Kinetics and Mechanism of the Complex Formation Reactions of Cobalt(II) with Chloride, Bromide, Iodide, and Azide Ions, 2,2′-Bipyridine, 2,2′:6′,2″-Terpyridine, and Tris(2-pyridyl)amine in Hexamethylphosphoric Triamide

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Synopsis. The kinetics of the complex formation reactions of cobalt(II) with chloride, bromide, iodide, and azide ions, 2,2′-bipyridine (bpy), 2,2′:6′,2″-terpyridine (terpy), and tris(2-pyridyl)amine (tpya) has been studied by stopped-flow spectrophotometry in hexamethylphosphoric triamide (HMPA) at a constant ionic strength of 0.06 mol dm^{-3}. The reaction mechanism is discussed on the basis of the obtained formation rate constants, activation enthalpies, and activation entropies. An associative interchange mechanism for the complex formation reaction of cobalt(II) with halide ions is suggested.

There are few accumulated kinetic data for the complex formation reactions of tetrahedral metal(II) ions with complexing ligands,[1] although the kinetics of octahedral metal(II) ions has been significantly investigated.[2] This is due to the formation of tetrahedral complexes severely restricted and to their fast reaction rates in tetrahedral complexes. We have reported that metal(II) ions are four-coordinated in HMPA and that four-coordinate tetrahedral $[MX_n(hmpa)_{4-n}]^{(2-n)+}$ (M=Co, Zn; X=Cl, Br, I) are formed stepwise.[3,4] In spite of the remarkably strong donicity of HMPA compared with other oxygen-donor solvents such as water, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO),[5] where the metal(II) ions show six-coordination, unusual exothermicity for $[MX]^+$ (M=Co, Zn; X=Cl, Br) in HMPA has been observed in contrast to endothermicity in DMF or DMSO. The origin of the unusual thermodynamic behavior of the complexation for $[CoCl(hmpa)_3]^+$ was interpreted on the basis of structural data, which both Co–O (HMPA) and Co–Cl bond lengths within the tetrahedral complexes are reduced in comparison within the octahedral ones.[6] This suggests that not only the thermodynamic but also the kinetic behavior of the complexation of metal ions with ligands under a tetrahedral environment may be different from that under the usual octahedral environment. No kinetic data have been obtained so far regarding the formation reaction of metal ions with halide ions in HMPA. We therefore explored the kinetics of the complex formation reactions of cobalt(II) with halide (X=Cl, Br, I) ions, azide ion, 2,2′-bipyridine (bpy), 2,2′:6′,2″-terpyridine (terpy), and tris(2-pyridyl)-amine (tpya) in HMPA. The mechanism of the complex formation reactions for cobalt(II) with ligands is discussed on the basis of the linear free energy relationship as well as the isokinetic relationship. The thermodynamic parameters of complexation of $[Co(tpya)]^{2+}$ and $[CoN_3]^+$ are also reported in HMPA.

Experimental

Materials. All of the chemicals used were of reagent grade. The HMPA solvate of cobalt(II) perchlorate $Co(ClO_4)_2 \cdot 4HMPA$ was prepared according to a method described in the literature.[7] Tetraethylammonium halide was recrystallized from ethanol and then dried in vacuo under over P_2O_5 at room temperature. Terpy and tpya were used without further purification. Bpy and HMPA were purified as described elsewhere.[8]

Kinetic Measurements. The complex formation reactions were followed spectrophotometrically at 650 nm in the Cl^-, Br^-, and N_3^- systems, at 675 nm in the I^- system, and at 633 nm in the bpy, terpy, and tpya systems by using a Union Giken stopped-flow spectrophotometer RA-401 with a thermostated cell compartment. The absorption spectra were measured using a Shimadzu recording spectrophotometer UV-200 with a thermostated cell compartment. The ionic strength was adjusted to 0.06 mol dm^{-3} with sodium perchlorate.

