1014 © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 1014—1021 (1982) [Vol. 55, No. 4

Effect of Nucleophiles on the Rates of Dissociation and Racemization of the Tris(1,10-phenanthroline)iron(II) Ion in Aqueous Solutions

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(Received May 13, 1981)

The rates of dissociation and racemization of the tris(1,10-phenanthroline)iron(II) ion were obtained in aqueous solutions containing fourteen kinds of nucleophile. They ranged from 0.7 to 9.3 and from 0.9 to 3.2 times the rates in pure water, respectively. The results were analyzed by considering simultaneous reactions of free and ion-paired complex ions. The rate constants of the dissociation (ligand release) of the complex existing in ion-pairs increased in the following order of the counter-ions: $I^- < Br^- < Cl^- < (H_2O) < NO_2^- < CH_3COO^- < OCN^- < N_3^- < F^- < OH^- \approx CN^-$; here H_2O is regarded as a nucleophile for the free complex ion. This order is similar to that of proton affinities of nucleophiles. The results show that the dissociation is accelerated by σ donation from the nucleophile, suggesting an ion-pair interchange mechanism. The intramolecular racemization rate constant, given by total recemization rate constant minus dissociation rate constant, increased in the following order of nucleophiles: $OH^- \approx CN^- \approx F^- \approx Cl^- < Br^- \approx NO_2^- < (H_2O) < CH_3COO^- < OCN^- < I^- < N_3^- <$ (thiourea) $\approx SCN^- \approx SeCN^- <$ (pyridine). This suggests that the polarizability of nucleophiles has a greater effect than their basicity. The operation of π interaction between the complex ion and the nucleophile in the transition state is also suggested. The ion-association constants obtained from the rate data were in the range of 1 to 8 (I=1.0, 32.0 °C).

Intramolecular twist mechanisms[1] are among the basic reaction mechanisms of the stereochemical rearrangement of metal chelates. The nature of these mechanisms, however, does not seem to be fully understood.[2] Although such mechanisms are suggested in many systems, firm evidence for the mechanism has been presented for only a few cases.[3] The $[Fe(phen)_3]^{2+}$ (phen=1,10-phenanthroline) ion is one of the few inert complexes which racemize by an intramolecular twist mechanism.[4] Thus, studies of the racemization of this complex are expected to give information concerning the characteristics of the twist mechanism.

A variety of different mechanisms have been proposed for substitution reactions of the iron(II) complex. Margerum *et al.*[5] studied the nucleophilic substitution of $[Fe(phen)_3]^{2+}$ with hydroxide, cyanide, and azide. They proposed a mechanism in which nucleophiles enter into the "pocket" between ligands to form an inner-sphere ion-pair with the complex ion and interact with the metal center. An associative mechanism has been proposed for the nucleophilic ligand substitution of $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$.[6] Gillard[7] proposed a mechanism for hydrolysis involving nucleophilic attack at a chelate-ring carbon adjacent to a nitrogen atom. Recently, Lawrance *et al.*[8] proposed a dissociative interchange mechanism based on the values of activation volume obtained from high-pressure experiments. The conjugate base mechanism proposed for the base hydrolysis of cobalt(III) complexes does not seem to be operative in the present case, where the complex has no readily ionizable protons.

In the present study, the kinetics of dissociation and racemization of $[Fe(phen)_3]^{2+}$ were investigated in the presence of nucleophiles to clarify the dissociation mechanism in which nucleophiles are involved and to gain further understanding of the nature of the twist mechanisms.

Experimental

Materials. All the chemicals used were of guaranteed reagent grade except potassium azide, cyanate, and selenocyanate, and were obtained from Wako Pure Chemical Industries, Ltd. unless otherwise noted.

Complex: (+)-$[Fe(phen)_3](ClO_4)_2 \cdot 2H_2O$ was synthesized and resolved according to the method of Dwyer and Gyarfas.[9] $[\alpha]_{589}=1380°$.

Nucleophiles: Potassium fluoride, chloride, bromide, iodide, thiocyanate, cyanide, acetate, nitrite (Merck), and azide (Alpha), and thiourea were recrystallized from water. Potassium cyanate (Kanto) was recrystallized twice from water below 40 °C to minimize decomposition. Potassium selenocyanate was recrystallized from aqueous alcohol (1:5.5). Pyridine was fractionally distilled using a Widmer distilling column 30 cm long (bp 116.0—116.1 °C). Potassium hydroxide was used without further purification. The concentrations of the solutions of potassium thiocyanate, cyanide, cyanate, and selenocyanate were determined by argentometry. The concentration of the solution of potassium nitrate was determined by iodometry, that of potassium fluoride by the colorimetric method with a zirconium lake of 4-dimethylaminoazobenzene-4′-arsonic acid,[10] and that of potassium acetate by alkalimetry after passing the solution through a column of H-form cation-exchange resin. The solutions of potassium chloride, bromide, iodide, and azide, as well as those of thiourea, were prepared by weighing well-dried reagents.

Other Reagents: Nickel(II) chloride hexahydrate was recrystallized from water. Nickel(II) perchlorate hexahydrate was synthesized from nickel(II) carbonate and perchloric acid. The concentrations of nickel(II) solutions were determined by chelatometry. Other chemicals were used without further purification.

