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The Kinetics and Mechanisms of the Racemization of Tris(*N*,*N*′-dimethylethanediimine)iron(II)

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Tris(*N*,*N*′-dimethylethanediimine)iron(II) (trivial name: tris(glyoxal-bis-*N*-methylimine)iron(II)1)), $[\mathrm{Fe(gmi)_3}]^{2+}$, has been resolved for the first time, and its racemization mechanism has been investigated in acid solutions. A mechanism similar to that for tris(2,2′-bipyridine)iron(II) was verified from the acid dependence of the racemization rate. At 69.4 °C, 30% of the racemization proceeded by means of an intramolecular bond-rupture mechanism and the remainder by means of an intramolecular twist mechanism. The activation enthalpy and the activation entropy for the twist path were 148($\Delta H^{\neq}$/kJ mol^{-1}) and 110($\Delta S^{\neq}$/J K^{-1} mol^{-1}) respectively. These values were compared with 127 and 114 for $[\mathrm{Fe(bpy)_3}]^{2+}$ (bpy=2,2′-bipyridine) and with 119 and 91 for $[\mathrm{Fe(phen)_3}]^{2+}$ (phen=1,10-phenanthroline). The racemization rate was larger in organic solvents, increasing in the order water<nitromethane<formamide<dimethyl sulfoxide, which is the same as the order for the bpy and phen complexes. The rate was less dependent on the solvent in the order $[\mathrm{Fe(phen)_3}]^{2+} > [\mathrm{Fe(bpy)_3}]^{2+} > [\mathrm{Fe(gmi)_3}]^{2+}$. A salt effect on the racemization rates was also observed.

The intramolecular twist mechanism2) is one of the basic mechanisms of the stereochemical rearrangement of metal chelates. The nature of the mechanism, however, does not seem to be fully understood.3) Many investigations have been made concerning the intramolecular stereochemical rearrangement of stereochemically nonrigid complexes by means of dynamic nuclear magnetic resonance spectroscopy.4) The mechanisms proposed in these studies have, however, been mainly based on indirect evidence. On the other hand, the studies of inert complexes based on rather classical kinetic methods have given more definitive evidence to show the reaction mechanisms.5)

Tris(1,10-phenanthroline)iron(II)6) is one of the few examples of such inert complexes which racemize by means of an intramolecular twist mechanism. Iron(II) forms very stable, strongly colored complexes not only with bpy and phen, but also with *N*,*N*′-dialkyl-1,2-diimines.7) The racemization of the simple *N*,*N*′-dialkyl-1,2-diimine complex, $[\mathrm{Fe(gmi)_3}]^{2+}$ (gmi=$\mathrm{CH_3N{=}CH{-}CH{=}NCH_3}$), has been studied to disclose whether or not a twist mechanism also occurs in this case, and to gain a better understanding of the characteristics of the twist mechanism.

Experimental

Materials. *Preparation and Resolution of the Complexes*: Tris(*N*,*N*′-dimethylethanediimine)iron(II) iodide, $[\mathrm{Fe(gmi)_3}]\mathrm{I_2 \cdot 3H_2O}$, was prepared by Krumholtz's method.1) The complex was resolved for the first time by the fractional crystallization of its $(+)_{589}$-tartratoantimonate. Racemic iodide (2.0 g, 3.6×10^{-3} mol) was dissolved in water (10.5 cm^3), and, to the resulting solution, silver $(+)_{589}$-tartratoantimonate (2.8 g, 7.2×10^{-3} mol) was added with vigorous stirring. The stirring was continued for several minutes, during which double decomposition was completed to yield the solution of the $(+)_{589}$-tartratoantimonate of the racemic complex and the insoluble silver iodide. After the latter was filtered off, the solution was heated to 40 °C and ethanol was slowly added to it until the solution became slightly cloudy. The solution was then kept overnight at 0 °C to give a crystalline precipitate. Crystals of the $(+)_{589}$-tartratoantimonate of this complex, $(-)_{589}$-$[\mathrm{Fe(gmi)_3}]$(Sbtart)$_2$, were filtered off from the solution, and the crystals of $(+)_{589}$-$[\mathrm{Fe(gmi)_3}]$(Sbtart)$_2$ were precipitated by adding ethanol to the filtrate. By repeating the fractional crystallization five times, 0.15 g of $(+)_{589}$-diastereomer ($\Delta\varepsilon_{570}=+32$) and 0.32 g of $(-)_{589}$-diastereomer ($\Delta\varepsilon_{570}=-30$) were obtained. These diastereomers were converted into active bromide by the use of the anion-exchange resin, Dowex 2-X8, by the column method. The $[\alpha]_{589}$ values for $(+)_{589}$- and $(-)_{589}$-enantiomers were +950° and −900° respectively. Anal. $(+)_{589}$-$[\mathrm{Fe(gmi)_3}]\mathrm{Br_2 \cdot 3H_2O}$: Found: C, 27.40; H, 5.49; N, 15.96; Calcd for $\mathrm{C_{12}H_{30}N_6O_3Br_2Fe}$: C, 27.61; H, 5.75; N, 16.10.