Results and Discussion

Thermodynamic Parameters of Formation of $[Co(tpya)]^{2+}$ and $[CoN_3]^+$. Figure 1 (A) shows the dependence of the absorption spectra of cobalt(II) com-

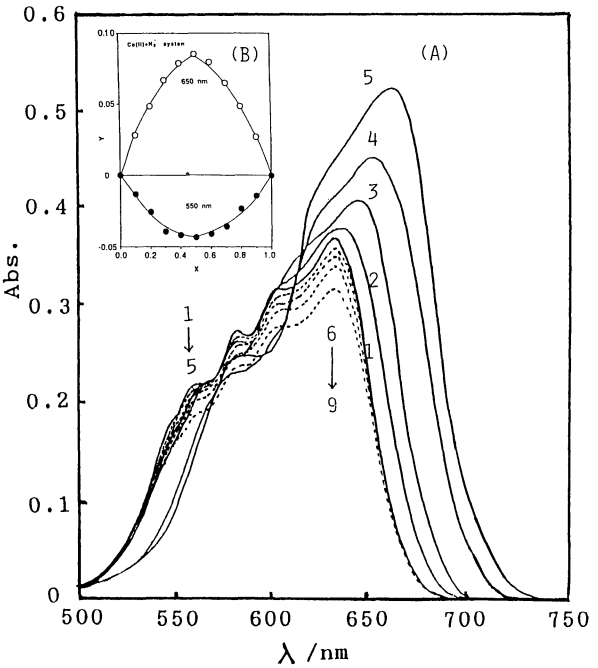

Fig. 1. (A) Absorption spectra of cobalt(II) azide (——) and tpya(– – –) HMPA solutions at 500—750 nm at 25 °C. [Co(II)]=1×10^{-3} mol dm^{-3}, $[N_3^-]_0$/10^{-4} mol dm^{-3}: (1) 0 (2) 4 (3) 6 (4) 15 (5) 20, $[tpya]_0$/10^{-4} mol dm^{-3}: (6) 6 (7) 10 (8) 50 (9) 100. (B) Curves of continuous variation in Co(II)+N_3^- system at 550 and 650 nm at 25 °C. [Co(II)]+$[N_3^-]_0$=1×10^{-3} mol dm^{-3}.

Table 1. Observed Formation and Rate Constants (25 °C), and Thermodynamic Parameters of the Complex Formation Reactions of Cobalt(II) with Halide and N_3^- Ions, Bpy, Terpy, and Tpya in HMPA[a)]

L	$\log K_1$	ΔH_1°	ΔS_1°	$\log k_f$	$\Delta H_f^\ddagger$	$\Delta S_f^\ddagger$
		kJ mol^{-1}	J mol^{-1} K^{-1}		kJ mol^{-1}	J mol^{-1} K^{-1}
Cl^-	6.7[b)]	−15.2	78	5.01(0.02)	49.0(5.4)	14(1)
Br^-	5.53[b)]	−2.7	97	4.70(0.03)	41.6(3.2)	−15(1)
I^-	2.69[b)]	12.9	95	1.35(0.03)	32.1(0.6)	−111(2)
N_3^-	4.28(0.03)	−25.1(0.4)	69(8)	4.70(0.04)	45.6(3.0)	−6(4)
bpy	5.84[c)]	—	—	3.61(0.10)	44.7(4.0)	−26(2)
terpy	4.87[c)]	—	—	2.22(0.10)	28.4(2.0)	−108(8)
tpya	1.45(0.05)	−5.6(0.4)	9(9)	2.05(0.02)	21.3(3.0)	−130(9)

a) Values in parentheses refer to σ. b) Ref. 3. c) Ref. 9.

plexes upon the concentrations of tpya and N_3^- ion in HMPA at $[[Co(hmpa)_4]^{2+}]_0=1.0\times10^{-3}$ mol dm^{-3}. The curves of continuous variation for the Co(II)+N_3^- system at 550 and 650 nm indicates that 1 : 1 complexes are predominantly formed between cobalt(II) and N_3^- as shown in Fig. 1 (B). Similar data were obtained in the tpya system. The values of K_1 were calculated by using the continuous variation method as described in previous work.[9)] The results are summarized in Table 1, together with kinetic data.

The geometry for $[CoN_3]^+$ is tetrahedral since the spectral changes are similar in the cobalt(II)+halide ion system.[3)] On the other hand, the monotonous decreases of the absorbances in the tpya system are attributed to the formation of an octahedral cobalt(II) complex, which shows no absorption in this region.[9)] Therefore, the geometry change from tetrahedral to octahedral upon the formation of $[Co(tpya)]^{2+}$ occurs in HMPA.

