(6) J. Heinrich and J. Surovy, *Sb. Pr. Chem. Fak. SVST*, 207 (1966); *Chem. Abstr.*, **66**, 79839z (1967).
(7) Reference 3, p 118.
(8) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Vol. 1, Elsevier, New York, N.Y., 1965, p 527.
(9) I. M. Kolthoff, R. Belcher, V. A. Stenger, and G. Matsuyama, "Titration Methods", Vol. III, Interscience, New York, N.Y., 1957, p 419.
(10) H. L. Ward, *J. Phys. Chem.*, **30**, 1316 (1926).
(11) R. L. Bohon and W. F. Claussen, *J. Am. Chem. Soc.*, 73, 1571 (1951).
(12) G. Scatchard, *Chem. Rev.*, **8**, 329 (1931); J. H. Hildebrand and R. L. Scott, "Regular Solutions", Prentice-Hall, New York, N.Y., 1962, pp 129–131.
(13) P. Pfeiffer and B. Werdelmann, *Z. Anorg. Chem.*, **261**, 203 (1950).
(14) J. D. Miller and R. H. Prince, *J. Chem. Soc.*, 4706 (1965).
(15) A. Zalkin, D. H. Templeton, and T. Ueki, *Inorg. Chem.*, **12**, 1641 (1973).
(16) A. Jensen, F. Basolo, and H. M. Neumann, *J. Am. Chem. Soc.*, **80**, 2354 (1958).
(17) O. P. Anderson, *J. Chem. Soc., Dalton Trans.*, 1237 (1973).
(18) A. F. Kapustinskii and K. B. Yatsimirskii, *Zh. Obsch. Khim.*, **19**, 2191 (1949); *J. Gen. Chem. USSR*, **19**, 1665 (1949).
(19) In the following energy considerations the standard states for gases and solutions are defined as the hypothetical systems which are both ideal and contain 1 mol l.$^{-1}$. The symbol ΔG refers to a standard free-energy change between standard states so defined. In the absence of information about activity coefficients, the latter are taken to be unity in numerical calculations.
(20) G. C. Sinke, *J. Chem. Thermodyn.*, **6**, 311 (1974).
(21) N. Bjerrum, *K. Dan. Vidensk. Selsk.*, 7, No. 9 (1926).
(22) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
(23) G. N. LaMar and G. R. van Hecke, *Inorg. Chem.*, **12**, 1767 (1973).
(24) L. S. Frankel, T. R. Stengle, and C. H. Langford, *Chem. Commun.*, 394 (1965).

The Rates of Racemization and Dissociation of the Tris(1,10-phenanthroline)iron(II) Cation in Various Solvents[1,2]

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Received August 4, 1975

Abstract: Rates of racemization and dissociation of $[Fe(phen)_3]^{2+}$ were measured in water, methanol, acetone, formamide, *N,N*-dimethylformamide, acetonitrile, and acetic acid, and in mixtures of water with methanol, acetone, formamide, and *N,N*-dimethylformamide. The rate of racemization was also measured in mixtures of water with glycerol and ethylene glycol. In all cases the dissociation rate was much slower than the racemization rate, indicating that racemization is predominantly intramolecular in all these solvents. Ion association (with ClO_4^-), when it occurs, has a retarding effect on the rate of racemization. The effect of a solvent on the racemization rate appears to be due to solvation of the aromatic phenanthroline ligands in the transition state, and to the viscous resistance to reorganization of the solvent in the vicinity of the complex ion when the latter undergoes inversion. Supporting this view is the fact that the rate constants can be empirically represented by the equation $\log k = c - (0.26\Delta G_{\text{ligand}}/2.303RT) - 0.48 \log (\eta V_m)$, where ΔG_{ligand} is the free energy of solvation of the aromatic ligands, η is the coefficient of viscosity of the solvent, and V_m is the molar volume of the solvent. The effect of solvent on the dissociation rate appears to be due to solvation of the ligands in the transition state, and the solvent's ability to act as a replacing ligand.

