA) has a tendency to form complexes of a tetrahedral configuration.[7,8] In this paper, we measured spectrophotometrically the substitution reaction rates of HMPA for NN (NN=2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dmbpy), or 1,10-phenanthroline (phen)) on the tetrahedral complexes $[Co(NN)(hmpa)_2]^{2+}$ in pure HMPA and in nitrobenzene, acetone, 1,2-dichloroethane, and nitromethane at various concentrations of HMPA for the purpose of clarifying the reaction mechanism and the effect of the bulkiness of HMPA on the mechanism. The reaction rates were successfully measured by the conventional technique because, in general, bidentate ligands are exchanged more slowly than unidentate ones. The flexibilities of ligand molecules vary among bpy, dmbpy, and phen. Therefore, when one of those ligands is exchanged with HMPA which is more bulky than the original ligand, the reaction mechanism is strongly affected by the nature of the original ligands. When the reaction proceeds by an associative mechanism, the solvent effect may be stronger than for a dissociative mechanism.

Experimental

Materials. $[Co(hmpa)_4](ClO_4)_2$ and $[Cu(hmpa)_4](ClO_4)_2$ were prepared by methods described in the literature.[9,10] The recrystallizations of $NaClO_4$ and bpy were carried out by procedures we have described previously.[7] Anhydrous phen and dmbpy were used without further purification. The purifications of HMPA and nitromethane were carried out according to our previous description. Nitrobenzene and 1,2-dichloroethane were dried over calcium chloride and molecular sieves 4A, and then distilled under reduced pressure and at atmospheric pressure, respectively. Acetone was dried over calcium sulfate and molecular sieves 4A, and then distilled at atmospheric pressure.

Rate Measurements. The complex $[Co(NN)(hmpa)_2]^{2+}$ was prepared by mixing appropriate amounts of $[Co(hmpa)_4]^{2+}$ and bpy, dmbpy, or phen in HMPA or in one of the inert solvents in advance. The reaction was then initiated by mixing a solution of $[Co(NN)(hmpa)_2]^{2+}$ with a solution of $[Cu(hmpa)_4]^{2+}$ at a concentration in excess of the concentration of $[Co(NN)(hmpa)_2]^{2+}$ in a given solvent. The NN liberated by substitution was removed from the reaction system by its rapid complexation with $[Cu(hmpa)_4]^{2+}$. The reaction rate was followed by observing the increase in the absorbance at 580 nm using a Shimadzu Model UV-200S Spectrophotomer with a thermostated cell compartment. The ionic strength was adjusted at 0.06 $mol\ dm^{-3}$ with sodium perchlorate or tetraethylammonium perchlorate.

Results and Discussion

Absorption Spectra of $[Co(dmbpy)(hmpa)_2]^{2+}$ and $[Co(phen)(hmpa)_2]^{2+}$ in HMPA and in Inert Solvents. As shown in Fig. 1, the absorption spectra of both $[Co(dmbpy)(hmpa)_2]^{2+}$ in HMPA and $[Co(phen)(hmpa)_2]^{2+}$ in acetone are quite similar to that of $[Co(bpy)(hmpa)_2]^{2+}$ in HMPA, which is already reported to be tetrahedral.[8] Therefore, $[Co(dmbpy)(hmpa)_2]^{2+}$ and $[Co(phen)(hmpa)_2]^{2+}$ in the respective solvents are deduced to be also tetrahedral. In other solvents, the same results were obtained.

Rate Constants of the Substitution Reaction. In any of the solvents used, the reaction obeys Eq. 1 under the

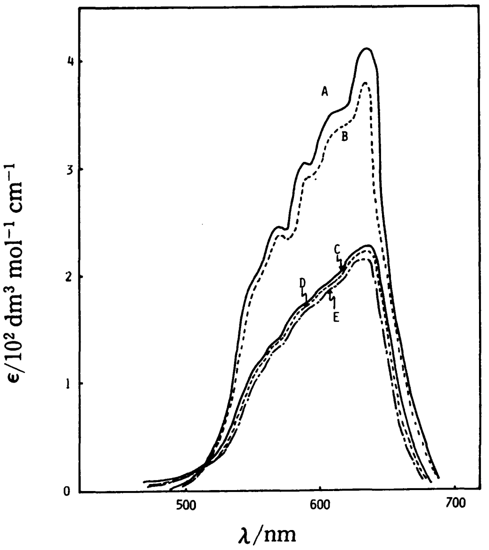


Fig. 1. Absorption spectra of $[Co(hmpa)_4]^{2+}$ in acetone (A: ——) and in HMPA (B: ----), and $[Co(dmbpy)(hmpa)_2]^{2+}$ in HMPA (C: ——), $[Co(phen)(hmpa)_2]^{2+}$ in acetone (D: ----), and $[Co(bpy)(hmpa)_2]^{2+}$ in HMPA (E: -·-·-).