Tris(1,10-phenanthroline)iron(II) perchlorate was resolved through precipitation as $(+)_{589}$-tartratoantimonate according to the method of Dwyer and Gyarfas;8) $[\alpha]_{589}=+1460°$. The resolution of tris(2,2′-bipyridine)iron(II) perchlorate through precipitation as iodide $(+)_{589}$-tartratoantimonate was carried out in a manner similar to that previously described;9) $[\alpha]_{589}=+4970°$.

Solvent: Nitromethane was refluxed with urea, dried with anhydrous sodium sulfate, and distilled. Dimethyl sulfoxide was distilled under reduced pressure, treated with alumina, and distilled again under reduced pressure. Formamide was dried with anhydrous sodium sulfate and distilled twice under reduced pressure.

Other Reagents: Guaranteed-grade potassium chloride and potassium iodide were recrystallized from water. Guaranteed-grade hydrochloric acid was purified by azeotropic distillation. Guaranteed-grade potassium thiocyanate was recrystallized from an aqueous ethanolic (1:1) solution. All the other chemicals were of a guaranteed grade and were used without purification.

Experimental Procedure. *Racemization and Dissociation of* $[Fe(gmi)_3]^{2+}$: The optically active bromide was dissolved in a given solvent ($(0.42-2.5)\times10^{-4}$ M††), containing other chemicals whenever necessary. Aliquots of the solution were sealed in eleven small test tubes. They were placed in a thermostat(±0.1 °C) and taken out, one by one, at proper intervals. They were then cooled in ice water, and their circular dichroism(CD) strength was measured at 570 nm and their absorbance, at 560 nm. The apparent racemization (rate constant: k_r^{app}) was studied by following the loss of optical activity for one to five half-lives. From the changes in the absorbance of the solution during the apparent racemization, the dissociation rate (rate constant: k_d) was calculated. Both the apparent racemization and the

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†† 1 M=1 mol dm^{-3}.

dissociation were first-order with respect to the metal-complex concentration in the time range of the experiments. The net rate of racemization (rate constant: k_r^{net}) was obtained as $k_r^{net}=k_r^{app}-k_d$.

Racemization of $[Fe(bpy)_3]^{2+}$ *and* $[Fe(phen)_3]^{2+}$: The (0.5—1.0) × 10^{-4} M solutions of optically active perchlorates were placed in a thermostatted (±0.1 °C) quartz cell, and the change in the optical rotation (at 510 nm for the phenanthroline complex, 525 nm for the bipyridine complex) was followed on a recorder. The temperature was measured during the reaction by putting a thermister directly in the solution. The reactions were followed for one to two half-lives.

Dissociation of $[Fe(bpy)_3]^{2+}$ *and* $[Fe(phen)_3]^{2+}$: The 0.5 × 10^{-4} M solutions of the complex were placed in a thermostatted (±0.1 °C) quartz cell, and the change in the absorbance (at 510 nm for the phen complex, 520 nm for the bpy complex) of the solution was followed on a recorder.

The racemization and dissociation rate constants were calculated by the usual method for first-order reactions. The racemization rate constant was defined as $k_r=[\ln(\alpha_0/\alpha_t)]/t$, where α_0 and α_t are the optical rotations or the CD strengths at time zero and t respectively.

Apparatus. A JASCO ORD/UV-5 with a CD attachment was used for measuring the CD strength and the optical rotation, and for recording the CD spectra. A Hitachi 323 Spectrometer was used for recording the absorption spectra, and Hitachi 101 and 124 Spectrophotometers, for measuring the absorbances.