Kinetic Studies. Dissociation Rates: The dissociation rates were obtained at 32 °C from the changes in the absorbance at 510 nm of the solution containing 5×10^{-5} mol dm^{-3} $[Fe(phen)_3](ClO_4)_2$. Nickel(II) chloride (5.19×10^{-4} mol dm^{-3}) was added as the scavenger of the liberated phenanthroline[11] except in the solutions containing KCN and KOH.

A sodium citrate solution of 1.0×10^{-2} mol dm^{-3} was added to the solutions containing potassium cyanate, potassium acetate, and pyridine to prevent the precipitation of any iron hydroxide which might be produced in the course of the reaction. A 1.0×10^{-3} mol dm^{-3} citric acid solution was added to the solutions containing potassium azide and potassium nitrite, and a 2.0×10^{-3} mol dm^{-3} solution of disodium dihydrogen ethylenediaminetetraacetate (Na_2H_2edta) was added to the solutions containing potassium hydroxide for the same reason. The hydroxide ion concentration of the solution was corrected for the Na_2H_2edta added.5a) The reactions were followed for four half-lives, and were found to be of the first order in the metal-complex concentration in the time range studied. The data were analyzed by the usual method of the first order reactions. The dissociation rates obtained were reproducible within $\pm1\%$. They were independent of the nickel(II) concentration in the range of $(0.02—1.0)\times10^{-2}$ mol dm^{-3}; the rates obtained in Ni(II)-containing KCl solutions agreed with that obtained in acidic solution. The other added reagents had little effect on the dissociation rate, at least at their concentrations up to 1×10^{-2} mol dm^{-3}; the dependence of the rate on the reagent concentration was checked. For the systems containing KSCN and KSeCN, the dissociation rate could not be obtained because of the precipitation of the complex. Without Ni(II) ions, however, no precipitations nor absorbance changes were observed at least for thirty minutes, and the racemization rate could be obtained.

Racemization Rates: A 1.0 ml portion of a 5×10^{-4} mol dm^{-3} solution of the optically active iron-complex perchlorate, cooled with ice water, was added to a thermostated (32.0 °C) solution containing a nucleophile; the resultant solution was adjusted to a volume of 10.0 ml with water at 32.0 °C, and mixed immediately. After being kept for one minute in a thermostat, the solution was transferred into a thermostated (32.0 °C) quartz cell (5 cm path length) and the change in optical rotation of the solution at 546 nm was followed on a recorder using a Union PM-101 automatic polarimeter. Correction was made for the reproducible instrumental error which occurred when the absorbance of the solution decreased in the course of the kinetic measurement. All the reactions were followed for at least four half-lives. The reactions were first order in the concentration of the optically active metal complex in the time range studied.

The racemization rate constant was defined as $k_r=[\ln(\alpha_0/\alpha_t)]/t$, where α_0 and α_t mean the optical rotations at times zero and t, respectively. The reproducibility of the rate data was estimated to be within $\pm5\%$ from the standard deviation of the multiple measurements under the same experimental conditions.

pH Measurements. After each kinetic run, the pH value of the solution was measured by a Radiometer PHM26 pH-meter. In each case, the pH value was at least 2.0 greater than the pK_a value of the nucleophile contained. More than 99% of the nucleophiles thus existed in the free base form, so that the concentrations of the nucleophilic free bases assumed to be equal to those of the nucleophiles added.

Results and Discussion

Rates of Dissociation. Table 1 gives the rate constants for dissociation (k_d) and racemization (k_r) of the complex in aqueous solutions containing various nucleophiles at different concentrations. In the potassium azide system, the final absorbance value of the solution (A_∞) increased with the increase in citric acid and potassium azide concentrations of the solution. This would be caused by the formation of the mixed complex of nickel or iron with citrate and azide ions. However, linear relationships existed between $\log(A_t-A_\infty)$ and the time for four half-lives (A_t represents the absorbance at time t). The rate was not affected by nickel(II) and citric acid concentrations in the range studied. The rate constants thus obtained are considerably greater than those obtained by Margerum *et al.*,5b) who reported the slowing-down of the apparent dissociation rate after the first 15% decrease in the absorbance. The rate expression proposed by them (Eq. 10) is also different from that proposed here (Eq. 6).

Table 1. The racemization and dissociation rate constants (k_r and k_d) of $[Fe(phen)_3]^{2+}$ in various ionic media at 32.0 °C