Table 1. The dependence of k_{obsd} on [Cu(II)] at $[[Co(bpy)(hmpa)_2]^{2+}] = 8\times10^{-4}$ mol dm^{-3} in HMPA

$\frac{[[Cu(hmpa)_4]^{2+}]}{10^{-2}\,\mathrm{mol\,dm^{-3}}}$	$\frac{T}{°C}$	$\frac{k_{obsd}}{10^{-2}\,\mathrm{s^{-1}}}$
2.00	16.0	1.58
2.00	16.0	1.35
2.00	20.0	2.30
2.00	20.0	2.70
0.50	25.0	3.39
1.00	25.0	3.90
1.50	25.0	3.30
1.50	25.0	3.27
2.00	25.0	3.93
2.00	25.0	3.21
2.00	25.0	3.29
2.00	25.0	3.10
2.00	25.0	3.10
2.00	29.0	4.43
2.00	29.0	4.43
2.00	29.0	4.55
2.00	34.0	7.02

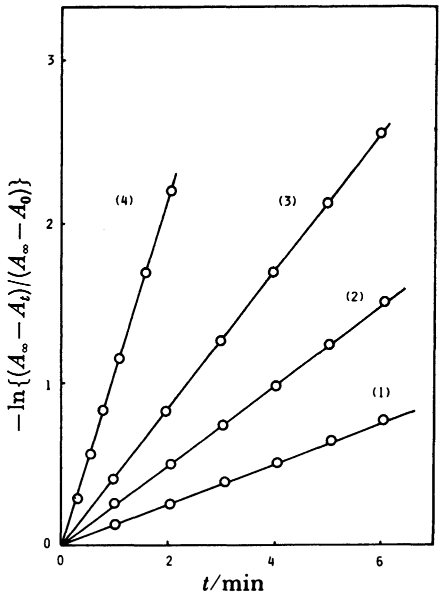


Fig. 2. Plots of $-\ln(A_\infty-A_t)/(A_\infty-A_0)$ *vs.* t at $[Co(II)] = 8\times10^{-4}$ mol dm^{-3} and $[Cu(II)] = 1.0\times10^{-2}$ mol dm^{-3} for the dmbpy complex in HMPA. Temperatures are (1) 15°C, (2) 20°C, (3) 25°C, and (4) 30 °C.

condition of [Cu(II)] of a large excess over $[Co(II)] = 8\times10^{-4}$ mol dm^{-3},

$$\ln(A_\infty-A_t)/(A_\infty-A_0) = -k_{obsd}t, \tag{1}$$

where A_0, A_t, and A_∞ are the absorbances at 580 nm at times 0, t, and infinity, respectively, and k_{obsd} is the observed first-order rate constant. An example of the linear relationship based on Eq. 1 is shown in Fig. 2. The measured absorbances need not be corrected because the disappearing $[Cu(hmpa)_4]^{2+}$ and the produced Cu(II)–NN complex exhibit an isosbestic point at 580 nm. In all the solvents used, k_{obsd} was independent of [Cu(II)]; the experimental results in the case of the bpy complex in HMPA are given in Table 1. Essentially similar data were also obtained in the other solvents. Since the liberated NN reacts rapidly with $[Cu(hmpa)_4]^{2+}$, the following Reaction 2 and the rate equation 3 are deduced.

$$[Co(NN)(hmpa)_2]^{2+} + 2hmpa \xrightarrow{k_{obsd}} [Co(hmpa)_4]^{2+} + NN, \tag{2}$$

$$-\frac{d[[Co(NN)(hmpa)_2]^{2+}]}{dt} = k_{obsd}[[Co(NN)(hmpa)_2]^{2+}]. \tag{3}$$

Dependence of k_{obsd} *on the HMPA Concentration and Reaction Mechanism.* The dependence of k_{obsd} on the HMPA concentration in the inert solvents can be classified into the following three types as shown in Figs. 3—5.

Type 1): As is shown in Fig. 3, k_{obsd} at first increases with increase in HMPA concentration and then reaches a constant value above a certain concentration of HMPA; this trend is also seen for the bpy and dmbpy complexes in nitrobenzene and for the phen complex in acetone, nitrobenzene, and nitromethane.