Results and Discussion

CD Spectrum. Figure 1 shows the absorption and CD spectra of the resolved complex. The CD spectrum of the complex is very similar to those of the bpy and phen complexes;[10] the positive and negative CD peaks near 20×10^3 cm^{-1} are attributed to charge-transfer transitions by analogy with the corresponding bands in the bpy and phen complexes. The CD peak at 28.5×10^3 cm^{-1} is that of the d-d transition ($^1T_{2g}\leftarrow{}^1A_{1g}$ in octahedral approximation), in agreement with the assignment of the absorption band near 28.5×10^3 cm^{-1} by Ito *et al.*[11] On the other hand, the CD peaks at (25—26) × 10^3 cm^{-1} of $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ were suggested to be of metal-to-ligand charge-transfer transitions.[10] In view of the d-d spectral parameters of $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$,[12] a d-d absorption band ($^1T_{2g}\leftarrow{}^1A_{1g}$ in O_h approximation) is suspected to exist around (25—26) × 10^3 cm^{-1}, though it is hidden by the strong CT-bands. Thus, the CD peaks of tris(1,2-diimine)-iron(II) at (25—30) × 10^3 cm^{-1} are probably of $^1T_{2g}\leftarrow{}^1A_{1g}$ d-d transition. The observed intensities of these CD peaks of magnetically forbidden d-d transitions may be attributed to a trigonal distortion of the complex and to mixing with charge-transfer transition.

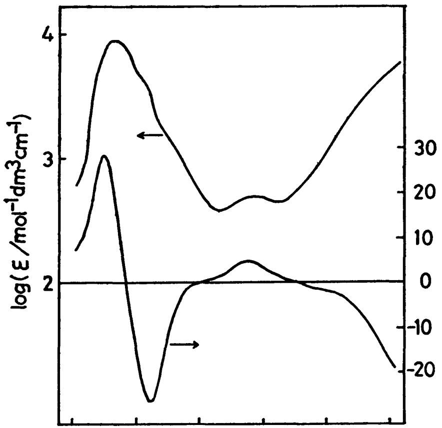

Fig. 1. Absorption (AB) and circular dichroism (CD) spectra of $(+)_{589}[Fe(gmi)_3]Br_2$ in aqueous solution.

Kinetics and Mechanism of Racemization. *Racemization in a Neutral Solution*: The apparent racemization, as measured by the change in optical activity, was first-order throughout approximately 90% of the reaction. The CD strength throughout the spectrum diminished monotonously to zero as the reaction proceeded. The decrease in absorbance (*A*) observed during this apparent racemization gave a straight line in the graph of log *A* *vs.* time. The decrease in absorbance was attributed to the dissociation of the complex, since the monotonous absorbance change occurred over the whole range of the absorption spectrum. The dissociation of the complex was an irreversible reaction, probably due to the immediate hydrolysis of the dissociated ligand. The formation of the bis complex from the tris complex was regarded as rate-determining;[13] *i.e.*, once one gmi ligand has been released from the tris complex, the complex will decompose irreversibly to yield an aqua-complex. Thus, the net racemization of this complex will take place exclusively by means of intramolecular mechanisms and not by intermolecular ligand-exchange processes. The net racemization rates were not affected by the presence of possible decomposition products of the complex (methylamine and/or glyoxal).

Racemization in an Acidic Solution: The decomposition of the complex is known to be acid-catalyzed,[14] and the rate expression is known to be similar to that for $[Fe(bpy)_3]^{2+}$,[6] which dissociates through an intermediate with one bond ruptured. In order to clarify the role of this process in the racemization, the racemization rate was measured at various acid concentrations. The results are depicted in Fig. 2. The observed acid dependence of the rates can be explained by the reaction scheme shown in Fig. 3. In the reaction scheme, k_r^t and $k_r^{b.r.}$ represent the rate constants of an intramolecular twist racemization process and that of an intramolecular bond-rupture racemization process respectively.

The rate constant for the apparent racemization, k_r^{app}, can be expressed as:

$$k_r^{app} = k_r^t + k_1\left(\frac{k_2+k_r^{b.r.}+k_3[H^+]}{k_{-1}+k_2+k_r^{b.r.}+k_3[H^+]}\right), \qquad (1)$$

if the steady-state approximation is applied to the bond-rupture intermediate. The rate constant of acid dissociation, k_d, can be expressed as:

$$k_d = k_1\left(\frac{k_2+k_3[H^+]}{k_{-1}+k_2+k_3[H^+]}\right). \qquad (2)$$

The net rate of racemization is given by: $k_r^{net}=k_r^{app}-k_d$.

