Kinetics of Structural Rearrangement Accompanying the Substitution Reaction on Complex [Co(terpy)(hmpa)$_3$]$^{2+}$(terpy=2,2′ : 6′,2″-Terpyridine) in Hexamethylphosphoric Triamide

Yuriko ABE* and Goro WADA

Department of Chemistry, Nara Women's University, Nara 630

(Received February 1, 1982)

Synopsis. The reaction of structural rearrangement accompanying the substitution of hexamethylphosphoric triamide (HMPA) for 2,2′:6′,2″-terpyridine (terpy) from octahedral [Co(terpy)(hmpa)$_3$]$^{2+}$ to tetrahedral [Co(hmpa)$_4$]$^{2+}$ proceeds through a five-coordinated intermediate in HMPA. The following values for the first-order rate constant at 25 °C, ΔH_d^*, and ΔS_d^* were obtained: $k_d = 3.55 \times 10^{-5}$ s^{-1}, $\Delta H_d^* = 105.4$ kJ mol^{-1}, and $\Delta S_d^* = +15.9$ J K^{-1} mol^{-1}.

There are few kinetic data for reactions involving structural interconversions.[1-5] This is probably due to the high reaction rates except for the cases which can be measured by tempertaure jump or NMR, and to the severe thermodynamic requirements of their investigation.

In this report, we studied spectrophotometrically the kinetics of structural rearrangement reactions accompanying HMPA substitution for terpy from octahedral [Co(terpy)(hmpa)$_3$]$^{2+}$ to tetrahedral [Co(hmpa)$_4$]$^{2+}$ in HMPA, for the purpose of clarifying the rearrangement mechanism and the effect of the bulkiness of HMPA on its mechanism. The reaction rate was successfully measured by a conventional technique, since terdentate ligands generally undergo ligand exchange more slowly than unidentate ones.

Experimental

Materials. [Co(hmpa)$_4$](ClO$_4$)$_2$ and [Cu(hmpa)$_4$](ClO$_4$)$_2$ were prepared by methods described in the literature.[6,7] Terpy was used without further purification. The purification of HMPA was carried out as previously described.[8,9]

Rate Measurements. The complex [Co(terpy)(hmpa)$_3$]$^{2+}$ was prepared from appropriate amounts of [Co(hmpa)$_4$]$^{2+}$ and terpy in HMPA in advance and the reaction was initiated by mixing a solution of [Co(terpy)(hmpa)$_3$]$^{2+}$ with a solution of [[Cu(hmpa)$_4$]$^{2+}$] in a large excess over [[Co(terpy)(hmpa)$_3$]$^{2+}$] in HMPA. Cu(II) was used in order to remove the free terpy by its rapid complexation.[10] The reaction rate was followed by observing the increase in the absorbance at 580 nm by use of a Shimadzu Spectrophotometer Model UV-200S with a thermostated cell compartment. The measured absorbances were not corrected because the absorbance due to Cu(II) was approximately constant during the course of the reaction. The ionic strength was adjusted at 0.1 mol dm^{-3} with sodium perchlorate.

Results and Discussion

Rate Constants and Activation Parameters. The reaction obeys the following rate equation (1) under the conditions of [Cu(II)] of a large excess over [Co(II)] = 8×10^{-4} mol dm^{-3},

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

where A_0, A_t, and A_∞ are the absorbances at times 0, t, and infinite at 580 nm, respectively. As shown in Fig. 1, the values of k_{obsd} were found to be linearly dependent upon the Cu(II) concentration. In the similar reactions (such as those of M(II)-terpy complexes (M(II)=Mn(II), Fe(II), Co(II), Ni(II), Zn(II), or Cd(II)) in H_2O,[10] and of Mn(II)-terpy in methanol,[11]) no dependence of the rate constant upon either [Hg(II)] or [Cu(II)] has been observed, where Hg(II) or Cu(II) only acts to scavenge the free terpy. Therefore, this result in HMPA is particularly interesting. The correlation of k_{obsd} with [Cu(II)] in HMPA can be empirically expressed by the following equation;

$$k_{obsd} = k_d + k_a[\mathrm{Cu(II)}] , \quad (2)$$

in which k_d is a first-order rate constant with respect to [Co(II)] and k_a is a second-order rate constant with respect to [Co(II)] and [Cu(II)]. By plotting $\ln k_d$ or $\ln k_a$ *vs.* $1/T$, ΔH^* and ΔS^* were obtained as follows: $\Delta H_d^* = 105.4$ kJ mol^{-1} and $\Delta S_d^* = +15.9$ J K^{-1} mol^{-1} for the k_d path, and $\Delta H_a^* = 72.3$ kJ mol^{-1} and $\Delta S_a^* = -54.0$ J K^{-1} mol^{-1} for the k_a path, respectively.

Reaction Mechanism. The reaction with the first-order rate constant k_d corresponds to the following equation:

$$\underset{\text{octahedral}}{[\mathrm{Co(terpy)(hmpa)_3}]^{2+}} + \mathrm{hmpa} \longrightarrow \underset{\text{tetrahedral}}{[\mathrm{Co(hmpa)_4}]^{2+}} + \mathrm{terpy} . \quad (3)$$

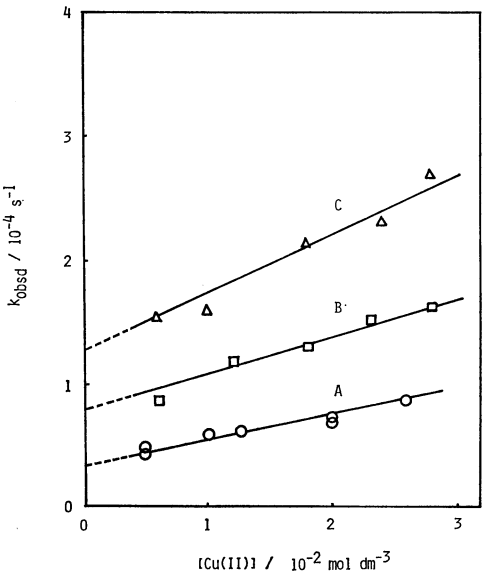

Fig. 1. The dependence of k_{obsd} on the Cu(II) concentrations at 25 °C (A), 30 °C (B), and 35 °C (C).

