1848 © 1994 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 67, 1848—1854 (1994) [Vol. 67, No. 7

Axial Substitution Reaction of Substituted Pyridine on Chloro(5,10,15,20-tetraphenylporphinato)chromium(III) in Toluene with Special Reference to the Substituent Effect

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(Received February 25, 1994)

Equilibria and kinetics for the axial substitution reaction of pyridine and substituted pyridines (L) coordinated to chloro(5,10,15,20-tetraphenylporphinato)chromium(III) [Cr(tpp)(Cl)] by 1-methylimidazole as an entering ligand in toluene have been studied spectrophotometrically. Equilibrium constants, rate constants, and activation parameters for the substitution of L from the six-coordinated [Cr(tpp)(Cl)(L)] complex have been obtained. It has been demonstrated that equilibrium constants of the substitution reaction depend on the basicity of the axial ligands and that a good linear relationship between the activation parameters and the basicity of L is in accord with the reaction mechanism with a limiting dissociative activation mode.

Metalloporphyrins have drawn the interest of numerous chemists because of their importance in biological functions and their own specific chemical properties. Much attention has been focused on the axial substitution reaction of the metalloporphyrins.[1—44)] One of the most dramatic chemical phenomena caused by the porphyrin ligand is a labilizing effect on the substitution rate of the complex at its axial coordination site in solution. This effect amounts to several orders of magnitude in rate; it depends on the metal ion, oxidation state, porphyrin ligand, and solvent. Many efforts have been exerted to elucidate the mechanism of the axial labilizing effect, especially for the metalloporphyrins of chromium(III),[1—10)] cobalt(III),[11—23)] and rhodium(III)[24,25)] ions which are substitution inert, and it has been accepted that the mechanism of the axial substitution is dissociative (D mechanism) or dissociative-interchange (I_d mechanism).[8,10,22)] In addition, Sweigard et al. have studied the substitution of iron(III) porphyrins, and pointed out the role of hydrogen bonding between the complex and the entering ligand in acetone.[29—38)]

In this work, equilibria and kinetics for the axial substitution reaction of monoligated chloro(5,10,15,20-tetraphenylporphinato)chromium(III) ([Cr(tpp)(Cl)(L)]) by 1-methylimidazole (1-Meim) in toluene (Eq. 1) have been measured spectrophotometrically.

$$[\mathrm{Cr(tpp)(Cl)(L)}] + \text{1-Meim} \rightleftharpoons [\mathrm{Cr(tpp)(Cl)(1\text{-}Meim)}] + \mathrm{L}, \qquad (1)$$

where L represents pyridine and substituted pyridines.[46)] In an inert solvent such as toluene, there should be no complexity in the reaction process because of the inability of the solvent coordination to the chromium(III) ion. Our purpose is to clarify the mechanism of the axial substitution in terms of the substituent effect at *meta-* and *para-*position of pyridine on the kinetic parameters for the reaction. Electron-withdrawing and electron-donating substituents on substituted pyridines at *meta-* and *para-*position may affect the rate of substitution reaction. This effect will be discussed together with the influence of the substituents on the equilibrium constant for reaction 1.

Experimental

Reagents. The Cr(III)-tpp complex, chloro(5,10,15,20-tetraphenylporphinato)chromium(III) [Cr(tpp)(Cl)], was prepared and purified according to published procedures.[47)] 3-Acetylpyridine and 4-acetylpyridine were dried by molecular sieves 4A and then distilled under reduced pressure. 1-Methylimidazole, pyridine, and other substituted pyridines were purified by the literature method.[48)] Toluene was dried by standing with sodium, and then distilled.

Measurements. The constant temperature of reaction solutions was maintained (±0.1 °C) with a circulating thermostatted water bath. UV-visible absorption spectra were recorded on a JASCO UVIDEC 660 spectrophotometer. Kinetic measurements were performed with a stopped-flow spectrophotometer (Unisoku). The concentrations of the leaving and entering ligands were kept in a large excess over that of the Cr(III)-tpp complex to guarantee the pseudo-first-order conditions. The total concentration of the complex was in the range of $(0.5—1.2)\times10^{-5}$ mol kg^{-1}. An appropriate wavelength around the Soret band was chosen for following the reaction for each reaction system. The pseudo-first-order rate constant, k_0, was evaluated by fitting the absorbance-time traces with a non-linear least-squares program, and the k_0 value obtained was the average of 5 to 8 runs. Reproducibility of the k_0 value was better than ±3%.