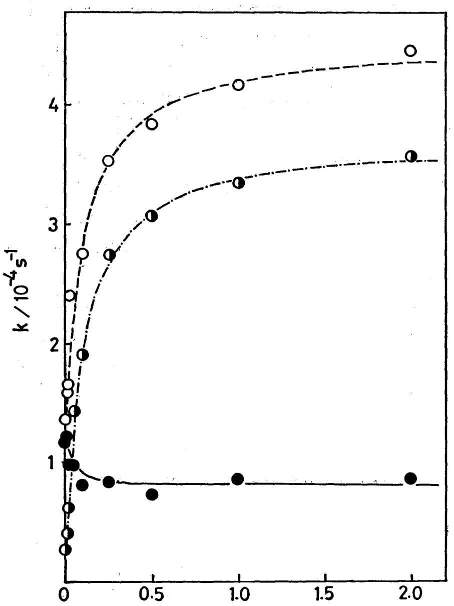

Fig. 2. Influence of acid concentration on the racemization and dissociation rate constants of $[Fe(gmi)_3]^{2+}$ at 69.4 °C and $I=2.00$ (HCl–KCl).
○: k_r^{app}, ◑: k_d, ●: k_r^{net}.

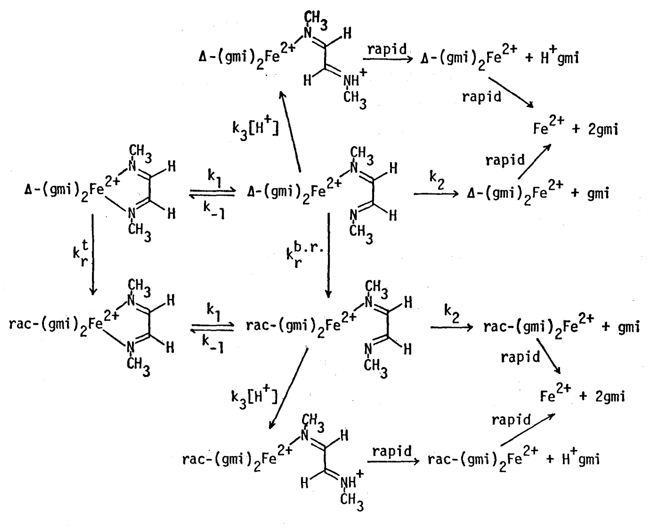

Fig. 3. The reaction scheme.

When $[H^+]$ is sufficiently low, the values of k_r^{app} and k_d will be approximately equal to the respective limiting values given by:

$$k_r^{\circ} = k_r^{t} + k_1\left(\frac{k_2+k_r^{b.r.}}{k_{-1}+k_2+k_r^{b.r.}}\right), \tag{3}$$

$$k_d^{\circ} = k_1\left(\frac{k_2}{k_{-1}+k_2}\right). \tag{4}$$

Then, Eqs. 1 and 2 can be transformed into:

$$k_r^{app} = (k_1+k_r^{t}) - \frac{k_{-1}+k_2+k_r^{b.r.}}{k_3}\frac{k_r^{app}-k_r^{\circ}}{[H^+]}, \tag{5}$$

$$k_d = k_1 + \frac{k_{-1}+k_2}{k_3}\frac{k_d-k_d^{\circ}}{[H^+]}. \tag{6}$$

In Fig. 4, the k_r^{app} and k_d values, observed in aqueous HCl–KCl solutions ($I=2.00$) at 69.4 °C, are plotted against $(k_r^{app}-k_r^{\circ})/[H^+]$ and $(k_d-k_d^{\circ})/[H^+]$ respectively. The values, $k_r^{app}=(1.39\pm0.02)\times10^{-4}\ s^{-1}$ and $k_d=(2.7\pm0.1)\times10^{-5}\ s^{-1}$, observed in 2 M KCl were taken as the k_r° and k_d° values respectively. The intercepts and the slopes of the lines shown in Fig. 4 give $k_1=(3.70\pm0.10)\times10^{-4}\ s^{-1}$, $(k_{-1}+k_2)/k_3=(0.102\pm0.005)$ mol dm^{-3}, $(k_1+k_r^{t})=(4.52\pm0.12)\times10^{-4}\ s^{-1}$, and $(k_{-1}+k_2+k_r^{b.r.})/k_3=(0.125\pm0.010)$ mol dm^{-3}. These values, together with $k_r^{\circ}=(1.39\pm0.02)\times10^{-4}\ s^{-1}$ and $k_d^{\circ}=(2.7\pm0.1)\times10^{-5}\ s^{-1}$, lead to $k_{-1}/k_2=12.7\pm0.9$, $k_3/k_2=(129\pm13)$ mol^{-1} dm^3, and $k_r^{b.r.}/k_2=1.41\pm0.41$. The curves in Fig. 2 are the theoretical ones for k_r^{app}, k_d, and k_r^{net}, obtained on the basis of the above values.