The Determination of Rate Constants. In the case of the bpy and terpy systems, the complex formation reaction was followed by a pseudo-first-order rate law under conditions of $[Co(II)]=(0.5—1.5)\times10^{-2}$ mol dm^{-3} of a large excess over $[L]=5\times10^{-4}$ mol dm^{-3} (L=bpy, terpy). The dependence of the pseudo-first-order rate constant k_{obsd} on the concentration of Co(II) was given by $k_{obsd}=k_f[Co^{2+}]+k_d$, where k_f is a second-order rate constant for the formation of the $[Co(L)]^{2+}$ complex, and k_d is a first-order rate constant for the dissociation of the $[Co(L)]^{2+}$ complex. Under the present experimental conditions, the dissociation reaction was negligible, since the plots of k_{obsd} vs. [Co(II)] lay along a straight line starting from the origin. In the halide ions, N_3^-, and tpya systems, the reactions obeyed the pseudo-first-oder rate law by using a later reaction time close to equilibrium under the condition of $[Co(II)]=(0.8—1.0)\times10^{-3}$ mol dm^{-3} of a slight excess over $[L]=5\times10^{-4}$ mol dm^{-3}, where the formation of $[Co(L)_2]^{2+}$ and higher complexes was negligible. The value of k_{obsd} is given by $k_{obsd}=k_f\{[Co^{2+}]+1/K_1\}$,[10)] where $[Co^{2+}]$ is the concentration of Co^{2+} at infinite time. The obtained formation rate constants at 25 °C, activation enthalpies, and entropies are listed in Table 1.

Reaction Mechanism. It is now generally accepted that the complex formation reaction of metal ions with ligands proceeds by a stepwise mechanism, preceded by the formation of an outer-sphere complex between the metal ion and the ligand as expressed by Scheme 1 for the monodentate ligand:

$$[Co(hmpa)_4]^{2+}+X^- \overset{K_{os}}{\rightleftharpoons} [Co(hmpa)_4]^{2+}\ X^- \xrightarrow{k_1} [CoX(hmpa)_3]^+ + hmpa.$$

Scheme 1.

For the halide and N_3^- ions as monodentate ligands, the second-order rate constant k_f for the formation reaction is written as $k_f=K_{os}k_1/(1+K_{os}[Co^{2+}])$ by using the equilibrium and rate constants defined in Scheme 1. Since $1 \gg K_{os}[Co^{2+}]$ under the present experimental conditions, the equation reduces to $k_f=K_{os}k_1$. The equilibrium constant K_{os} for the formation of an outer-sphere complex can be calculated according to the Eigen[11)] and Fuoss[12)] equation:

$$K_{os}=\frac{4\pi N_A a^3}{3000}e^{-U(\varepsilon)/kT},$$

$$U(\varepsilon)=\frac{z_M z_L e^2}{\varepsilon a}-\frac{z_M z_L e^2\kappa}{\varepsilon(1+\kappa a)},\ \kappa^2=\frac{8\pi N_A e^2 I}{1000\varepsilon kT},$$

where N_A is Avogadro's constant; a is the distance of closest approach of two ions; k is the Boltzmann constant; $z_M e$ and $z_L e$ are the charges of the metal ion and the ligand, respectively; ε is the bulk dielectric constant; and I is the ionic strength. In the calculation, the a values were taken to be about 8.3×10^{-8}, 8.4×10^{-8}, and 8.6×10^{-8} cm for the Cl^-, Br^-, and I^- systems, respectively. The obtained K_{os} values are 139, 134, and 130 mol^{-1} dm^3 for the Cl^-, Br^-, and I^- systems, respectively, which are similar values among the halide ions. These results depend on the bulkiness of the hmpa molecule. Thus, the change of k_f values for a variation of the entering ligand is mainly that of the k_1 values in the Eq. $k_f=K_{os}k_1$. Figure 2 shows the plot of $\log k$ vs. $\log K_1$, where the linear free energy relationship (L. F. E. R.) holds for the halide ions in HMPA. The value of the slope for the formation reaction is nearly 1, in contrast to being nearly zero for the backward reaction; i.e. complex formation is strongly affected by the halide ions as the entering ligand, but is not affected by the hmpa molecule as the leaving ligand. This suggests that the geometry in the transition state is similar to that in the product, where the halide ion penetrates deeply into the first coordination sphere. It is therefore proposed that the complex formation reaction of cobalt(II)