No effect of added water on either the visible absorption spectra or the reaction rates was confirmed up to $[\mathrm{H_2O}] = 4\times10^{-2}$ mol kg^{-1}, as determined by a Mitsubishi Kasei CA-06 Karl Fischer titrator.

Results

Equilibria. The equilibrium constant K for the axial substitution reaction (Eq. 2) was determined by a conventional spectrophotometric method;

$$[\mathrm{Cr(tpp)(Cl)(L)}] + \mathrm{X} \overset{K}{\rightleftharpoons} [\mathrm{Cr(tpp)(Cl)(X)}] + \mathrm{L}, \qquad (2)$$

where X is py or 1-Meim, and $K = [\mathrm{Cr(tpp)(Cl)(X)}][\mathrm{L}]$-

Table 1. Equilibrium Constants and Thermodynamic Parameters for Substitution Reaction of the Axial Ligand L of the [Cr(tpp)(Cl)(L)] Complex by the Entering Ligand X[a]

$L(B/\mathrm{kJ\,mol^{-1}})$[b]	X	T/°C	K	ΔH° / $\mathrm{kJ\,mol^{-1}}$	ΔS° / $\mathrm{J\,K^{-1}\,mol^{-1}}$
3-CNpy (843)	py	15.0	$(4.14\pm0.11)\times10$	-9.1 ± 0.3	-0.5 ± 1.0
		25.0	$(3.67\pm0.08)\times10$		
		35.0	$(3.24\pm0.07)\times10$		
		45.0	$(2.90\pm0.08)\times10$		
3-Clpy (866)	py	15.0	9.92 ± 0.56	-6.2 ± 0.9	-2.5 ± 2.7
		25.0	8.71 ± 0.65		
		35.0	8.27 ± 0.68		
		45.0	7.71 ± 0.68		
3-Acpy (876)	1-Meim	15.0	$(7.56\pm0.09)\times10^2$	-16.2 ± 0.5	-1.3 ± 1.4
		25.0	$(6.01\pm0.06)\times10^2$		
		35.0	$(4.82\pm0.05)\times10^2$		
		45.0	$(4.00\pm0.03)\times10^2$		
py (892)	1-Meim	15.0	$(3.98\pm0.09)\times10^2$	-14.6 ± 0.4	-0.7 ± 1.4
		25.0	$(3.31\pm0.04)\times10^2$		
		35.0	$(2.68\pm0.04)\times10^2$		
		45.0	$(2.26\pm0.03)\times10^2$		
3-Mepy (905)	1-Meim	15.0	$(2.72\pm0.05)\times10^2$	-15.4 ± 0.3	-6.8 ± 0.8
		25.0	$(2.15\pm0.02)\times10^2$		
		35.0	$(1.79\pm0.02)\times10^2$		
		45.0	$(1.48\pm0.03)\times10^2$		
3,5-$\mathrm{Me_2}$py (911)	1-Meim	15.0	$(1.86\pm0.02)\times10^2$	-14.0 ± 0.4	-5.0 ± 1.1
		25.0	$(1.53\pm0.04)\times10^2$		
		35.0	$(1.26\pm0.01)\times10^2$		
		45.0	$(1.08\pm0.01)\times10^2$		
4-CNpy (851)	py	15.0	$(1.13\pm0.02)\times10$	-2.0 ± 0.5	13.4 ± 1.7
		25.0	$(1.15\pm0.02)\times10$		
		35.0	$(1.07\pm0.02)\times10$		
4-Acpy (877)	1-Meim	15.0	$(8.66\pm0.10)\times10^2$	-15.8 ± 0.3	1.4 ± 1.0
		25.0	$(6.95\pm0.06)\times10^2$		
		35.0	$(5.64\pm0.05)\times10^2$		
4-Mepy (909)	1-Meim	15.0	$(1.06\pm0.03)\times10^2$	-12.7 ± 0.7	-5.3 ± 2.4
		25.0	$(8.69\pm0.29)\times10$		
		35.0	$(7.50\pm0.31)\times10$		
3-CNpy[c]	1-Meim	25.0	$(1.21\pm0.03)\times10^4$	-23.6 ± 0.6	-1.2 ± 1.7
3-Clpy[c]	1-Meim	25.0	$(2.88\pm0.22)\times10^3$	-20.8 ± 1.0	-3.2 ± 3.0
4-CNpy[c]	1-Meim	25.0	$(3.62\pm0.07)\times10^3$	-16.5 ± 0.7	12.7 ± 2.2