Type 2): The value of k_{obsd} is independent of the HMPA concentration in the case of the phen complex in 1,2-dichloroethane as shown in Fig. 4.

Type 3): The correlation of k_{obsd} with the concentration of HMPA can be empirically expressed by the sum of two terms; the zeroth and the first order with respect to the HMPA concentrations.

$$k_{obsd} = k_d + k_a[hmpa] \tag{4}$$

This is seen in the cases for the bpy and dmbpy complexes in acetone, 1,2-dichloroethane, and nitromethane; the examples for the bpy complex are shown in Fig. 5.

Judging from the above features of the reaction, two mechanisms may be considered for the substitution reaction of NN with $[Co(NN)(hmpa)_2]^{2+}$. One is a

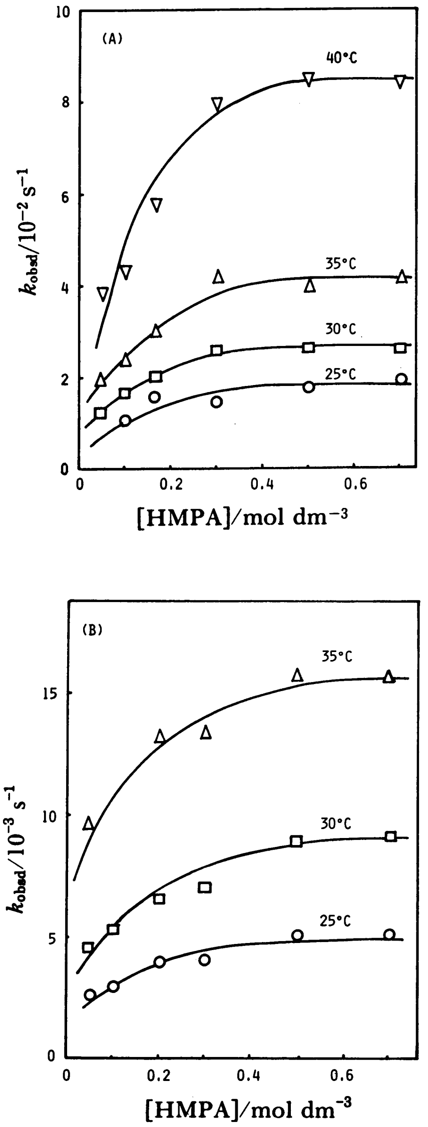


Fig. 3. The dependence of k_{obsd} on the HMPA concentration for the bpy (A) and dmbpy (B) complexes in nitrobenzene at 25 °C (○), 30 °C (□), 35 °C (△), and 40 °C (▽).

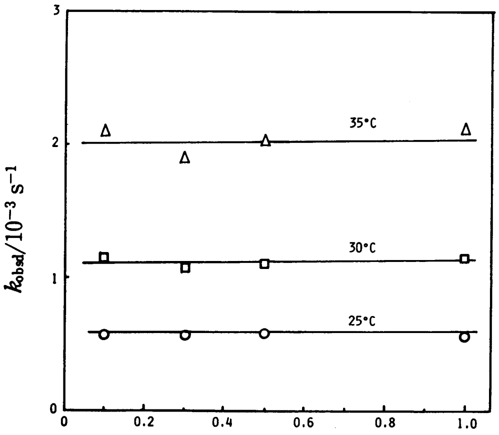


Fig. 4. The dependence of k_{obsd} on the HMPA concentration for the phen complex in 1,2-dichloroethane at 25 °C (○), 30 °C (□), and 35 °C (△).

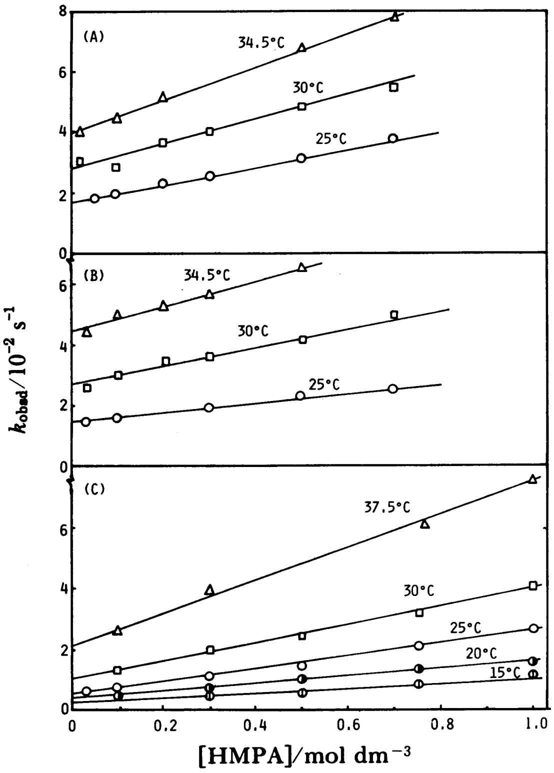
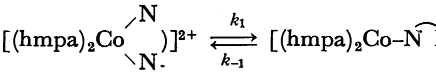