The role of solvent in bimolecular reactions, or in unimolecular reactions that involve a formal separation of charge, has been extensively investigated.[3] By comparison, relatively little attention has been paid to solvent effects in unimolecular reactions involving no formal separation of charge. The racemization reaction of certain complex ions, particularly those occurring by an intramolecular mechanism, should provide interesting examples of such unimolecular reactions.

Investigations of solvent effects on racemization reactions are reported in the literature for several complex ions: the trisphenanthroline and tris(bipyridine) complexes of Ni(II),[4,5] the tris(oxalato)chromate(III) ion,[6] and the trisphenanthroline and tris(bipyridine) complexes of Fe(II).[5,7]

Davies and Dwyer[5] suggested that the racemization of $[Ni(bpy)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ occurred by an intramolecular process, but later measurements[8,9] of both racemization and dissociation rates showed the two rates to be experimentally the same, indicating racemization by dissociation.

The racemization rates have been measured[6] for $[Cr(ox)_3]^{3-}$ in mixtures of water with methanol, ethanol, isopropyl alcohol, dioxane, acetone, and glycerol. The rates all decrease with increasing organic component in the solvent. The mechanism is thought to be dissociative.

Seiden, Basolo, and Neumann[7] measured the rates of racemization and dissociation of $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ in methanol-water mixtures and found racemization rates to be appreciably faster than dissociation. This evidence suggests that the Fe(II) complexes favor intramolecular racemization in organic solvents. Accurate determination of the rate was difficult because of the rapidity of reaction in these solutions and the large absorbancies at the wavelengths normally used for polarimetry.

The acid dependence of the rate of racemization of $[Fe(bpy)_3]^{2+}$ suggests that a partial dissociation mechanism may be operative here.[10] In this mechanism only one end of the bipyridine ligand comes loose from the iron atom, the other nitrogen atom remaining bonded to it. Since rearrangement may occur before the free nitrogen atom becomes reattached, racemization may occur. In the $[Fe(phen)_3]^{2+}$ system, each ligand is constrained by the steric rigidity of the ring system, and both nitrogen atoms must be coordinated at the same time. Racemization of $[Fe(phen)_3]^{2+}$ in water is acid independent, which supports this view. The rate of racemization of $[Fe(phen)_3]^{2+}$ is strongly dependent on the solvent composition; there is almost a hundredfold increase in the rate on going from water to methanol.[7] The racemization in water at 25 °C was found to be 89% intramolecular, and the percentage increased as the methanol content of the solvent increased.[7] For these several reasons it was decided that the $[Fe(phen)_3]^{2+}$ system would provide a good model for investigating solvent effects.

Table I. Experimental Rate Constants for Dissociation of $Fe(phen)_3(ClO_4)_2$ in Mixed Solvents at 25.0°C

Mole % organic component[a]	10^4k, sec^{-1}			
	Methanol	Acetone	*N,N*-dimethylformamide	Formamide
0	0.776			
	0.770			
20	0.92	1.52	2.44	1.88
	0.98	1.54	2.50	1.90
40	1.61	2.57	4.45	2.49
	1.66	2.63	4.50	2.50
60	2.31	3.11	5.20	2.50
	2.38	3.16	5.35	2.51
80	2.28	2.42	4.44	2.13
	2.33	2.57	4.53	2.18
100	0.40	0.060	2.37	1.83
			2.38	1.86

[a] Other solvent component is water.