a) Errors represent the standard deviation. b) The figure in the parenthesis represents the gas phase basicity B of L.[49] c) Thermodynamic parameters for these reaction systems were calculated by using the equilibrium constant of the substituted py/py system and that of the py/1-Meim system (see in text).

$[\mathrm{Cr(tpp)(Cl)(L)}]^{-1}[\mathrm{X}]^{-1}$. UV-visible absorption spectra of solutions which contain the Cr(III)-tpp complex, leaving ligand L, and entering ligand py or 1-Meim were measured at various temperatures between 15.0 and 45.0 °C. Concentrations of Cr(III)-tpp and L were kept constant, while that of X was varied. Absorption spectra of the solution containing Cr(III)-tpp (1.3×10^{-5} $\mathrm{mol\,kg^{-1}}$), 3-Mepy (4.45×10^{-2} $\mathrm{mol\,kg^{-1}}$), and 1-Meim (6.25×10^{-5}—2.68×10^{-2} mol kg^{-1}), for example, change gradually with the increase of the concentration of 1-Meim. Changes in spectra were thus attributed to the substitution of 3-Mepy by 1-Meim as indicated in Eq. 2. There may be the possibility of the dissociation of the axial Cl ligand by addition of bases as found in the case of Fe(III) porphyrin complexes.[31,33,35,36] In the present case, the fact that the spectrum change according to Eq. 2 corresponds to the single step substitution is evidence for the strong stability of the Cr–Cl bond. It has been also demonstrated by the conductivity measurements that the dissociation of chloride ion never occurs for [Cr(tpp)(Cl)] in toluene.[47] Equilibrium constants were determined by simultaneously analyzing the absorbance data at several wavelengths between 350 and 500 nm by use of a non-linear least-squares fitting program. In the case where leaving ligands are 3-CNpy, 3-Clpy, and 4-CNpy, the equilibrium constant for the substitution of these ligands by 1-Meim (reaction 1) is too large to be determined directly by the method described here. We have, therefore, calculated these constants by using the equilibrium constant K for the substitution reaction of these ligands by py and the equilibrium constant $K=[\mathrm{Cr(tpp)(Cl)(1\text{-}Meim)}][\mathrm{py}][\mathrm{Cr(tpp)(Cl)(py)}]^{-1}[\mathrm{1\text{-}Meim}]^{-1}$. Temperature dependence of the equilibrium constants gives the enthalpy change (ΔH°) and the entropy change (ΔS°) for the substitution reaction. Obtained equilibrium constants at various temperatures and thermodynamic parameters are summarized in Table 1.

Kinetics. Rates of the axial substitution of substituted pyridines by 1-Meim (reaction 1) were measured spectrophotometrically. Reaction conditions where the substitution proceeds substantially at completion were adopted so as to eliminate the contribution of the backward reaction. Under the pseudo-first-order conditions, first-order plots were linear for at least four half-lives for all reaction systems. The reaction is of the first order with respect to [Cr(tpp)(Cl)(L)]. The rate law is thus given by Eq. 3:

$$-\mathrm{d}[\mathrm{Cr(tpp)(Cl)(L)}]/\mathrm{d}t = k_0[\mathrm{Cr(tpp)(Cl)(L)}], \tag{3}$$

where k_0 is a conditional first-order rate constant, which depends on the concentrations of leaving and entering ligands in the bulk solution. At a constant concentration of free L in the bulk solution, k_0 values increase with an increase of [1-Meim] and approach the limited value at higher concentrations of 1-Meim, while they decrease with an increase of [L] in the bulk at a constant 1-Meim concentration, as shown in Fig. 1 in the case of L=4-Acpy as an example. These features can be interpreted by a dissociative mechanism indicated by Eqs. 4 and 5