Racemization Mechanism: The results discussed above indicate that, in a solution containing no hydrochloric acid at 69.4 °C, 70% of the racemization of $[Fe(gmi)_3]^{2+}$ occurred by way of an intramolecular twist mechanism, and the remainder, by means of an intramolecular bond-rupture mechanism. Thus, complexes with flexible ligands, such as bpy and gmi, racemize intramolecularly by means of a bond-rupture mechanism as well as by means of a twist mechanism. This is in contrast to $[Fe(phen)_3]^{2+}$, which is known to

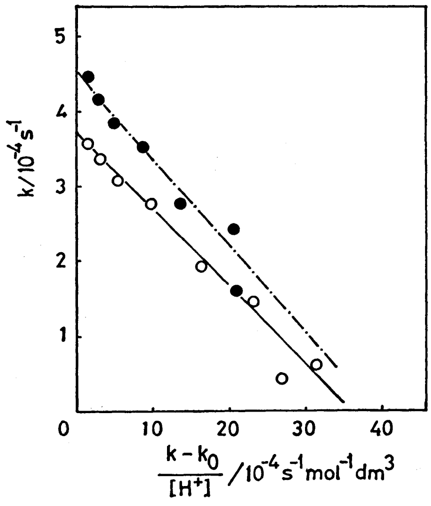

Fig. 4. Plots of k_r^{app} *vs.* $(k_r^{app}-k_r^{\circ})/[H^+]$ for apparent racemization (●) and k_d *vs.* $(k_d-k_d^{\circ})/[H^+]$ for dissociation (○) of $[Fe(gmi)_3]^{2+}$ at 69.4 °C and $I=2.00$ (HCl–KCl).

TABLE 1. THE RACEMIZATION AND DISSOCIATION RATE CONSTANTS OF $[Fe(gmi)_3]^{2+}$ IN VARIOUS MEDIA

t / °C	k_r^{app} / $10^{-5}\ s^{-1}$	k_r^{net} / $10^{-5}\ s^{-1}$	k_r^{app} / $10^{-5}\ s^{-1}$	k_d / $10^{-5}\ s^{-1}$
A. Water			C. 0.25 M HCl	
50.0	1.13±0.01	0.93±0.03	2.79±0.08	2.27±0.01
58.8	4.45±0.15	4.01±0.15	9.55±0.17	6.33±0.20
59.4	5.07±0.09	4.42±0.09	—	—
69.2	22.4±0.4	19.2±0.4	41.5±1.0	28.3±1.7
B. 2 M KCl			D. 2 M HCl	
50.0	0.62±0.01	0.50±0.01	2.41±0.02	2.15±0.01
58.9	2.66±0.17	2.35±0.17	9.54±0.17	7.49±0.16
69.2	13.9±0.2	11.6±0.2	38.7±2.7	32.3±1.0

TABLE 2. THE RATE CONSTANTS OF THE RACEMIZATION AND DISSOCIATION OF $[Fe(bpy)_3]^{2+}$ AND $[Fe(phen)_3]^{2+}$ IN 2 M HCl

$[Fe(bpy)_3]^{2+}$				$[Fe(phen)_3]^{2+}$			
$\frac{t}{°C}$	$\frac{k_r}{10^{-3}\,s^{-1}}$	$\frac{t}{°C}$	$\frac{k_d}{10^{-3}\,s^{-1}}$	$\frac{t}{°C}$	$\frac{k_r}{10^{-3}\,s^{-1}}$	$\frac{t}{°C}$	$\frac{k_d}{10^{-4}\,s^{-1}}$
15.0	0.219	15.0	0.159	20.0	0.214	20.5	0.283
20.0	0.543	19.9	0.400	22.6	0.339		0.287
22.4	0.705	22.4	0.588	25.0	0.493		
25.0	1.208	25.0	0.850	27.65	0.745	27.6	0.971
27.5	1.73	27.5	1.26	30.25	1.110		0.987
30.1	2.41	30.0	1.90	32.65	1.745		
	2.52			35.1	2.50	35.3	3.61
32.5	3.80	32.5	2.59				3.73
	3.94						

TABLE 3. THE APPARENT RACEMIZATION RATE CONSTANTS IN IONIC MEDIA[a]