Added salt (mol dm^{-3})		$k_r/10^{-3}$ s^{-1}		$k_d/10^{-3}$ s^{-1}		$(k_r-k_d)/10^{-3}$ s^{-1}	
		Obsd	Calcd a)	Obsd	Calcd a)	Obsd	Calcd
KCl							
0.00	—	1.94±0.09 (20) b)	1.94	0.255	0.254 c)	1.69	1.69
0.10	—	1.99	1.90	—	0.254	1.74	1.65
0.20	—	1.80, 1.81	1.88	0.254	0.254	1.55	1.63
0.30	—	1.86	1.86	—	0.254	1.61	1.61
0.40	—	1.72—1.82 (3)	1.83	0.254	0.254	1.51	1.58
0.60	—	1.82, 1.88	1.79	0.255	0.254	1.59	1.55
0.80	—	1.82, 1.85	1.76	0.254	0.254	1.58	1.51
1.00	—	1.70—1.79 (5)	1.74	0.251	0.254	1.49	1.49
KBr	KCl						
0.20	0.80	1.75	1.77	0.244	0.244	1.51	1.53
0.40	0.60	1.76	1.80	0.237	0.237	1.52	1.56
0.60	0.40	1.72, 1.88	1.82	0.231	0.231	1.57	1.59
0.80	0.20	1.80	1.84	0.225	0.225	1.58	1.61
1.00	0.00	1.83—1.86 (3)	1.85	0.221	0.221	1.62	1.65
KI	KCl						
0.20	0.80	2.10	2.13	0.231	0.230	1.87	1.90
0.40	0.60	2.24	2.23	0.213	0.214	2.03	2.02

Table 1. (Continued)

Added salt (mol dm^{-3})		$k_r/10^{-3}$ s^{-1}		$k_d/10^{-3}$ s^{-1}		$(k_r-k_d)/10^{-3}$ s^{-1}	
		Obsd	Calcd$^{a)}$	Obsd	Calcd$^{a)}$	Obsd	Calcd
0.60	0.40	2.36	2.27	0.201	0.202	2.16	2.07
0.80	0.20	2.36	2.30	0.193	0.192	2.17	2.11
1.00	0.00	2.22—2.37 (4)	2.31	0.185	0.184	2.10	2.13
0.10	—	—	—	0.233	0.236	—	—
0.20	—	—	—	0.227	0.225	—	—
0.40	—	—	—	0.208	0.210	—	—
0.50	—	—	—	0.206	0.204		
0.60			—	0.200	0.199	—	—
0.80	—	—	—	0.191	0.191	—	—
KI							
0.011	—	1.95	1.93	—	—	—	—
0.099	—	2.03	2.05	—	—	—	—
0.247	—	2.13, 2.17	2.15	—	—	—	—
0.422	—	2.17, 2.23	2.21	—	—	—	—
0.629	—	2.28, 2.28	2.26	—	—	—	—
0.760	—	2.38	2.28	—	—	—	—
0.837	—	2.23, 2.33	2.31	—	—	—	—
KF	KCl						
0.20	0.80	1.96	1.88	0.403	0.397	1.56	1.48
0.40	0.60	1.96	2.04	0.566	0.569	1.39	1.47
0.60	0.40	2.31	2.24	0.765	0.769	1.55	1.47
0.80	0.20	2.41	2.46	0.982	0.996	1.43	1.46
1.00	0.00	2.75	2.72	1.260	1.251	1.49	1.47
0.20	—	—	—	0.589	0.576	—	—
0.40	—	—	—	0.775	0.790	—	—
0.60	—	—	—	0.959	0.970	—	—
0.80	—	—	—	1.127	1.124	—	—
KN_3	KCl						
0.10	0.90	1.85	—	—	—	—	—
0.20	0.80	2.12, 2.15	2.16	0.522	0.526	1.61	1.63
0.30	0.70	2.29	—	—	—	—	—
0.40	0.60	2.47, 2.63	2.51	0.722	0.715	1.83	1.79
0.50	0.50	2.72	—	—	—	—	—
0.60	0.40	2.72, 3.04	2.79	0.855	0.852	2.03	1.93
0.80	0.20	2.91—3.17 (5)	3.03	0.950	0.956	2.07	2.07
1.00	0.00	3.11—3.40 (5)	3.24	$1.044^{d)}$	1.038	2.21	2.20
0.20	—	—	—	0.660	0.662	—	—
0.40	—	—	—	0.825	0.823	—	—
0.60	—	—	—	0.932	0.923	—	—
0.80	—	—	—	0.996	0.992	—	—
KSCN	KCl						
0.10	0.90	2.09	2.01	—	—	—	—
0.20	0.80	2.24	2.20	—	—	—	—
0.30	0.70	2.32	2.34	—	—	—	—
0.40	0.60	2.26, 2.48	2.45	—	—	—	—
0.60	0.40	2.70	2.61	—	—	—	—
0.80	0.20	2.73	2.72	—	—	—	—
1.00	0.00	2.72—2.87 (3)	2.77	—	—	—	—
0.021	—	2.00	2.01	—	—	—	—
0.043	—	2.02	2.07	—	—	—	—
0.070	—	2.03	2.12	—	—	—	—
0.078	—	2.15	2.13	—	—	—	—
0.100	—	2.23	2.16	—	—	—	—
0.162	—	2.40	2.25	—	—	—	—
0.205	—	2.03	2.30	—	—	—	—
0.30	—	2.27	2.39	—	—	—	—
0.40	—	2.53	2.47	—	—	—	—
0.50	—	2.42, 2.55	2.54	—	—	—	—
0.60	—	2.62	2.60	—	—	—	—

TABLE 1. (Continued)