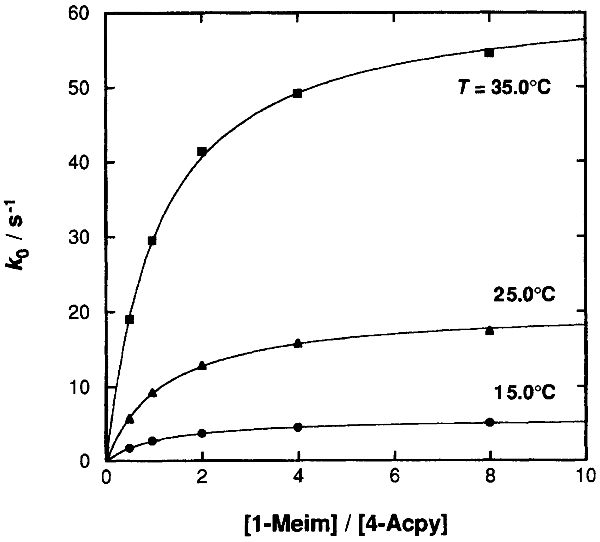

Fig. 1. Dependence of the conditional first-order rate constant k_0 on the ratio of [1-Meim]/[4-Acpy] at various temperatures. The concentration of the Cr(III)-tpp complex is 1.12×10^{-5} mol kg^{-1}. Total concentration of 1-Meim and 4-Acpy is in the range of 3.0×10^{-3}—5.1×10^{-2} mol kg^{-1}. The solid curves were calculated by using the activation parameters obtained.

$$[\mathrm{Cr(tpp)(Cl)(L)}] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Cr(tpp)(Cl)}] + \mathrm{L}, \tag{4}$$

$$[\mathrm{Cr(tpp)(Cl)}] + \mathrm{1\text{-}Meim} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [\mathrm{Cr(tpp)(Cl)(1\text{-}Meim)}]. \tag{5}$$

Since the contribution of the k_4 path to k_0 can be neglected, judging from the equilibrium constant under the present conditions, the steady-state approximation to the five-coordinated [Cr(tpp)(Cl)] intermediate gives Eq. 6:

$$k_0 = k_1[\mathrm{1\text{-}Meim}](k_2[\mathrm{L}]/k_3 + [\mathrm{1\text{-}Meim}])^{-1}. \tag{6}$$

Values of k_1 and k_2/k_3 at each temperature were determined by fitting k_0 obtained at various concentrations of L and 1-Meim to Eq. 6 by use of a least-squares program, and are listed in Table 2. Eyring's plots of k_1 and k_2/k_3 for all reaction systems proved linear within the experimental errors. Therefore, enthalpy and entropy of activation were determined by fitting simultaneously the variable-temperature data to Eq. 6 and the Eyring equation, and are summarized in Table 2.

Although the rate constant k_4 for the dissociation of 1-Meim from the [Cr(tpp)(Cl)(1-Meim)] complex has not been measured directly in the present work, it can be evaluated by the following relationship: $K=k_1k_3k_2^{-1}k_4^{-1}$. The fact that substantially the same value for k_4 was obtained from each reaction system

Table 2. Rate Constants for Substitution Reaction of the Axial Ligand L of the [Cr(tpp)(Cl)(L)] complex by 1-Meim[a)]