Fig. 5. The dependence of k_{obsd} on the HMPA concentration for the bpy complex in acetone (A), 1,2-dichloroethane (B), and nitromethane (C) at 15 °C (◐), 20 °C (◑), 25 °C (○), 30 °C (□), and 34.5 °C or 37.5 °C (△).

dissociative mechanism, in which one of the two cobalt-nitrogen bonds is first broken, followed by the reaction of the three-coordinated intermediate with an HMPA. The other is an associative mechanism, in which Co(II) first reacts with an HMPA, resulting in a five-coordinated intermediate.

The following reaction scheme may be valid when the substitution reaction proceeds by the dissociative mechanism.



$$[(\mathrm{hmpa})_2\mathrm{Co}\overset{\diagup \mathrm{N}}{\underset{\diagdown \mathrm{N}}{\quad}})]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [(\mathrm{hmpa})_2\mathrm{Co}\text{-}\mathrm{N}\frown\mathrm{N}]^{2+} \qquad (5)$$

$$[(\mathrm{hmpa})_2\mathrm{Co}\text{-}\mathrm{N}\frown\mathrm{N}]^{2+} + \mathrm{hmpa} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [(\mathrm{hmpa})_3\mathrm{Co}\text{-}\mathrm{N}\frown\mathrm{N}]^{2+} \qquad (6)$$

$$[(\mathrm{hmpa})_3\mathrm{Co}\text{-}\mathrm{N}\frown\mathrm{N}]^{2+} + \mathrm{hmpa} \xrightarrow{k_3} [(\mathrm{hmpa})_4\mathrm{Co}]^{2+} + \mathrm{NN} \qquad (7)$$

Application of the steady-state method to the unstable intermediates, $[(\mathrm{hmpa})_2\mathrm{Co}\text{–}\widehat{\mathrm{NN}}]^{2+}$ and $[(\mathrm{hmpa})_3\mathrm{Co}\text{–}\widehat{\mathrm{NN}}]^{2+}$, leads to Eq. 8.

$$k_{obsd} = \frac{k_1k_2k_3[\mathrm{hmpa}]^2}{k_{-1}k_{-2} + k_{-1}k_3[\mathrm{hmpa}] + k_2k_3[\mathrm{hmpa}]^2} \qquad (8)$$

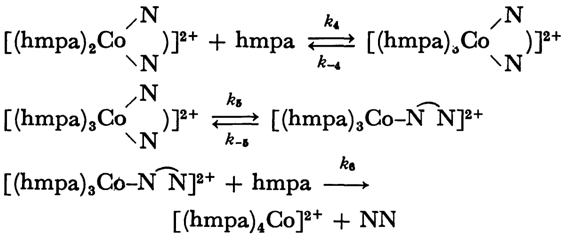
By rearranging Eq. 8, the following equation is derived;

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2}\frac{1}{[\mathrm{hmpa}]} + \frac{k_{-1}k_{-2}}{k_1k_2k_3}\frac{1}{[\mathrm{hmpa}]^2}. \qquad (9)$$

On the other hand, for the associative mechanism, Reactions 10—12 are considered.

Table 2. Rate constants at 25 °C, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of the dissociative mechanism and the associative mechanism for bpy, dmbpy, and phen complexes in HMPA, nitrobenzene, acetone, 1,2-dichloroethane, and nitromethane