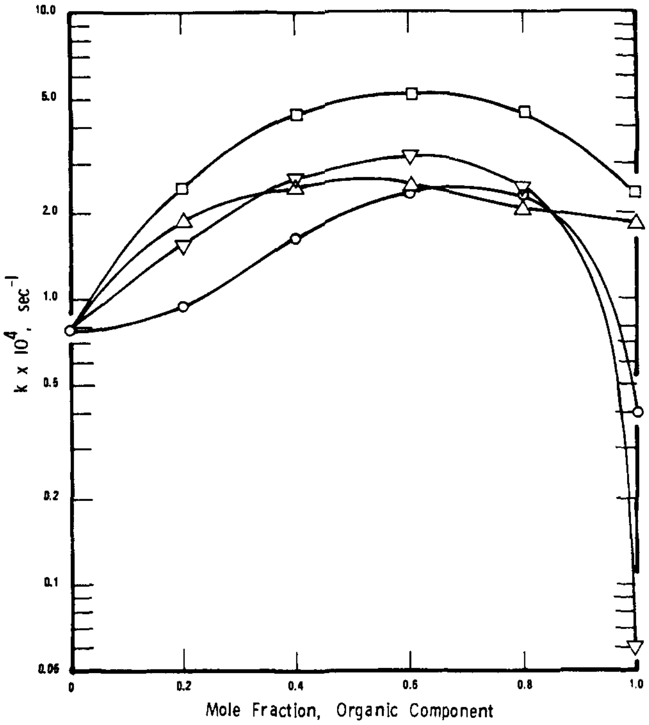

Figure 1. Rate of dissociation at 25.0 °C as a function of solvent composition: methanol, ○; acetone, ▽; formamide, △; *N,N*-dimethylformamide, □.

Table II. Racemization Rates of $Fe(phen)_3^{2+}$ in Water

Temp, °C	10^4k, sec^{-1}
12.0	0.695
15.2	1.40
18.8	2.20
24.9	6.50, 6.53
35.6	33.2

Experimental Section

Materials. Preparations of anhydrous $[Fe(phen)_3](ClO_4)_2$ and purification of solvents are described in the accompanying article.[11] The method of preparing optically active *l*-$[Fe(phen)_3](ClO_4)_2 \cdot 3H_2O$ was a variation of the procedure of Dwyer and Gyarfas[12] involving diastereoisomeric resolution with antimony *d*-tartrate. Because of the rapid racemization of $[Fe(phen)_3]^{2+}$ in hot water, nearly 100% resolution into $[l\text{-}Fe(phen)_3][d\text{-}C_4H_2O_6)_2Sb_2] \cdot 8H_2O$ is achieved.

Hexaquonickel(II) perchlorate was prepared from $Ni(OH)_2$ and 70% perchloric acid and crystallized from water. Before use in kinetic runs the water was removed from the $Ni(H_2O)_6(ClO_4)_2$ by heating for several hours to 90 °C under a vacuum of less than 0.5 mm of Hg.

Rates of Dissociation. The disappearance of $[Fe(phen)_3]^{2+}$ was followed at 510 mμ with a Beckman DU spectrophotometer using 1.00-cm glass stoppered silica cells inside a thermostated cell compartment. The reaction involves the rate determining dissociation of one phenanthroline ligand from $[Fe(phen)_3]^{2+}$ followed by the rapid dissociation of the other two phenanthroline ligands.[10] A large excess of Ni(II) as $Ni(ClO_4)_2$ was used to react with the dissociated phenanthroline.[7,13,14]

In each kinetic run a solution of $Ni(ClO_4)_2$ in the appropriate solution was first prepared and placed in a thermostat. A portion of $Fe(phen)_3(ClO_4)_2$ was then dissolved in this solution, and the solution transferred to the spectrophotometer cell. About 25 absorbance readings were taken, and these gave good first-order behavior. The rate constants were reproducible within about 2%. The initial concentrations of the reactants were: $Fe(phen)_3^{2+}$, 1.5×10^{-4} *M*; Ni^{2+}, 1.5×10^{-2} *M*. The dissociations in acetic acid and acetonitrile were very slow and were followed for only approximately one half-life.

Rates of Racemization. Racemization rates were determined with a slightly modified Bendix-Ericsson automatic polarimeter. A tungsten lamp in combination with a Corning colored glass filter having maximum transmittance at 610 mμ was used as the light source. The 610-mμ region is just outside the sharp increase in absorbance of the 510-mμ band of $[Fe(phen)_3]^{2+}$, and just inside the cutoff region of the photomultiplier.