L	T/°C	k_1/s^{-1}	k_2/k_3	$\Delta H_1^\ddagger$ kJ mol^{-1}	$\Delta S_1^\ddagger$ J K^{-1} mol^{-1}	$\Delta H_2^\ddagger-\Delta H_3^\ddagger$ kJ mol^{-1}	$\Delta S_2^\ddagger-\Delta S_3^\ddagger$ J K^{-1} mol^{-1}
py	15.0	2.33±0.02	0.94±0.02	86.0±0.5	61.0±1.5	−1.6±1.0	−6.1±3.3
	25.0	8.24±0.07	0.93±0.02				
	35.0	(2.57±0.02)×10	0.90±0.02				
3-CNpy	10.0	(5.63±0.04)×10	1.10±0.02	77.3±0.9	62.0±2.9	−1.3±1.6	−3.9±5.5
	17.5	(1.33±0.02)×10^2	1.07±0.02				
	25.0	(3.10±0.05)×10^2	1.10±0.03				
3-Clpy	15.0	(2.59±0.03)×10	1.05±0.02	81.0±0.8	63.7±2.6	1.0±1.5	4.0±4.9
	25.0	(8.52±0.10)×10	1.14±0.03				
	35.0	(2.49±0.05)×10^2	1.09±0.04				
3-Acpy	15.0	4.33±0.04	1.02±0.02	84.3±0.5	60.0±1.6	−1.0±1.0	−3.6±3.2
	25.0	(1.44±0.02)×10	0.96±0.03				
	35.0	(4.54±0.04)×10	0.98±0.02				
3-Mepy	15.0	1.56±0.01	0.92±0.02	84.5±0.8	52.1±2.7	−1.2±1.7	−5.2±5.6
	25.0	5.23±0.06	0.90±0.02				
	35.0	(1.64±0.02)×10	0.89±0.02				
3,5-Me$_2$py	15.0	0.941±0.01	0.83±0.01	86.7±0.4	55.9±1.3	−1.1±0.7	−5.3±2.4
	25.0	3.30±0.02	0.80±0.02				
	35.0	(1.06±0.06)×10	0.80±0.01				
4-CNpy	10.0	(1.50±0.01)×10	1.21±0.02	82.0±0.6	67.6±2.0	−1.9±1.2	−5.2±4.2
	17.5	(3.66±0.03)×10	1.13±0.02				
	25.0	(9.13±0.08)×10	1.16±0.02				
4-Acpy	15.0	5.81±0.04	1.12±0.02	85.2±0.4	65.9±1.5	−1.2±1.0	−2.8±3.4
	25.0	(2.04±0.02)×10	1.19±0.02				
	35.0	(6.25±0.06)×10	1.08±0.02				
4-Mepy	25.0	2.42±0.02	1.04±0.02	88.2±0.6	58.3±1.8	−1.7±1.4	−5.4±4.4
	35.0	7.89±0.11	0.98±0.03				
	45.0	(2.42±0.02)×10	1.00±0.02				

a) Errors represent the standard deviation.

indicates the validity of the reaction mechanism proposed. The averaged value of k_4 was determined to be (2.59±0.14)×10^{-2}s^{-1} at 25.0 °C. Similarly, the activation parameters for the k_4 path were estimated from ΔH° and ΔS° of each reaction and respective activation parameters for the k_1, k_2, and k_3 paths: $\Delta H_4^\ddagger$= 101.7±1.9 kJ mol^{-1} and $\Delta S_4^\ddagger$=65.9±6.4 J K^{-1} mol^{-1}.

Discussion

Systematic study of the equilibrium constant K and the rate constants k_1 and k_2/k_3 has revealed that the relation between these constants and the basicity of the leaving ligand L obeys fairly well the linear free energy relationship (LFER). Although it would be preferable to base the relation on values corresponding to the donor ability of the nitrogen atom of L in toluene, such values are not available. pK_a value of the conjugate acid of the ligand in water is usually used as a measure of the basicity of the ligand. Such a pK_a value, however, depends somehow on the specific interaction between the substituent of substituted pyridines and water molecules. Since the medium is toluene in the present work, we prefer to use the energy of protonation to the base in the gas phase,[49)] where there is no solute-solvent interaction.

Figure 2 shows the LFER between K for reaction 1, k_1, or k_2/k_3 and the gas phase basicity of L. The substituent effect at the *meta*- and *para*-positions of pyridine is not steric, but electronic. The protonation energy may reflect the availability of the nitrogen lone-paired electrons for σ bonding. Thus, the decrease in k_1 with an increase of the gas phase basicity strongly supports the conclusion that the k_1 process is a dissociation of the ligand L. The same correlation is observed for the equilibrium constant K. Moreover, the correlation with the ligand basicity is parallel for K and k_1. These findings strongly indicate that the potential energy of the transition state for the ligand dissociation process (k_1 path) is independent of the nature of the leaving ligand L and that L is almost completely dissociated in the activated state for the k_1 path (see Fig. 3). Therefore, the limiting dissociative mechanism should be operative.