Added salt (mol dm^{-3})		$k_r/10^{-3}$ s^{-1}		$k_d/10^{-3}$ s^{-1}		$(k_r-k_d)/10^{-3}$ s^{-1}	
		Obsd	Calcd[a]	Obsd	Calcd[a]	Obsp	Calcd
KOCN	KCl						
0.20	0.80	2.23	2.17	0.408	0.415	1.82	1.75
0.40	0.60	2.29	2.39	0.564	0.561	1.73	1.83
0.60	0.40	2.57	2.57	0.702	0.692	1.87	1.88
0.80	0.20	2.74	2.72	0.814	0.810	1.93	1.91
1.00	0.00	2.85, 2.88	2.85	0.906	0.916	1.96	1.93
KSeCN	KCl						
0.10	0.90	2.18	2.17	—	—	—	—
0.20	0.80	2.41	2.40	—	—	—	—
0.40	0.60	2.51	2.64	—	—	—	—
0.60	0.40	2.83	2.76	—	—	—	—
0.80	0.20	2.76	2.83	—	—	—	—
1.00	0.00	2.83, 3.02	2.89	—	—	—	—
KNO_2	KCl						
0.20	0.80	1.75, 1.88	1.81	0.271	0.270	1.61	1.54
0.40	0.60	1.85, 1.89	1.87	0.290	0.287	1.60	1.58
0.60	0.40	1.91, 1.94	1.92	0.306	0.305	1.63	1.61
0.80	0.20	1.94, 1.95	1.95	0.323	0.322	1.63	1.63
1.00	0.00	1.97, 2.01	1.99	0.340[d]	0.340	1.67	1.65
KCH_3COO	KCl						
0.20	0.80	1.93	1.87	0.280	0.280	1.55	1.59
0.40	0.60	1.92	1.97	0.308	0.310	1.61	1.66
0.60	0.40	2.10	2.05	0.332	0.340	1.77	1.71
0.80	0.20	2.04	2.12	0.380	0.370	1.66	1.75
1.00	0.00	2.14—2.26 (3)	2.18	0.401	0.400	1.80	1.78
0.40	—	—	—	0.335	0.333	—	—
0.60	—	—	—	0.357	0.359	—	—
KOH	KCl						
0.016	0.98	1.91	1.94	0.488	0.481	1.42	1.47
0.036	0.96	2.16	2.20	0.783	0.761	1.38	1.45
0.056	0.94	2.46	2.46	1.018	1.036	1.44	1.43
0.076	0.92	2.63	2.72	1.284	1.307	1.35	1.41
0.080[e]	0.90	2.89	2.78	1.343	1.372	1.55	1.42
0.096	0.90	3.02	2.99	1.605	1.573	1.41	1.40
KCN	KCl						
0.020	0.98	2.30	2.21	0.736	0.710	1.56	1.53
0.040	0.96	2.72	2.68	1.110	1.148	1.61	1.57
0.060	0.94	3.08	3.14	1.587	1.570	1.49	1.59
0.080	0.92	3.46, 3.79	3.61	1.981	1.976	1.64	1.63
0.100	0.90	4.05, 4.08	4.07	2.357	2.367	1.71	1.66
Thiourea	KCl						
0.10	1.00	—	—	0.231	—	—	—
0.20	1.00	1.97	2.00	0.225	—	1.75	1.78
0.40	1.00	2.27	2.22	0.217	—	2.05	2.00
0.60	1.00	2.39	2.37	0.209	—	2.18	2.16
0.80	1.00	2.42	2.49	0.203	—	2.22	2.29
0.90	1.00	—	—	0.189	—	—	—
1.00	1.00	2.61	2.58	0.189	—	2.42	2.39
Pyridine	KCl						
0.20	1.00	3.14, 3.32	3.15	0.274	—	2.96	2.87
0.40	1.00	3.98	4.14	0.305	—	3.67	3.84
0.60	1.00	4.66	4.90	0.346	—	4.31	4.56
0.80	1.00	5.50, 6.05	5.50	0.389	—	5.39	5.11
1.00	1.00	5.64—6.15 (3)	5.98	0.433	—	5.52	5.54

a) Calculated with Eq. 6 or 9 using the $K^{IP}_{c(X)}$ and $k^{IP}_{d(X)}$ or $k^{I,IP}_{r(X)}$ values given in Table 2. b) The value in parentheses is the number of observations. c) In KCl solutions, the value of k_d was assumed to be independent of the KCl concentration. d) The value changed only within ±1% in 0—1×10^{-2} mol dm^{-3} citric acid. e) Containing 1.0×10^{-2} mol dm^{-3} Na_2H_2-edta.

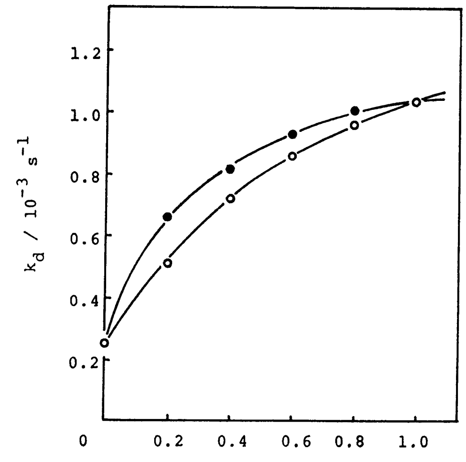

Fig. 1. The dissociation rate constants of $[Fe(phen)_3]^{2+}$ in potassium azide solutions. The solid circles show the rate constants observed in the solutions without ionic-strength adjustment and the open circles are those in the solutions of constant ionic strength ($I=1.0$, adjusted with KCl).