Ligand	Solvent	Dissociative mechanism			Associative mechanism		
		$k_d(=k_1)$ / $10^{-3}\,\mathrm{s^{-1}}$	$\Delta H_1^{\ddagger}$ / $\mathrm{kJ\,mol^{-1}}$	$\Delta S_1^{\ddagger}$ / $\mathrm{J\,K^{-1}\,mol^{-1}}$	$k_a\left(=\frac{k_4k_5}{k_{-4}+k_5}\right)$ / $10^{-3}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$	$\Delta H_a^{\ddagger}$ / $\mathrm{kJ\,mol^{-1}}$	$\Delta S_a^{\ddagger}$ / $\mathrm{J\,K^{-1}\,mol^{-1}}$
bpy	HMPA	(14)	(85)	(+7)	(3)	(55)	(−105)
	Nitrobenzene	14.5	89.2	+13.4	—	—	—
	Acetone	13.4	80.8	−9.6	32.1	50.7	−81.6
	1,2-Dichloroethane	13.0	85.8	+8.4	14.3	65.3	−60.7
	Nitromethane	6.0	87.5	+3.8	25.7	61.5	−72.0
dmbpy	HMPA	6.64	89.2	+11.7	—	—	—
	Nitrobenzene	5.53	83.3	−1.7	—	—	—
	Acetone	5.60	84.6	−5.0	10.1	63.2	−71.2
	1,2-Dichloroethane	4.50	85.0	−5.4	7.86	54.0	−103.4
	Nitromethane	2.28	89.2	+2.9	6.57	52.3	−111.3
phen	HMPA	0.680	97.1	+20.5	—	—	—
	Nitrobenzene	0.862	90.4	0.0	—	—	—
	Acetone	0.654	86.7	−16.3	—	—	—
	1,2-Dichloroethane	0.580	96.7	+16.7	—	—	—
	Nitromethane	0.555	100.9	+36.2	—	—	—



$$[(\mathrm{hmpa})_2\mathrm{Co}\langle{}^{\mathrm{N}}_{\mathrm{N}}\rangle)]^{2+} + \mathrm{hmpa} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [(\mathrm{hmpa})_3\mathrm{Co}\langle{}^{\mathrm{N}}_{\mathrm{N}}\rangle)]^{2+} \tag{10}$$

$$[(\mathrm{hmpa})_3\mathrm{Co}\langle{}^{\mathrm{N}}_{\mathrm{N}}\rangle)]^{2+} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [(\mathrm{hmpa})_3\mathrm{Co{-}}\widehat{\mathrm{N\ N}}]^{2+} \tag{11}$$

$$[(\mathrm{hmpa})_3\mathrm{Co{-}}\widehat{\mathrm{N\ N}}]^{2+} + \mathrm{hmpa} \xrightarrow{k_6} [(\mathrm{hmpa})_4\mathrm{Co}]^{2+} + \mathrm{NN} \tag{12}$$

Again, by use of the steady-state method for $[(\mathrm{hmpa})_3\text{-}\mathrm{Co}\langle{}^{\mathrm{N}}_{\mathrm{N}})]^{2+}$ and $[(\mathrm{hmpa})_3\mathrm{Co{-}}\widehat{\mathrm{NN}}]^{2+}$, k_{obsd} is expressed by the following equation 13.

$$k_{\mathrm{obsd}} = \frac{k_4k_5k_6[\mathrm{hmpa}]^2}{k_{-4}k_{-5}+(k_{-4}+k_5)k_6[\mathrm{hmpa}]} \tag{13}$$

By rearranging Eq. 13, Eq. 14 holds;

$$\frac{1}{k_{\mathrm{obsd}}} = \frac{k_{-4}+k_5}{k_4k_5}\,\frac{1}{[\mathrm{hmpa}]} + \frac{k_{-4}k_{-5}}{k_4k_5k_6}\,\frac{1}{[\mathrm{hmpa}]^2}. \tag{14}$$

If the plots of $1/k_{\mathrm{obsd}}$ *vs.* $1/[\mathrm{hmpa}]$ are linear without passing the origin, the reaction may proceed by the dissociative mechanism with the third term on the right-hand side in Eq. 9 negligibly small. Examples are seen in the case of the dmbpy complex in nitrobenzene and the phen complex in acetone of the Type 1 as shown in Fig. 6. Essentially similar data are obtained in other solvents. Therefore, the reaction of Type 1 proceeds by the dissociative mechanism. Accordingly, k_1 and k_{-1}/k_2 can be obtained, respectively, from the intercept and slope of the straight line. These results are summarized, respectively, in Tables 2 and 3.

In the case of Type 2, plotting $1/k_{\mathrm{obsd}}$ *vs.* $1/[\mathrm{hmpa}]$ will give a straight line parallel to the abscissa, and therefore this type of the reaction can be deduced to proceed through the dissociative mechanism with k_{-1}/k_2 nearly equal to zero. Thus, k_{obsd} becomes nearly equal to k_1, suggesting that Reaction 5 is the rate-determining step in the dissociative mechanism.