Interestingly, the ratio of the rate constants k_2/k_3 shows little change even in the variation of L and falls into a very narrow range around unity (see Table 2 and Fig. 2). This fact indicates the very slight discriminating ability of the five-coordinated intermediate [Cr(tpp)(Cl)] toward the nucleophiles and the high reactivity of this intermediate, and thus reconfirms the validity of the steady-state approximation assumed in deriving Eq. 6. The ratio k_2/k_3 is available for other bulky L, and its value is 1.52×10^{-2} for L=quinoline,[10] 7.3×10^{-4} for L=PPh_3,[10] 4.2×10^{-2} for L=$P(OPr)_3$,[6] and 5×10^{-3} for L=$P(C_2H_4CN)_3$[6] at 25 °C. These values are much smaller than unity, which indicates that the steric hindrance around the donor atom of the ligand should slow down the recombination rate of these bulky ligands to [Cr(tpp)(Cl)]. On the other hand, circumstances around the donor nitrogen atom of the substituted pyridines used in the present work are almost the same in terms of the steric hindrance.

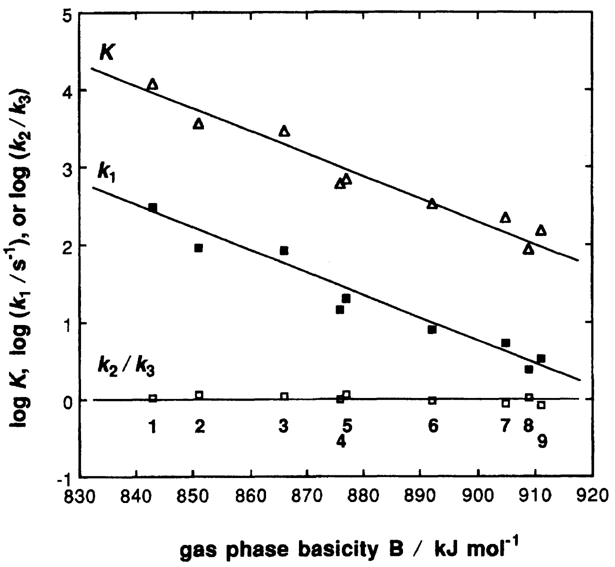

Fig. 2. Relationship between the equilibrium constant K, the rate constant k_1, or the ratio of rate constants k_2/k_3 at 25.0 °C and the gas phase basicity B of the axial ligand L. The ligands are: 3-CNpy (1), 4-CNpy (2), 3-Clpy (3), 3-Acpy (4), 4-Acpy (5), py (6), 3-Mepy (7), 4-Mepy (8), 3,5-Me_2py (9).

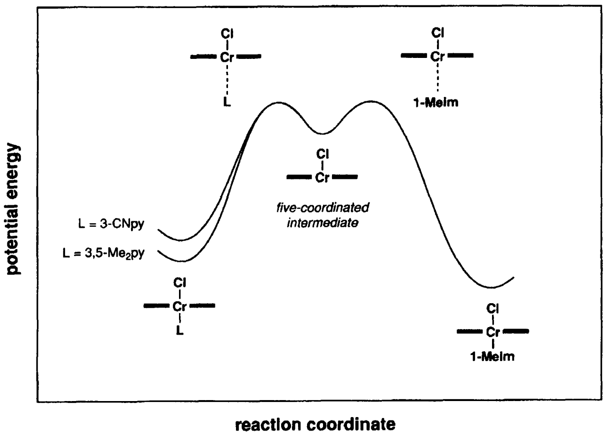

Fig. 3. Potential energy along the reaction coordinate for the reaction: [Cr(tpp)(Cl)(L)]+1-Meim⟶[Cr(tpp)(Cl)(1-Meim)]+L. Two reaction systems are shown for L=3-CNpy and L=3,5-Me_2py.