The effect of nucleophiles on the reaction rate is discussed separately in two groups: anionic and neutral nucleophiles.

Anionic Nucleophiles: An example of the results is shown in Fig. 1. The ion-pair formation mechanism[12] reasonably accounts for the observed dissociation rates. In the systems without added KCl, the proposed mechanism is as follows:

$$[Fe(phen)_3]^{2+} + X^- \xrightleftharpoons{K^{IP}_{(X)},\ K^{IP}_{c(X)}} [Fe(phen)_3]^{2+}\cdot X^-, \tag{1}$$

$$[Fe(phen)_3]^{2+} \xrightarrow{k^0_d} Fe^{2+} + 3\,phen, \tag{2}$$

$$[Fe(phen)_3]^{2+}\cdot X^- \xrightarrow{k^{IP}_{d(X)}} Fe^{2+} + 3\,phen + X^-, \tag{3}$$

$$K^{IP}_{(X)} = \frac{[Fe(phen)_3{}^{2+}\cdot X^-]}{[Fe(phen)_3{}^{2+}][X^-]}\frac{f_1}{f_2 f_1} \simeq K^{IP}_{c(X)}\frac{1}{f_2}, \tag{4}$$

where $K^{IP}_{(X)}$ and $K^{IP}_{c(X)}$ represent the thermodynamic and the concentration ion-association constant for reaction (1) and where k^0_d and $k^{IP}_{d(X)}$ are the rate constants for reactions (2) and (3), respectively. The symbol f_z means the activity coefficient of the ion with a charge of $\pm z$; $\log f_z$ can be expressed as:

$$\log f_z = -\frac{z^2 A\sqrt{I}}{1+Ba\sqrt{I}} + bI, \tag{5}$$

where $A=0.5181$ $mol^{-1/2}$ $dm^{3/2}$, $B=0.3305\times10^8$ cm^{-1} $mol^{-1/2}$ $dm^{3/2}$ at 32 °C in water, and the parameters, a and b, are taken to be $(7-12)\times10^{-8}$ cm and $0.1\,z^2$, respectively. Then, the observed dissociation rate constant, k_d, is expressed as:

$$k_d = \frac{k^0_d + k^{IP}_{d(X)}K^{IP}_{c(X)}f_2[X^-]}{1+K^{IP}_{(X)}f_2[X^-]}. \tag{6}$$

The $K^{IP}_{(X)}$ and $k^{IP}_{d(X)}$ were obtained by the weighted least-squares fit[13] to Eq. 6 of the kinetic data. The $K^{IP}_{(X)}$ was transformed to the ion-association constant ($K^{IP}_{c(X)}$) at $I=1.0$ by means of Eqs. 4 and 5.

The following equations were added to Eqs. 1—3 for the systems in which the ionic strength was adjusted to 1.0 with added KCl.

$$[Fe(phen)_3]^{2+} + Cl^- \xrightleftharpoons{K^{IP}_{c(Cl)}} [Fe(phen)_3]^{2+}\cdot Cl^- \tag{7}$$

$$[Fe(phen)_3]^{2+}\cdot Cl^- \xrightarrow{k^{IP}_{d(Cl)}} Fe^{2+} + 3\,phen + Cl^- \tag{8}$$

Then, the observed dissociation rate constant is expressed as:

$$k_d = \frac{k^0_d + k^{IP}_{d(Cl)}K^{IP}_{c(Cl)}[Cl^-] + k^{IP}_{d(X)}K^{IP}_{c(X)}[X^-]}{1+K^{IP}_{c(Cl)}[Cl^-]+K^{IP}_{c(X)}[X^-]}. \tag{9}$$

Since the dissociation rate constants were almost unaffected by the KCl concentration (Table 1), the value of $K^{IP}_{c(Cl)}$ was obtained in the following way.

TABLE 2. THE ION-ASSOCIATION CONSTANTS OF $[Fe(phen)_3]^{2+}$ WITH NUCLEOPHILES ($K^{IP}_{c(X)}$) AND THE DISSOCIATION AND INTRAMOLECULAR RACEMIZATION RATE CONSTANTS ($k^{IP}_{d(X)}$ AND $k^{i,IP}_{d(X)}$) OF THE COMPLEX IN ION-PAIRS AT THE CONSTANT IONIC STRENGTH OF 1.0 (KCl)