Table 3. The values of k_{-1}/k_2 for bpy, dmbpy, and phen complexes in nitrobenzene, acetone, and nitromethane at 25 °C, 30 °C, and 35 °C

Ligand	Solvent	k_{-1}/k_2 / $\mathrm{mol\,dm^{-3}}$ 25 °C	30 °C	35 °C
bpy	Nitrobenzene	0.076	0.067	0.080
dmbpy	Nitrobenzene	0.053	0.049	0.032
phen	Nitrobenzene	0.048	0.081	0.116
	Acetone	0.047	0.052	0.055
	Nitromethane	0.101	0.125	0.096

If either the first and the third terms on the right-hand side in Eq. 9 in the dissociative mechanism or the second term on the right-hand side in Eq. 14 in the associative mechanism can be neglected, k_{obsd} will become equal to $(k_1k_2/k_{-1})[\mathrm{hmpa}]$ for the dissociative path or equal to $\{k_4k_5/(k_{-4}+k_5)\}[\mathrm{hmpa}]$ for the associative path, respectively. In the case of Type 3, however, the plots of k_{obsd} *vs.* [hmpa] actually show linearities without passing through the origin as expressed by Eq. 4 (as shown in Fig. 5). Accordingly the reaction can not be simply explanined by either of the two above assumptions. When the reaction of Type 3 is assumed to proceed by both the dissociative and associative mechanisms simultaneously, Eq. 4 can be well explained. The first-order rate constant k_d corresponds to the rate constant k_1 which is independent of the HMPA concentrations as the Type 2. Necessarily, the term of the [HMPA] dependence in Eq. 4 is due to the associative mechanism, where the second term on the right-hand side in Eq. 14 is negligibly small. Therefore, the total rate constant k_{obsd} is given by the sum of the following two terms;

$$k_{\mathrm{obsd}} = k_1 + \frac{k_4k_5}{k_{-4}+k_5}[\mathrm{hmpa}] \tag{15}$$

k_d and k_a in Eq. 4 corresponding to k_1 and $k_4k_5/(k_{-4}+k_5)$.

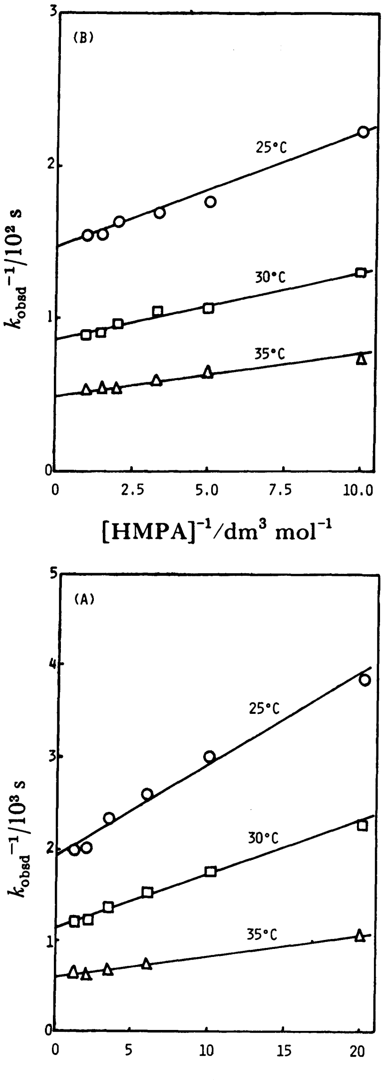


Fig. 6. Plots of k_{obsd}^{-1} *vs.* $[hmpa]^{-1}$ for the dmbpy complex in nitrobenzene (A) and for the phen complex in acetone (B) at 25 °C (○), 30 °C (□), and 35 °C (△).

The values of k_d and k_a in the inert solvents at 25 °C are summarized in Table 2.

Temperature Dependence of k_{obsd} *and Activation Parameters.* The rates of the substitution reactions were measured at various temperatures, and the values of sets of ($\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$) and ($\Delta H_a^{\neq}$ and $\Delta S_a^{\neq}$) were obtained by plotting ln k_1 or ln k_a *vs.* $1/T$; these values are summarized in Table 2. In the associative mechanism, the values for $\Delta H_a^{\neq}$ and $\Delta S_a^{\neq}$ are only the apparent ones because the apparent rate constant k_a is composed of rate constants of the elementary processes.

General Discussion. Table 2 gives a survey of the two schemes of the reaction through the single path of the dissociative mechanism and the simultaneous paths of the dissociative and associative mechanisms.