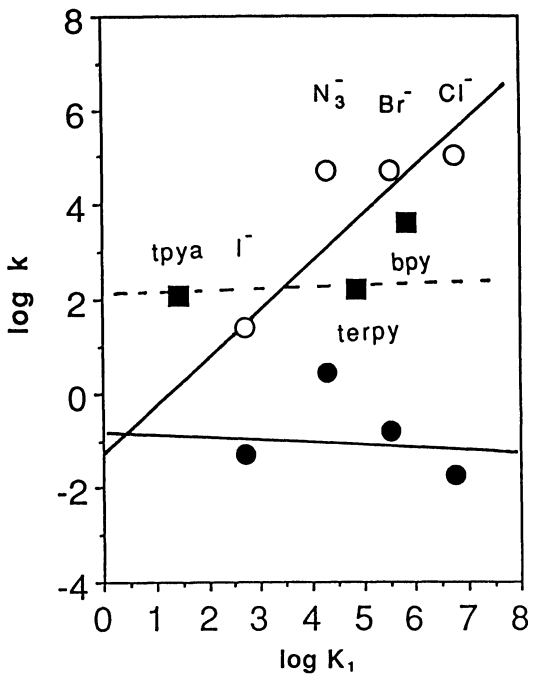

Fig. 2. Linear free energy relationship between log k and log K_1 in HMPA. ○, ■; k_f, ●; k_b.

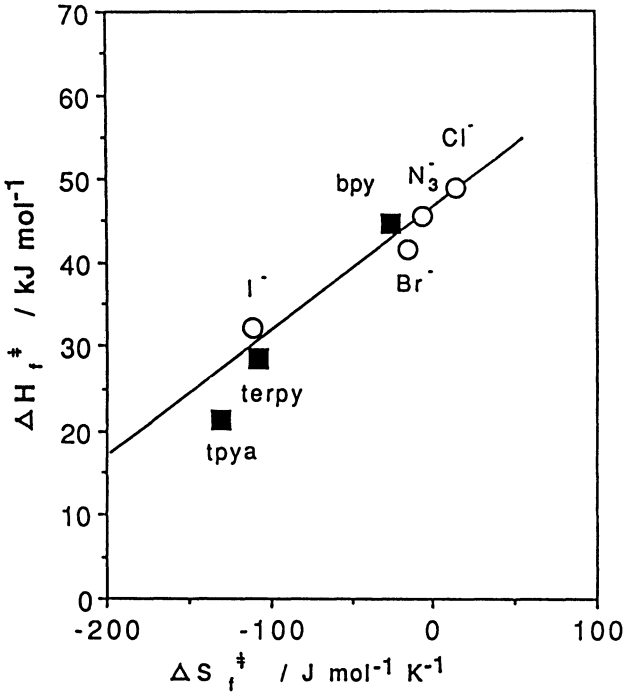

Fig. 3. Isokinetic relationship between $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ in HMPA.

with halide ions occurs via an associative interchange mechanism in HMPA. Figure 3 shows the plot of $\Delta H_f^{\ddagger}$ vs. $\Delta S_f^{\ddagger}$, where the isokinetic relationship holds among the ligands used. It is suggested that the complex formation reaction between cobalt(II) and halide ions proceeds by the same mechanism.

We have pointed out that the rate-determining step of the dissociation reaction of the tetrahedral $[Co(bpy)]^{2+}$ ion is the formation of both a five-coordinated intermediate coordinated by two nitrogen atoms and a three-coordinated one coordinated by one nitrogen atom with one end of the ligand left free in HMPA.[8] We thus postulate the rate-determining step of the formation reaction of $[Co(bpy)]^{2+}$ to be the formation of a chelate-ring-closure, not that of monodentate species.[2] In the terpy system, the chelate-ring-closure formation as well as in the bpy system is the rate-determining step.[13] The k_f, $\Delta H_f^{\ddagger}$, and $\Delta S_f^{\ddagger}$ values are similar in the terpy and tpya systems, though the K_1 values are largely different in both systems. This indicates that the reaction mechanism in the tpya system is similar to that in the terpy system. It is interesting that the isokinetic relationship holds in all systems (as shown in Fig. 3) in spite of the occurence of the geometry change from tetrahedral to octahedral in the terpy and tpya systems.

Comparison among the Mechanisms in HMPA and in the Other Solvents. In H_2O, MeOH, CH_3CN, and DMF, the solvent exchange on Co^{2+} ion occurs by a dissociative mechanism.[14] The complex formation of cobalt(II) with such ligands as NH_3, *N,N*-dimethyl-4-(2-pyridylazo)aniline, and glycinate ion also proceeds via a dissociative mechanism[15] in H_2O, where the solvated Co^{2+} ion and its complexes are octahedral. On the other hand, the present investigation of the complex formation reaction of the tetrahedral cobalt(II) ion with halide ions suggests an associative mechanism in HMPA. The tetrahedral cobalt(II) ion seems to prefer a higher coordination number in the transition state.

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