Nucleophile	pK_a	$k^{IP}_{d(X)}/10^{-3}$ s^{-1}	$k^{i,IP}_{r(X)}/10^{-3}$ s^{-1}	$K^{IP}_{c(X)}$	
				Dissociation	Racemization
I	−10	0.165±0.003	2.20±0.09	3.5±0.4	6 ±4
Br	−7	0.210±0.003	1.58±0.11	3.1±1.3	2 ±5
Cl	−4	0.250±0.003	1.37±0.04	2.0±1.0	1.7±0.6
H_2O	−1.7	0.254±0.002	1.74±0.09	—	—
SCN	−0.7	<0.4	3.04±0.17[a]	—	3.4±1.5
Thiourea	0.4	—	2.53±0.18	—	5 ±3
F	3.2	1.78 ±0.03	1.48±0.12	1.9±0.1	1.0±0.9
NO_2	3.4	0.391±0.005	1.64±0.06	1.6±0.2	6 ±11
OCN	3.5	1.14 ±0.06	1.94±0.09	2.9±1.3	17 ±20
SeCN	—	<0.13	2.99±0.10[a]	—	9 ±4
N_3	4.7	1.18 ±0.01	2.4 ±0.3	5.7±0.2	2 ±3
CH_3COO	4.7	0.475±0.011	1.79±0.07	2.0±0.2	6 ±4
Pyridine	5.3	—	6.4 ±0.3	—	5 ±2
CN	9.2	14.2 ±1.6	1.60±0.17	5.0±2.0	5 ±7
OH	15.7	13.6 ±2.0	1.43±0.14	3.2±1.8	0.7±10

a) Rate constants for the total racemization. Other values are for the intramolecular racemization.

Using Eq. 6, an analysis of the kinetic data was made for the systems of various ionic strength containing KI, KN_3, KF, KCH_3COO, and KNO_2 to obtain the values of $k^{IP}_{d(Cl)}$ and $K^{IP}_{c(X)}$. These values were substituted in Eq. 9. The kinetic data for similar systems of the constant ionic strength with added KCl were analyzed with this equation to evaluate $k^{IP}_{d(Cl)}$ and $K^{IP}_{c(X)}$. The latter kinetic data were analyzed again using the resulting $k^{IP}_{d(Cl)}$ and $K^{IP}_{c(X)}$ values to re-evaluate $k^{IP}_{d(X)}$ and $K^{IP}_{c(X)}$. The values thus obtained are in agreement with those derived above from the data for the solutions of variable ionic strength within the experimental error. These $k^{IP}_{d(X)}$ and $K^{IP}_{c(X)}$ values at $I=1.0$ are listed in Table 2.

Margerum[5)] reported the rate expression of the type

$$k_d = k_0 + k_1[X] + k_2[X]^2 + k_3[X]^3 \tag{10}$$

for the azide-, cyanide-, and hydroxide-assisted dissociation of $[Fe(phen)_3]^{2+}$. The square and cubic terms of nucleophile concentration in the rate equation were observed only for hydroxide ions. They were accounted for in terms of the mechanism of the multiple hydroxide attack to the complex, or the multiple hydroxide-association with the complex. However, the rate dependence of the type of Eq. 10 can also be fitted by Eq. 9 for the ion-pair formation mechanism. By substituting C_T(constant) for [Cl]+[X], Eq. 9 is transformed to

$$k_d = \frac{(k^0_d + k^{IP}_{d(Cl)}K^{IP}_{c(Cl)}C_T) + (k^{IP}_{d(X)}K^{IP}_{c(X)} - k^{IP}_{d(Cl)}K^{IP}_{c(Cl)})[X]}{(1+K^{IP}_{c(Cl)}C_T) - (K^{IP}_{c(Cl)} - K^{IP}_{c(X)})[X]}. \tag{11}$$

On the condition of $\left|\frac{(K^{IP}_{c(Cl)} - K^{IP}_{c(X)})[X]}{(1+K^{IP}_{c(Cl)}C_T)}\right| < 1$, the denominator of Eq. 11 can be expanded to an infinite series and Eq. 11 is then transformed to:

$$\begin{aligned}
k_d &= \{(k^0_d + k^{IP}_{d(Cl)}K^{IP}_{c(Cl)}C_T) + (k^{IP}_{d(X)}K^{IP}_{c(X)} - k^{IP}_{d(Cl)}K^{IP}_{c(Cl)})[X]\} \\
&\quad \times \left\{\frac{1}{(1+K^{IP}_{c(Cl)}C_T)} + \frac{(K^{IP}_{c(Cl)} - K^{IP}_{c(X)}}{(1+K_{c(Cl)}C_T)^2}[X] \right. \\
&\quad \left. + \frac{(K^{IP}_{c(Cl)} - K^{IP}_{c(X)})^2}{(1+K^{IP}_{c(Cl)}C_T)^3}[X]^2 + \cdots \right\} \\
&= \frac{(k^0_d + k^{IP}_{d(Cl)}K^{IP}_{c(Cl)}C_T)}{(1+K^{IP}_{c(Cl)}C_T)} + \left\{\frac{(k^0_d + k^{IP}_{d(Cl)}K^{IP}_{c(Cl)}C_T)(K^{IP}_{c(Cl)} - K^{IP}_{c(X)})}{(1+K^{IP}_{c(Cl)}C_T)^2} \right. \\
&\quad \left. + \frac{(k^{IP}_{d(X)}K^{IP}_{c(X)} - k^{IP}_{d(Cl)}K^{IP}_{c(Cl)})}{(1+K^{IP}_{c(Cl)}C_T)}\right\}[X] \\
&\quad + \left\{\frac{(k^0_d + k^{IP}_{d(Cl)}K^{IP}_{c(Cl)}C_T)(K^{IP}_{c(Cl)} - K^{IP}_{c(X)})^2}{(1+K^{IP}_{c(Cl)}C_T)} \right. \\
&\quad \left. + \frac{(K^{IP}_{c(Cl)} - K^{IP}_{c(X)})(k^{IP}_{d(X)}K^{IP}_{c(X)} - k^{IP}_{d(Cl)}K^{IP}_{c(Cl)})}{(1+K^{IP}_{c(Cl)}C_T)}\right\}[X]^2 + \cdots \\
&= k_0 + k_1[X] + k_2[X]^2 + \cdots.
\end{aligned} \tag{12}$$