We can expect some basicity-dependent part of the energy barrier as an electrostatic term during the recombination processes for the k_2 path, since all the ligands we have used are strong dipoles. Nitrogenous bases as axial ligands on the six-coordinated Fe(II)-tpp complexes in toluene can be photodissociated by a laser pulse.[42] The rate constants for the recombination reaction between the five-coordinated Fe(II)-tpp complex and the ligand, which vary in the range of 10^8—10^9 $M^{-1}\,s^{-1}$ at 25 °C (1 M=1 mol dm^{-3}), were found to decrease upon the increase of the basicity of the ligands. These findings were interpreted by the electrostatic repulsion between the dipole of the ligand and the dipole along the fourfold symmetry axis of the five-coordinated complex. The porphyrin dipole with negative nitrogens is induced because the iron atom displaces about 0.5 Å away from the porphyrin plane.[50] In the present case, on the other hand, the recombination rate constant k_2 does not depend on the basicity of the entering ligand L. This fact indicates that the five coordinated intermediate [Cr(tpp)(Cl)] has almost zero dipole moment and that the diffusion-controlled process should be rate-determining for the recombination reaction between [Cr(tpp)(Cl)] and L.

The activation enthalpy $\Delta H_1^\ddagger$ changes with the ligand

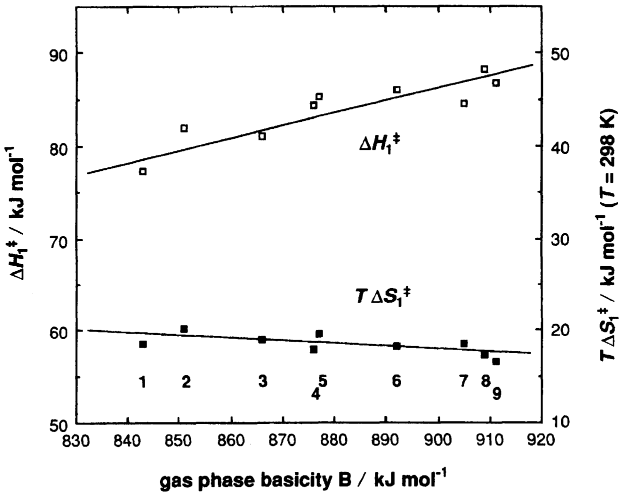

Fig. 4. Activation enthalpy $\Delta H_1^\ddagger$ and activation entropy $\Delta S_1^\ddagger$ for dissociation of L from [Cr(tpp)(Cl)(L)] as a function of the gas phase basicity of L. The ligands are as in Fig. 2.

basicity, as shown in Fig. 4. This tendency is again in accordance with the unimolecular dissociation process of the six-coordinated complex. The fairly large positive $\Delta S_1^\ddagger$ value of ca. 60 $\mathrm{J\,K^{-1}\,mol^{-1}}$ for the k_1 path in all the present reaction systems is also attributed to the dissociative mode of activation. The $\Delta H_1^\ddagger$ values are considerably smaller in comparison with the activation enthalpy of 110 $\mathrm{kJ\,mol^{-1}}$ for water exchange of aquated chromium(III) ion with the associative activation mode.[51)] The enhancement in rate arises from the small $\Delta H^\ddagger$ values and the large positive $\Delta S^\ddagger$ values in the present system. The cause of the axial labilization effect is, therefore, the stabilization of the five-coordinated intermediate of the metalloporphyrin, which leads to the change in the reaction mechanism from associative to dissociative.

This work was supported by Grants-in-Aid for Scientific Research in a Priority Area No. 04215213 and for Scientific Research No. 04403011 from the Ministry of Education, Science and Culture.

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46) Abbreviations: 1-Meim, 1-methylimidazole; py, pyridine; 3-CNpy, 3-cyanopyridine; 3-Clpy, 3-chloropyridine; 3-Acpy, 3-acetylpyridine; 3-Mepy, 3-methylpyridine; 3,5-$\mathrm{Me_2py}$, 3,5-dimethylpyridine; 4-CNpy, 4-cyanopyridine; 4-Acpy, 4-acetylpyridine; 4-Mepy, 4-methylpyridine.

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49) The gas phase basicity of a molecule is defined in terms of the hypothetical reaction:

$$\mathrm{L} + \mathrm{H}^+ \longrightarrow \mathrm{LH}^+$$

The gas phase basicity is the negative of the energy change associated with this reaction. These values are cited in *Journal of Physical and Chemical Reference Data*, Volume 13, The American Chemical Society and the American Institute of Physics for the National Bureau of Standards (1984).

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