$\frac{[KCl]}{M}$	$\frac{[HCl]}{M}$	$[Fe(gmi)_3]^{2+}$ $\frac{k}{10^{-4}\,s^{-1}}$ [b]	$[Fe(bpy)_3]^{2+}$ $\frac{k}{10^{-3}\,s^{-1}}$ [c]	$[Fe(phen)_3]^{2+}$ $\frac{k}{10^{-3}\,s^{-1}}$ [c]
0.00	0.00	2.24±0.04 (1.92±0.04)	2.17±0.14	1.92±0.02
0.25	0.00	1.87 (1.59)	—	—
1.00	0.00	1.67±0.01 (1.41±0.02)	1.88±0.10	1.76±0.02
2.00	0.00	1.39±0.02 (1.16±0.02)	1.68±0.01	1.70±0.03
2.00	0.00	1.43[d] (1.17)	1.19±0.01[e]	1.28±0.02[e]
1.75	0.25	3.52[d] (0.83)	1.96±0.05[e]	—
1.50	0.50	3.83[d] (0.73)	2.09±0.01[e]	—
1.00	1.00	4.17[d] (0.86)	2.43±0.03[e]	1.14±0.01[e]
0.00	2.00	4.45[d] (0.86)	2.46±0.06[e] (0.56±0.06)	1.12±0.02[e] (0.97±0.02)

a) Data in parentheses are net racemization rates. b) Data at 69.2 °C. c) Data at 32.0 °C. d) Data at 69.4 °C. e) Data at 30.0 °C.

TABLE 4. THE ACTIVATION PARAMETERS FOR THE REACTIONS OF $[Fe(1,2\text{-diimine})_3]^{2+}$ IN VARIOUS AQUEOUS IONIC MEDIA[a]

Complex	Medium	k_r^{app}		k_d		k_r^{net}	
		$\frac{\Delta H^*}{kJ\,mol^{-1}}$	$\frac{\Delta S^*}{J\,K^{-1}\,mol^{-1}}$	$\frac{\Delta H^*}{kJ\,mol^{-1}}$	$\frac{\Delta S^*}{J\,K^{-1}\,mol^{-1}}$	$\frac{\Delta H^*}{kJ\,mol^{-1}}$	$\frac{\Delta S^*}{J\,K^{-1}\,mol^{-1}}$
$[Fe(gmi)_3]^{2+}$	Water	140±1	94±4	—	—	141±1	96±3
	2.0 M KCl	147±2	108±6	139±1	73±2	148±3	110±9
	0.25 M HCl	127±2	59±5	119±4	33±13	148±5	112±15
	2.0 M HCl	131±4	71±11	128±2	60±6	149±24	109±72
$[Fe(bpy)_3]^{2+}$	2.0 M HCl	117±0	93±0	114±0	78±1	127±1	114±3
	1.0 M HCl[b]	—	—	112±2	71±4	106±8	50±29
$[Fe(phen)_3]^{2+}$	2.0 M HCl	120±0	93±0	128±0	104±0	119±1	91±2
	1.5 M HCl[b]	—	—	132±2	117±8	119±8	88±29

a) Calculated by least-squares method. Errors are the standard deviations. b) Data from Ref. 6.

undergo intramolecular racemization only by means of a twist mechanism because of the rigidity of the ligand. It is not clear whether a twist process proceeds *via* a trigonal or a rhombic intermediate and whether the bond-rupture intermediate is a square pyramid or a trigonal bipyramid.

Activation Parameters: Table 1 shows the racemization and dissociation rate constants of $[Fe(gmi)_3]^{2+}$ at various temperatures. Those of $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ are listed in Table 2 for the sake of comparison. The racemization rate constants in media of different salt and acid concentrations are given in Table 3. As has been described above for the case of $[Fe(gmi)_3]^{2+}$, the nearly identical values for the racemization rate constants at acid concentrations of 1 M and 2 M suggests that the net racemization rates of the complexes in 2 M HCl correspond to the rates of twist racemization. Table 4 shows the activation parameters of the three complexes for dissociation and twist racemization; the values obtained for $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ are in good agreement with the literature values[6] (see Table 4) except that the low ΔH^* and ΔS^* values previously reported for the twist racemization of $[Fe(bpy)_3]^{2+}$ may be accompanied by greater errors than those accompanied by the present values, because the number of experimental data is smaller in the former case.