For KF, KNO_2, KCH_3COO, KCN, and KOH, the observed dissociation rate constants were nicely expressed by Eq. 9 with the parameter values listed in Table 2, although the rate constants could also be expressed by Eq. 10. In fact, the kinetic data for hydroxide-assisted dissociation obtained by Margerum[5a)] can also be reproduced by Eq. 9 with a $K^{IP}_{c(X)}$ value of 1.0±0.7, consistent with the value of 3.2±1.8 obtained here. Thus, in our opinion, Eq. 10 may be regarded as an approximation to Eq. 9.

As shown in Table 2, the $k^{IP}_{d(X)}$ values increase in the order:

$$I^- < Br^- < Cl^- < (H_2O) < NO_2^- < CH_3COO^- < OCN^- < N_3^- < F^- < OH^- \approx CN^-,$$

where H_2O means free complex ions not forming ion-pairs. A good correlation is observed between the logarithm of $k^{IP}_{d(X)}$ and the pK_a value of the conjugate acid of the nucleophile, as shown in Fig. 2. Considering that pK_a is a measure of the σ-donating ability of a nucleophile, the dissociation is likely to proceed by an ion-pair interchange mechanism where the nucleophile in an ion-pair would interact directly with the central metal of the complex. The dissociation rate constant of the free complex cation follows the trend observed in Fig. 2, where a water molecule is regarded as a nucleophilic reagent for the free cation. Thus, the free cation would also dissociate by a similar interchange mechanism, *e.g. via* a 7-coordinate transition state with an H_2O ligand, as suggested by Burgess.[14)]

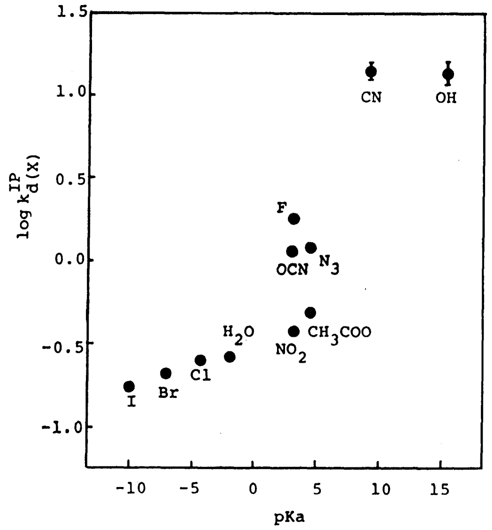

Fig. 2. The plot of the logarithm of $k^{IP}_{d(X)}$ *vs.* the pK_a value of nucleophile.

Alternative mechanisms which may account for the observed dissociation rates are: (i) dissociative mechanism, (ii) associative mechanism, and (iii) Gillard's mechanism. If dissociation of the complex proceeds dissociatively, the rate constant would be independent of the kind of nucleophile. As different rates were observed in the presence of different nucleophiles (Table 2), the dissociative mechanism can be excluded. Maestri *et al.*[15)] proposed an associative mechanism for the base hydrolysis of $[Cr(bpy)_3]^{3+}$ to account for the rate expression, $k^{obsd}=[OH^-]/(B+A[OH^-])$, a special case of Eq. 6 with $k^0_d=0$. The mechanism assumes that, as soon as the heptacoordinate complex is formed by the coordination of a water molecule, it undergoes an acid-base equilibrium, and that the conjugate-base form of the heptacoordinate complex (hydroxide associated species) tends to dissociate; the step of water coordination is considered to be rate-determining. A similar but slightly different mechanism may be considered to account for a rate expression of the type like Eq. 6; the mechanism assumes that a water molecule associated with the complex is subjected to nucleophilic proton subtraction to form a hydroxide-associated species which undergoes dissociation. In this mechanism, the rate constant for the proton subtraction would be proportional to the probability of the nucleophile approaching the complex (or, in a sense, the ion-association constant) and to the ease of the proton subtraction. As the former does not change very much, the latter may be correlated with the strength of the nucleophile as a base. Although the order in which the nucleophiles increase the dissociation rate of the complex is in general consistent with the trend of increasing basicity of the nucleophiles, the deceleration effect shown by halide ions cannot be explained by this mechanism. Gillard's mechanism supposes the direct nucleophilic attack to a carbon atom of the phenanthroline molecule. The order of nucleophilic reactivity obtained in this study is very different from that obtained from the rate of nucleophilic displacement of the iodide ion from methyl iodide.[16] Thus, Gillard's mechanism is not adequate to interpret the experimental results. Therefore, the ion-pair interchange mechanism proposed in this paper very probably takes place.