The sample cell for racemization rate measurements was a water jacketed Pyrex glass cell with a 4.93-cm path length and a 7.32-ml sample volume. For most runs the complex concentration was 3×10^{-4} M. Temperature control in the cell was better than ±0.1 °C. For normal or rapid rates the optical rotation was followed for at least ten half-lives, for slower rates four or five half-lives. For the very slow rates in glycerol, the rotation was followed for one or two half-lives, and the sample cell was removed from the polarimeter. Steam was passed through the cell jacket for about ten half-lives at 100 °C, based on an activation energy of at least 15 kcal. The contents of the cell were then cooled to the thermostat temperature, and an infinite time angle of rotation was measured.

The first-order rate constant for racemization is defined operationally as

$$-k = \frac{1}{(\alpha - \alpha_\infty)} \frac{d\alpha}{dt}$$

where α is the optical rotation at time t and α_∞ is the optical rotation at infinite time. The constant so defined is directly comparable with the dissociation rate constant.

Results

Rates of Dissociation. Table I lists the measured dissociation rate constants, which are reproducible within a few percent, in the four mixed solvent systems. Figure 1 shows the variation of the rate constant as a function of solvent composition. The rate constant in acetonitrile at 25° was observed to be 2.03×10^{-6} sec^{-1}, and in acetic acid, 7.6×10^{-7} sec^{-1}.

The data in methanol-water mixtures provide the only opportunity for comparison with earlier work. The rate constants are in close agreement with those reported by Seiden et al.[7] at 25.5 °C but are slightly larger in the region 0.6-0.8 mole fraction methanol.

Rates of Racemization. Tables II through VIII give the measured racemization rates of $[Fe(phen)_3]^{2+}$ in the various solvent systems. Normal rates at temperatures above 15 °C were reproducible within a few percent. For rapid rates and low temperatures, the disagreement increased to about 10%. The reproducibility of the measurements can be evaluated from the results in methanol (Table III).

Qualitatively the variation of rate with solvent composition is similar to the racemization rate data reported by Seiden, Basolo, and Neumann[7] for methanol-water mixtures at 0 °C, although their data are not at close enough

Table III. Racemization Rates in Methanol–Water Mixtures

Mole % methanol	10^4k, sec^{-1}			
	0.5°C	12.0°C	18.8°C	24.9°C
10	—	1.40	—	11.5
20	—	2.70, 2.75	—	20.8
30	—	4.53	—	32.2
40	—	7.12	—	53.2
41	—	7.37	—	—
50	—	10.8, 11.2	34.3	71.7
60	—	16.3, 16.8	—	102
70	—	23.8, 26.4	—	133
80	—	31.2, 31.9, 32.7	—	190
85	—	38.2, 39.2	—	—
87.5	—	43.2	—	—
89	—	41.6	—	—
90	7.65	41.5, 42.2, 43.0	—	212
91	—	41.1	—	—
92.5	—	42.5	—	—
95	—	40.9	—	—
100	7.61, 7.70	37.5, 37.8, 39.5	—	187