Dissociative Mechanism: Some features are found in the values of k_1, $\Delta H_1^{\neq}$, and $\Delta S_1^{\neq}$ for the dissociative mechanism in Table 2; k_1 values are nearly in the ranges $(1.3—1.5)\times 10^{-2}\ s^{-1}$ for bpy complex and $(4.5—5.6)\times 10^{-3}\ s^{-1}$ for dmbpy complex, respectively, in nitrobenzene, acetone, and 1,2-dichloroethane, and $\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$ values are 80—90 kJ mol^{-1} and approximately zero J K^{-1} mol^{-1} for both bpy and dmbpy complexes in all the solvents used. The constancy of these values would indicate that the inert solvents exhibit little influence on the cleavage of cobalt-nitrogen bonds, and moreover, the fact that $\Delta S_1^{\neq}$ values are not largely negative would support the occurrence of the three-coordinated intermediates in the course of the dissociative mechanism.

In HMPA, the mechanism of the substitution reaction is difficult to be analyzed because of the existence of the large excess of solvent HMPA. In the case of the dmbpy complex in HMPA, however, since the observed values, $k_{obsd}=6.64\times 10^{-3}\ s^{-1}$ at 25 °C, $\Delta H^{\neq}=89.2$ kJ mol^{-1} and $\Delta S^{\neq}=+11.7$ J K^{-1} mol^{-1}, are very close to those in inert solvents where the reactions proceed by the dissociative mechanism, the reaction of the dmbpy complex in HMPA may proceed also by the dissociative mechanism.

For the phen complex, the values, $k_{obsd}=(6—9)\times 10^{-4}\ s^{-1}$ at 25 °C, $\Delta H^{\neq}=(86—101)$ kJ mol^{-1}, and $\Delta S^{\neq}=(-16—+36)$ J K^{-1} mol^{-1}, are roughly constant, irrespective of the media used. Therefore, it can be concluded that the reaction in all the inert solvents used, as well as in HMPA, proceeds simply by the dissociative mechanism for the same reason as in the case of the dissociative mechanism for the bpy and dmbpy complexes.

If the reactions of Type 1 were hypothesized not to proceed by the dissociative mechanism but by a mechanism involving the formation of an outer-sphere associated complex between Co(II) and HMPA in the solvents used;

$$[Co(NN)(hmpa)_2]^{2+} + hmpa \overset{K_o}{\rightleftharpoons} [Co(NN)(hmpa)_2]^{2+}\cdot hmpa \qquad (16)$$

$$[Co(NN)(hmpa)_2]^{2+}\cdot hmpa \xrightarrow{k_i} \text{products}, \qquad (17)$$

the rate constant, k_{obsd}, would be expressed by the following equation:

$$k_{obsd} = \frac{k_i K_o[hmpa]}{1+K_o[hmpa]}. \qquad (18)$$

Then Eq. 18 is rearranged to give

$$\frac{1}{k_{obsd}} = \frac{1}{k_i} + \frac{1}{k_i K_o}\frac{1}{[hmpa]}. \qquad (19)$$

Therefore, k_i and K_o of the outer-sphere association mechanism might apparently correspond to k_1 and k_2/k_{-1} in Eq. 9 of the dissociative mechanism, respectively. If the reaction proceeds truly by the outer-sphere association mechanism, the values of K_o (the reciprocals of k_{-1}/k_2 in Table 3) could be shown to be about 8—31 dm^3 mol^{-1}. The values of K_o for the systems between $[Ni(H_2O)_6]^{2+}$ and HF, NH_3, or C_5H_5N in H_2O have been reported to be 0.15 dm^3 mol^{-1},[2,11] which is far smaller than 8—31 dm^3 mol^{-1} for the system between Co(II) and HMPA. Moreover, the $\Delta S_i^{\neq}$ value is supposed to be negative in process 17 for the associated complex between Co(II) and HMPA. However, the actually observed values of $\Delta S_i^{\neq}$ are approximately zero against the above supposition. Thus, the reaction of Type 1 is believed more probably to proceed through the dissociative mechanism than through the outer-sphere association one.