Although the complexes differ in hydrophobic properties, and thus in solvation, the entropies of activation for the twist racemization of the complexes are very similar. The large, positive activation entropies may be related to the formation of bond-expanded high-spin reaction intermediates[3] and/or to the rearrangement of the solvent sheath during the twist motion. These large, positive entropies of activation will lower the barrier for the operation of the twist mechanism by canceling a considerable part of the large activation enthalpies. The differences in activation enthalpies for the twist process between the complexes may come from differences in the ligand-field strength, which are shown by the CD spectra of the complexes. The ligand-field activation energies will become greater with the increase in the ligand-field strength if the reaction intermediates of racemization are similar for the three complexes. The observed activation parameters suggest that the ligand-field strength influences the ligand-field activation energy, but not so greatly as to change the mechanism.

The activation enthalpies of $[Fe(gmi)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ for the dissociation *via* bond-rupture intermediates are lower than those for the twist racemization, while the enthalpy of activation for the dissociation of $[Fe(phen)_3]^{2+}$ is higher than that for the twist racemization. Unlike the flexible bpy and gmi, the rigid phenanthroline ligand hardly serves at all as a monodentate ligand to form a bond-rupture intermediate leading to dissociation. Thus, two bonds have to be broken simultaneously in order for the ligand to be liberated from the complex, and a greater activation enthalpy is required for the dissociation of $[Fe(phen)_3]^{2+}$.

Salt Effects: The racemization of $[Fe(phen)_3]^{2+}$ was found to be retarded by KCl and accelerated by KI and KSCN. These salt effects have been attributed to ion-pair formation.[15] The salt effects on the racemization of $[Fe(gmi)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ have also been studied. The racemization rates of the complexes decreased with an increase in the KCl concentration, as is shown in Table 3. The racemization rates of $[Fe(gmi)_3]^{2+}$ increased in the presence of KSCN, but the addition of KI had no effect. The dissociation rates of $[Fe(gmi)_3]^{2+}$ increased in the presence of KSCN, but decreased slightly in the presence of KI. The results are shown in Fig. 5. Analyses of the data with due consideration of ion-pair formation[15] gave the racemization and dissociation rate constants of free and ion-paired complexes, and also the ion-association constants (Table 5). The curves in Fig. 5 were obtained by calculation on the basis of the values listed in Table 5.

The intramolecular racemization rates of the ion-pair increase in the order I≈Cl<SCN, and the dissociation rates, I<Cl<SCN. The sequence is similar to that for $[Fe(phen)_3]^{2+}$; this gives support for the previously proposed mechanism of the nucleophilic

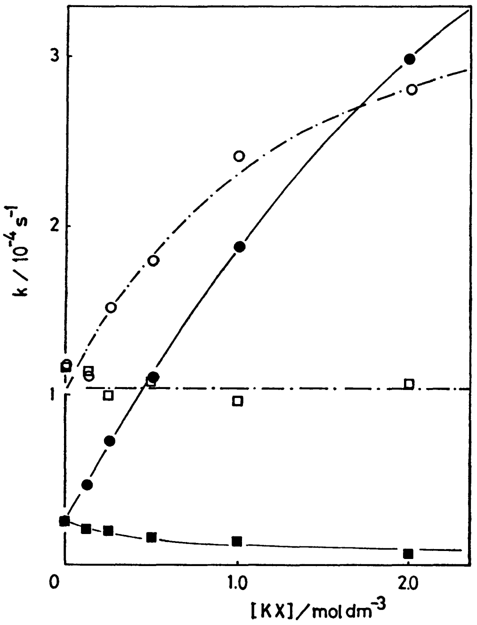

Fig. 5. Salt effects on the rates of racemization (open marks) and dissociation (full marks) at 69.1 °C and I=2.00 (KCl).
○,●: KSCN, □,■: KI.

Table 5. The ion-association constants of $[Fe(gmi)_3]^{2+}$ with an anion and the dissociation and intramolecular racemization rate constants of $[Fe(gmi)_3]^{2+}$ in an ion-pair

Counter ion	$k^{IP}_{d(X)}$ / 10^{-4} s^{-1}	$k^{i,IP}_{r(X)}$ / 10^{-4} s^{-1}	$K^{IP}_{c(X)}$/mol dm^{-3} Diss.	Racem.
H_2O[a)]	0.32±0.02	1.86±0.14	—	—
Cl^-	0.22±0.02	1.08±0.11	4.0±3.5	3.7±2.4
SCN^-	3.21±0.41	2.74±0.15	5.6±3.4	6.1±3.0
I^-	0.06±0.02	0.90±0.07	6.4±3.4	—

a) The value for a free ion.