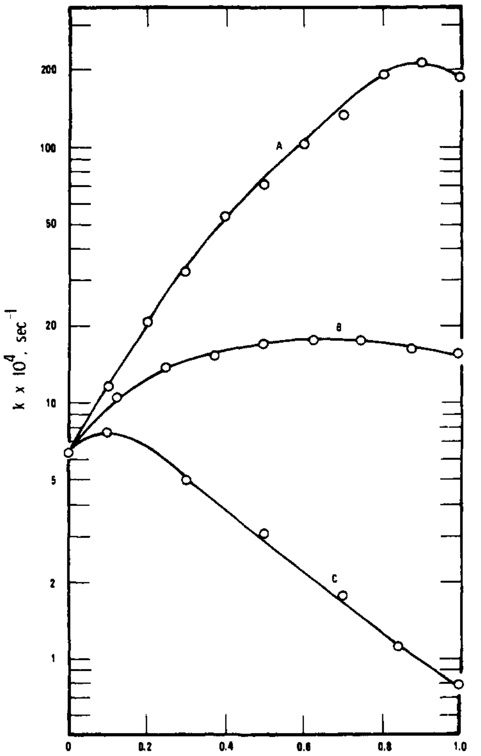

Figure 2. Rate of racemizarion at 25.0 °C in water-alcohol mixtures: curve A, methanol; curve B, ethylene glycol; curve C, glycerol.

intervals to show the maximum in rate constant at 0.9 mole fraction methanol (see Figure 2). The large number of measurements made between 0.8 and 1.0 mole fraction methanol confirms the existence of the maximum.

Figure 2 also shows the variation of the rate constant for racemization with mole fraction ethylene glycol for ethylene glycol-water mixtures at 25 °C, and the variation of the rate constant for racemization vs. mole fraction glycerol for glycerol-water mixtures at 25 °C.

The rate constant for racemization in acetonitrile at 25 °C was observed to be 1.47 × 10^{-2} and 1.49 × 10^{-2} sec^{-1} in two separate experiments, and in acetic acid, 3.65 × 10^{-3} and 3.77 × 10^{-3} sec^{-1} in two separate experiments.

Figure 3 shows the intramolecular rate constants at 25 °C as a function of the solvent composition for systems involving methanol, acetone, formamide, and *N,N*-dimethylformamide. The intramolecular racemization rate constant is the difference between the racemization rate constant, k_{rac}, and the dissociation rate constant, k_{diss}, at 25 °C. The racemization rate constants are either measured directly or extrapolated from Arrhenius plot of data at each solvent composition. The dissociation rate constants are either measured directly or interpolated from a plot of k_{diss} vs. mole fraction. In each solvent system the intramolecular process for racemization becomes more important compared to the dissociation route to racemization as the mole fraction of the organic component of the solvent increases.

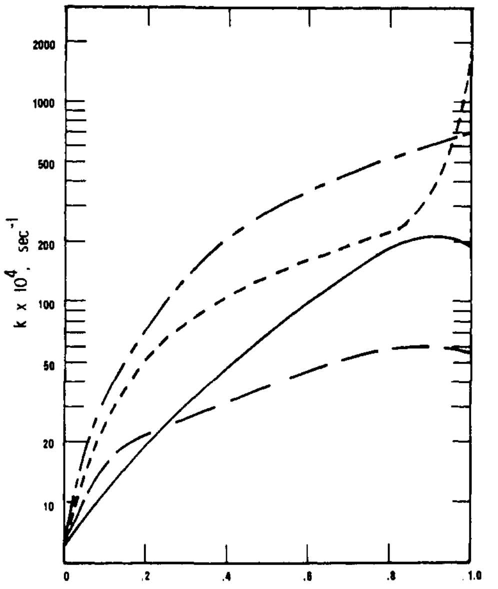

Figure 3. Rate of intramolecular racemization at 25.0 °C in aqueous solution containing: methanol, —; acetone, - - -; formamide, ——; *N,N*-dimethylformamide, ---.

The intramolecular racemization rate in water at 25 °C is 5.63 × 10^{-4} sec^{-1}, which is somewhat less than the value of 6.5 × 10^{-4} sec^{-1} found earlier.[10] This latter measurement, however, was made in 1.0 *M* HCl which may account for the difference.

Effect of Added Perchlorate Ion. Ion pairing is a phenomenon that would be expected to be significant in many of these solvent systems. Fortunately, the racemization measurements can be done at a complex concentration (3 × 10^{-4} *M* in this case) at which the extent of ion pairing is generally small. At this concentration the fraction, F_{IP}, of the complex present in ion pairs will be less than 0.1 when the equilibrium constant, K_{IP}, for formation of ion pairs is less than 200. Estimates of the value of this constant at 25 °C were made for various solvent media in the accompanying article.[11] The only solvent giving values of K_{IP} greater than 200 is acetone, and acetone-water mixtures will exceed this value when the mole fraction of acetone is greater than about 0.5.