Two possible reaction mechanisms may be considered for the substitution for terpy on $[Co(terpy)(hmpa)_3]^{2+}$. One is a dissociative mechanism, in which one of the three cobalt-nitrogen bonds is first broken and the reaction goes through a five-coordinated intermediate. The other is an associative mechanism, in which Co(II) first reacts with an HMPA molecule, resulting in a seven-coordinated intermediate or an outer-sphere associated complex. Since the coordination number of Co(II) is reduced from six to four, the former mechanism seems to be more probable. The fact that ΔS_d^* value is positive supports the dissociative mechanism which is represented as follows,

$$[(hmpa)_3Co\text{-}N\langle_{N}^{N}\rangle]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(hmpa)_3Co\text{-}N\langle_{N}^{N}\rangle]^{2+} \xrightarrow{k_2} . \quad (4)$$

Thus, k_d can be expressed as $k_1k_2/(k_{-1}+k_2)$.

The [Cu(II)] dependence in HMPA is similar to the case of the [Hg(II)] dependence of the reactions of Ni(II)-bidentate substituted pyridines in dimethyl sulfoxide.[12] Buck and Moore suggested that the reaction of the [Hg(II)] dependence proceeds by the attack of Hg(II) on a nitrogen atom whose bond with Ni(II) has been ruptured.[12] Therefore, it seems that the [Cu(II)] dependence in HMPA is also due to the reaction between the five-coordinated intermediate of Co(II) and Cu(II).

Comparison between Reactions in HMPA and in H_2O. When the equilibrium constant between the tetrahedral⇄octahedral configurations is expressed by $K_1=[[Co(terpy)(hmpa)_3]^{2+}]/[[Co(hmpa)_4]^{2+}][terpy]$, the reaction with the rate constant k_d corresponds to the backward reaction of the equilibrium. In the present study, the values of k_d obtained and the activation parameters in HMPA are as follows: $k_d=3.55\times10^{-5}$ s^{-1} at 25 °C, $\Delta H_d^*=105.4$ kJ mol^{-1}, and $\Delta S_d^*=+15.9$ J K^{-1} mol^{-1}, and the value of K_1 has been obtained as $K_1=7.4\times10^4$ dm^3 mol^{-1}.[9] In H_2O, where $[Co(H_2O)_6]^{2+}$ and $[Co(terpy)(H_2O)_3]^{2+}$ are both octahedral, those values are $k_d=1\times10^{-4}$ s^{-1} at 25 °C,[13] $\Delta H_d^*=82.0$ kJ mol^{-1},[13] $\Delta S_d^*=-1.7$ J K^{-1} mol^{-1},[13] and $K_1=2.5\times10^8$ dm^3 mol^{-1}.[14] Although the value of K_1 in HMPA differs considerably from that in H_2O, the values of k_d and the activation parameters in HMPA resemble those in H_2O.

Since the chelation by terpy in HMPA liberates only one molecule of HMPA in contrast with the liberation of as many as three water molecules in the case of water, the entropy effect would lead to the smaller K_1 in HMPA than in H_2O. Moreover, the coordinating HMPA molecules in $[Co(terpy)(hmpa)_3]^{2+}$ are closely packed. Accordingly, the complex is so unstable, due to its molecular bulkiness, that the equilibrium would be also unfavored, resulting in the smaller K_1 in HMPA than in H_2O. Although the reaction in HMPA is accompanied by a structural rearrangement, the similarity of k_d and the activation parameters in both media support the idea that the reaction proceeds by the same dissociative mechanism, independently of whether the solvent is HMPA or H_2O.

References

1) R. D. Farina and J. H. Swinehart, *J. Am. Chem. Soc.*, **91**, 568 (1969).
2) K. J. Ivin, J. Jamison, and J. J. McGarvey, *J. Am. Chem. Soc.*, **94**, 1763 (1972).
3) M. Cusumano, *J. Chem. Soc., Dalton Trans.*, **1976**, 2133.
4) J. D. Vitiello and E. J. Billo, *Inorg. Chem.*, **19**, 3477 (1980).
5) J. H. Coates, D. A. Hadi, S. F. Lincoln, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **20**, 707 (1981).
6) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962).
7) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 1158 (1963).
8) Y. Abe and G. Wada, *Bull. Chem. Soc. Jpn.*, **53**, 3547 (1980).
9) Y. Abe and G. Wada, *Bull. Chem. Soc. Jpn.*, **54**, 3334 (1981).
10) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).
11) D. J. Benton and P. Moore, *J. Chem. Soc., Dalton Trans.*, **1973**, 399.
12) D. M. W. Buck and P. Moore, *J. Chem. Soc., Dalton Trans.*, **1975**, 409.
13) T. Hogg and R. G. Wilkins, *J. Chem. Soc.*, **1962**, 341.
14) L. G. Sillén and A. E. Martell, "Stability Constants Supplements No. 1 Special Publication 25," ed by the Chemical Society, Alden Press, Oxford (1971).