TABLE 6. RECEMIZATION RATE CONSTANTS IN VARIOUS SOLVENTS

Solvent	$[\mathrm{Fe(gmi)_3}]^{2+}$ k / $10^{-5}\ \mathrm{s^{-1}}$ a)	$[\mathrm{Fe(bpy)_3}]^{2+}$ k / $10^{-4}\ \mathrm{s^{-1}}$ b)	$\mathrm{Fe(phen)_3}]^{2+}$ k / $10^{-4}\ \mathrm{s^{-1}}$ b)
Water	4.12±0.11	2.86±0.14	2.80±0.14
Nitromethane	7.8±0.6	7.7±0.7	13.0±0.7
Formamide	21.5±0.4	15.9±0.3	32.8±0.2
DMSO	38.0±0.1	146±7	450±100

a) Data at 59 °C. Corrected for decomposition. b) Data at 20.1 °C.

interaction of the anions with complex cations.[15]

Solvent Effects: In spite of several investigations carried out thus far,[16] the nature of the solvent effects on the racemization rates of tris(1,2-diimine)iron(II) is not yet well understood. In order to compare the effects of solvents on the racemization rates of $[\mathrm{Fe(gmi)_3}]^{2+}$, $[\mathrm{Fe(bpy)_3}]^{2+}$, and $[\mathrm{Fe(phen)_3}]^{2+}$, their racemization rates were observed in water, dimethyl sulfoxide (DMSO), nitromethane, and formamide. The results are summarized in Table 6. The net racemization rates were larger in organic solvents than in an aqueous solution. The dissociation rates of $[\mathrm{Fe(bpy)_3}]^{2+}$ and $[\mathrm{Fe(phen)_3}]^{2+}$ were reported to be not so large as the racemization rates in organic solvents.[16b,17] Thus, the increase in racemization rates in organic solvents can reasonably be considered to be due to the acceleration of the intramolecular process.

The abilities of the solvents accelerating the racemization were in the order DMSO>formamide>nitromethane>water for the three complexes. This order may be correlated with the polarizability of a solvent, by analogy with the fact that the effect of nucleophiles accelerating the intramolecular racemization of $[\mathrm{Fe(phen)_3}]^{2+}$ in an aqueous solution is correlated with their polarizability.[15] The electronic polarization of a solvent is related to its refractive index on the Na D line, the values being 1.476, 1.446, 1.380, and 1.333 for DMSO, formamide, nitromethane, and water respectively; this order of decreasing refractive index is consistent with the decreasing order of the accelerating ability of a solvent shown above. However, this cannot be extended to other solvents. The order of the ability to accelerate the racemization of $[\mathrm{Fe(phen)_3}]^{2+}$ was observed to be DMSO>acetone≈methanol > acetonitrile > formamide > nitrobenzene ≈ nitromethane>water,[18] whereas the order of the refractive index was nitrobenzene>DMSO>formamide >nitromethane>acetone > acetonitrile > water > methanol.

For the racemization of $[\mathrm{Ge(acac)_3}]^{+}$[19] and $[\mathrm{Ni(phen)_3}]^{2+}$[20] in organic solvents, the accelerating ability of the solvent was nicely correlated with Gutmann's donor number,[21] a parameter to express the electron-donating ability of a solvent molecule, although the mechanism for racemization differs from complex to complex. For the racemization of $[\mathrm{Fe(1,2\text{-}diimine)_3}]^{2+}$, the accelerating ability of a solvent may also be correlated with the donor number, the order of which is DMSO>methanol≳$\mathrm{H_2O}$≳acetone>acetonitrile>nitrobenzene>nitromethane, in rough agreement with the trend in the acceleration of the racemization, if water is regarded as an exception. The correlation of the racemization rate of $[\mathrm{Fe(1,2\text{-}diimine)_3}]^{2+}$ in organic solvents with the polarizability and/or donor number of the solvents may indicate the assistance of solvent molecules in the twist racemization.

As is shown in Table 6, the extent to which the rate is affected by the solvent is decreased in the order $[\mathrm{Fe(phen)_3}]^{2+}>[\mathrm{Fe(bpy)_3}]^{2+}>[\mathrm{Fe(gmi)_3}]^{2+}$. This order is consistent with the expectation that the most hydrophobic substance $[\mathrm{Fe(phen)_3}]^{2+}$ would interact with an organic solvent most strongly, and the least hydrophobic substance $[\mathrm{Fe(gmi)_3}]^{2+}$, least strongly. Thus, solvation plays some role in the racemization of tris(1,2-diimine)iron(II) complexes, as was suggested by Van Meter and Neumann.[16c]

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