To gain additional information about ion-pairing effects, the effect on the racemization rate of changing the complex concentration and of adding $NaClO_4$ was investigated. Table IX shows these results. Included in the table are estimated values of K_{IP}, and values of F_{IP} based on these estimates. Increasing concentration of ClO_4^- does not affect the rate much in methanol or *N,N*-dimethylformamide, but has significant effects on the rates in acetonitrile and acetone. The decrease of the rate constant with increasing perchlorate concentration indicates that ion pairs undergo racemization at a slower rate. Presumably the presence of a perchlorate ion in one of the pockets of the $[Fe(phen)_3]^{2+}$ ion exerts a configuration locking effect on the cation.

Table IV. Racemization Rates in Acetone–Water Mixtures

Mole % acetone		10^4k, sec^{-1}					
		7.1°C	11.3°C	15.2°C	19.4°C	24.9°C	28.9°C
11.5		—	—	7.02	13.2	30.3	56.0
19.9		—	7.09	12.1	22.3	48.9	—
30.1		—	11.0	19.7	38.0	69.5	—
40.1		—	16.3	29.8	47.3	104	—
50.2		11.4	22.5	36.3	65.4	—	—
60.0		14.2	27.5	43.7	77.5	—	—
69.9		17.0	33.6	55.0	92.5	—	—
80.2		18.3	34.4	59.0	102	—	—
89.3		24.5	—	117	156	—	—
		10^4k, sec^{-1}					
		0.15°C	5.47°C	9.45°C			
90.0		9.02	23.7	37.7			
		10^4k, sec^{-1}					
100	4.5°C	4.8°C	5.2°C	9.0°C	9.3°C	9.6°C	9.8°C
	141	151	169	214	211	250	273

Table V. Racemization Rates in *N,N*-Dimethylformamide–Water Mixtures

Mole %, DMF	Temp, °C	10^4k, sec^{-1}
10	13.87	6.07
	19.07	14.0
	22.89	25.2
	27.39	48.8
20	11.07	7.50
	14.26	12.4
	16.78	19.2
	19.92	31.7
30	9.50	12.7
	14.00	23.0
	17.87	43.7
	22.18	89.5
40	0.15	4.68
	5.47	11.5
	9.50	21.3
	14.00	43.3
50	0.17	8.87
	5.47	17.8
	9.45	33.0
60	0.30	10.1, 10.1
	5.10	25.9, 26.1
	9.95	49.2, 52.6
	14.52	102
	14.55	102
80	0.30	21.2
	0.50	20.2
	5.10	37.5, 38.4
	9.95	78.0, 74.6
	14.52	133
	14.55	134
100	0.70	20.8, 21.4
	5.10	42.1, 43.2
	9.95	103, 104
	14.52	163
	14.55	166

Table VI. Racemization Rates in Formamide–Water at 25.00°C

Mole fraction, formamide	10^4k, sec^{-1}
20	23.5, 23.8
40	34.6, 34.6
60	49.1, 49.8
80	61.5, 62.1
100	58.3, 58.3, 59.7, 60.0

Table VII. Racemization Rates in Ethylene Glycol–Water

Mole % glycol	$10^{-4}k$, sec^{-1}		
	21.36°C	25.20°C	30.23°C
12.5	—	10.5, 10.6	—
24.8	7.37, 7.37	13.7, 13.8	28.4, 28.6
37.5	—	14.9, 15.4	—
49.6	9.10, 9.29	16.9, 17.0	35.0, 35.0
62.5	—	17.7, 16.9	—
74.5	9.22, 9.25	16.7, 16.9	33.8, 33.9
87.5	—	15.5, 16.6	—
99.3	8.05, 8.15	15.5, 15.4	31.9, 32.0