Associative Mechanism: As have been shown in Table 2, the substitution reactions for the bpy and dmbpy complexes in acetone, 1,2-dichloroethane, and nitromethane proceed not only by the dissociative mechanism but also by the associative mechanism simultaneously, the k_a values being in the order: acetone$>$nitromethane $>$1,2-dichloroethane for the bpy complex and acetone$>$ 1,2-dichloroethane$>$nitromethane for the dmbpy complex. In nitrobenzene, on the other hand, the substitution does not occur by the associative mechanism in either complex. The values of $\Delta H_a^{\neq}=(50—65)$ kJ mol^{-1} for the associative mechanism are smaller than those about 80—90 kJ mol^{-1} for the dissociative mechanism, and the largely negative values of $\Delta S_a^{\neq}$ are compared with those of $\Delta S_1^{\neq}$ of approximately zero as shown in Table 2. This is reasonable for the associative mechanism with largely negative values of $\Delta S_a^{\neq}$ on account of the occurrence of the five-coordinated intermediates.

In the case of the bpy complex in HMPA, $k_{obsd}=3.4\times10^{-2}$ s^{-1} is larger than k_1 of the dissociative mechanism in inert solvents, and the apparent value of $\Delta S^{\neq}$, however, was found to be strongly negative. Therefore, the reaction occurs not only by the dissociative mechanism but also by the associative one. The values of the rate constants at various temperatures, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ for both mechanisms in HMPA were thus obtained from Eq. 4 by using [HMPA]$=5.8$ mol dm^{-3} and the averaged k_1 values in inert solvents, as shown in Table 2.

Steric Effect: In general, the associative mechanism has been accepted as the mechanism of substitution reactions of tetrahedral complexes.[3] However when a bulky ligand such as HMPA is exchanged, both the associative and dissociative mechanisms are known to occur simultaneously.[5] In the present investigation, the substitution reactions of bpy and dmbpy complexes have been found to proceed only by the dissociative mechanism in nitrobenzene, and by both mechanisms in parallel in inert solvents other than nitrobenzene. On the other hand, in the case of the phen complex, the reaction proceeds only by the dissociative mechanism in all the inert solvents used as well as in HMPA. It seems that this difference may be caused by the difference of the bond flexibility between two pyridine rings in bpy or dmbpy and phen. Since the carbon-carbon bond connecting two pyridine rings in bpy or dmbpy is allowed to rotate fairly freely, the degree of molecular flexibility is large. However, the carbon-carbon bond between two pyridine rings in phen is fixed, and therefore the molecular flexibility of phen should be small. Because the reaction of the associative mechanism proceeds *via* a five-coordinated intermediate which may be much sterically strained due to the bulkiness of HMPA molecules, the two pyridine rings may not become coplanar. Therefore, it is considered that the complexes of bpy and dmbpy with large flexibility are favorable for the associative mechanism. However in the case of the phen complex, the reaction occurs wholly *via* the dissociative mechanism which goes through a three-coordinated intermediate, first cleaving one of the two cobalt-nitrogen bonds to avoid the rigidity of the phen molecule.

Solvent Effect: The fact that the bpy and dmbpy complexes in nitrobenzene undergo ligand exchange only through the dissociative mechanism can not be accounted for simply by the steric hindrance between Co(II) and the bulky HMPA. Fujiwara and his coworkers reported[12] that an associated complex is formed between HMPA and nitrobenzene, both of which have large dipole moments, thus interacting strongly with each other in nonpolar solvents. Therefore, the bpy and dmbpy complexes as well as the phen complex are restricted from undergoing ligand exchange through the associative mechanism but simply allowed to go through the dissociative mechanism, with a three-coordinated intermediate in nitrobenzene. On the basis of the extent of the interaction between HMPA and solvent molecules, the sequence of k_a for the associative mechanism can also be explained. The rate constants, k_a, fall into the sequences: acetone$>$nitromethane$>$ 1,2-dichloroethane$\gg$nitrobenzene for the bpy complex, and acetone$>$1,2-dichloroethane$>$nitromethane$\gg$nitrobenzene for the dmbpy complex; these are almost in the reverse order of the values of their dipole moments, except for 1,2-dichloroethane with a small dielectric constant: acetone (2.9)$<$nitromethane (3.46)$<$nitrobenzene (4.21).

Conclusion. It can be concluded that the substitution reaction of bpy and dmbpy complexes proceeds only by the dissociative mechanism in nitrobenzene, and simultaneously by the dissociative and the associative mechanisms in parallel in inert solvents other than nitrobenzene. On the other hand, for the phen complex, the reaction proceeds simply by the dissociative mechanism in pure HMPA and in all the inert solvents used. Whether the substitution reaction proceeds by the dissociative mechanism or by the associative one, both the steric effect and the solvent effect seem to be important since HMPA is a bulky ligand and has a large dipole moment.

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