Pyridine and Thiourea: In the systems containing pyridine and thiourea, the kinetic data could not be reproduced by Eq. 6 nor by Eq. 9 (see Table 1). The coordination of pyridine molecules to the second coordination sphere of the complex may be important for the system containing pyridine. In the system containing thiourea, a steep decrease in the rate was observed at 0—0.1 and 0.8—0.9 mol dm^{-3} thiourea concentrations. This may reflect the change in water activity or in the solution structure around these thiourea concentrations, if a water molecule is coordinated to the complex ion in the transition state.

Rates of Racemization. The observed racemization rate constants (k_r) are listed in Table 1, along with the dissociation rate constants (k_d) obtained under the same experimental conditions. Since the complex racemizes intramolecularly and dissociatively, the intramolecular racemization rate is given by total racemization rate minus dissociation rate. The total racemization rates increased considerably with added nucleophiles, except in the systems containing KCl and KBr. On the other hand, the intramolecular racemization rates do not appreciably change for the systems containing KF, KCN, and KOH, increase slightly with increasing concentrations of KBr, KNO_2, and KCH_3COO, and increase considerably with the increase in the concentrations of KI, KSCN, KSeCN, KOCN, KN_3, thiourea, and pyridine. The KOH result is in contrast to the intramolecular twist racemization of (ethylenediaminetetraacetato)cobalt(III), for which the racemization was reported to be accelerated by the hydroxide ion.[17] The increase in intramolecular racemization rate of $[Fe(phen)_3]^{2+}$ with increasing nucleophile concentration can resonably be accounted for by considering ion-pair formation, as in the case of dissociation. An analysis similar to that used for the case of dissociation gave the intramolecular racemization rate constants for the ion-paired complex ion ($k_{r(X)}^{i,IP}$) and the ion-association constants ($K_{c(X)}^{i,IP}$); these are listed in Table 2. The variation in the racemization rate constant with different nucleophiles is smaller than that in the dissociation rate constant. The order for $k_{r(X)}^{i,IP}$ is: $OH^- \approx CN^- \approx F^- \approx Cl^- < Br^- < NO_2^- < H_2O < CH_3COO^- < OCN^- < I^- < N_3^- <$ thiourea $\approx SCN^- \approx SeCN^- <$ pyridine. This order of nucleophiles in accelerating the intramolecular racemization rate suggests the importance of the polarizability of nucleophiles rather than their basicity, which was suggested above to be important for nucleophile-assisted dissociation. The order seems to be in rough agreement with that proposed for the reactivity against platinum(II) complexes:[18] $OH^- < H_2O < Cl^- <$ pyridine $< Br^- < NO_2^- < N_3^- \approx SCN^- \approx I^- \approx$ thiourea $< R_3P$. The polarizability of the nucleophile was suggested to be important in determining this order. The absorption spectrum of the complex changed in the presence of KCl, KBr, KI, and KSCN, suggesting a short-range interaction between the complex and the nucleophiles. Red shifts (2—3 nm) of the visible and ultraviolet absorption bands of the complex are observed in the presence of KCl and KBr, while, for KI and KSCN, broadenings of the ultraviolet absorption band (266 nm) toward the longer wave length are observed in addition to the red shift of the visible band. A π interaction between the complex ion (possibly the phen ligand) and a nucleophile would be important for assisting the intramolecular racemization, in contrast to the importance of σ donation of a nucleophile to the central metal of the complex for assisting the dissociation. Thus, it may be said that the central metal of $[Fe(phen)_3]^{2+}$ acts as a hard acid in the dissociation assisted by nucleophilic attack and the ligand phenanthroline acts as a soft acid in the intramolecular racemization assisted by nucleophile. The large accelerating effect of pyridine on the racemization rate may be caused by the solvation-like effect on the complex cation. Remarkable effects of solvents in accelerating the racemization rates were reported for this complex.[19]

The Ion-association Constants. The ion-association constants obtained from the dissociation rates agreed with those obtained from the racemization rates within experimental uncertainties (Table 2). The order of magnitudes of the constants obtained are also in good agreement with the theoretical prediction[20] of $K_{c(X)}^{IP} = 1—7$ ($I = 1.0$, $a = (3—12) \times 10^{-8}$ cm). This can be taken as supporting the ion-pair mechanism for the dissociation and racemization discussed above. The ion-association constant of the complex with an anion increased in the order: $F^- < Cl^- < Br^- < I^-$. The order might seem to be contrary to the theoretical prediction, according to which $K_{c(X)}^{IP}$ increases with the increase in the reciprocal of the ionic radius of the nucleophile. However, the reversal of the order can be well understood by considering the hydration of nucleophiles. The hydration number increases with the increase in the reciprocal of the ionic radius. The effective radius of a hydrated ion would increase with the increase in the hydration number. The short-range interactions discussed above may also be a factor affecting the order given above.

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