Table VIII. Racemization Rates in Glycerol–Water

Mole % glycerol	Temp, °C	10^4k, sec^{-1}
10	24.42	6.35
	26.47	8.96
	28.49	12.3
	31.65	19.7
	35.51	36.3
30	25.00	4.70, 5.17
50	25.00	2.95, 3.20
70	25.00	1.75
84	24.77	1.00, 1.07
	24.80	0.95
	30.20	2.90
	33.76	5.39
	40.40	17.6
100	25.00	0.779, 0.798

Since the changes in the rate constant should parallel the values of F_{IP}, the effect on the rate provides a qualitative measure of whether the estimates of K_{IP} and F_{IP} are reasonable. The following conclusions are suggested: the estimate in methanol is too large; in acetonitrile, too small; in *N,N*-dimethylformamide and acetone, about right. The results with the highest perchlorate concentrations in pure acetone suggest that ion association has proceeded to the attachment of two perchlorates per cation.

Temperature Dependence. The Arrhenius parameters for racemization rates were determined by plotting log k vs. $1/T$. The numerical values of E_a and log A for several solvent systems are listed in Table X. A plot of E_a vs. mole fraction methanol is linear within the error limits of the data. A plot of E_a as a function of mole fraction acetone shows a minimum near 0.4 mole fraction acetone and a maximum near 0.9 mole fraction acetone, although the reality of the latter is not certain. For water the value of E_a of 28.3 kcal agrees with the earlier value[10] of 29 ± 2 kcal.

Discussion

In water at 25 °C racemization occurs by an intramolecular process 87.9% of the time, the remainder occurring by

Table IX. Dependence of Rate Constants for Racemization on Concentration of $Fe(phen)_3(ClO_4)_2$ and added $NaClO_4$

Molarity, $NaClO_4$	Molarity $Fe(phen)_3$-$(ClO_4)_2$	$[ClO_4^-]$	10^4k, sec^{-1}	F_{IP}
Pure Methanol at 25.0°C (K_{IP} = 193.2)				
0.0000	0.0003	0.0006	187	0.10
0.0061	0.0003	0.0067	183, 190	0.56
0.0183	0.0003	0.0189	178, 182	0.78
0.0426	0.0003	0.0432	162, 179	0.89
Pure Acetonitrile at 25.0°C (K_{IP} = 139.15)				
0.0000	0.0003	0.0006	147, 149	0.07
0.0058	0.0003	0.0064	93.6, 98.6	0.47
0.0175	0.0003	0.0181	96.2, 96.4	0.71
0.0407	0.0003	0.0413	91.0, 94.0	0.85
Pure *N,N*-Dimethylformamide at 0.30°C (K_{IP} = 72.6)				
0.0000	0.0003	0.0006	19.1, 21.8	0.04
0.0006	0.0003	0.0012	18.6, 18.8	0.08
0.0012	0.0003	0.0018	18.6, 18.8	0.11
0.0025	0.0003	0.0031	18.8, 19.1	0.18
Pure Acetone at 0.30°C (K_{IP} = 5031)				
0.0000	0.00026	0.00052	80.8	0.64
0.0000	0.00030	0.00060	60.9, 74.0	0.67
0.0000	0.00048	0.00096	61.0	0.75
0.0000	0.00052	0.00104	63.2	0.76
0.0000	0.00107	0.00214	60.0	0.86
0.0000	0.00114	0.00228	55.6	0.87
0.0000	0.00115	0.00230	61.2	0.87
0.0000	0.00168	0.00336	42.2	0.90
0.0000	0.00398	0.00796	20.2	0.95
0.0000	0.00401	0.00802	22.3	0.95
0.00040	0.00030	0.00100	8.15, 8.94	0.79
0.00080	0.00030	0.00140	6.55, 6.65	0.85
0.00172	0.00027	0.00227	5.56	0.91
0.00410	0.00022	0.00454	4.35	0.96
0.00988	0.00022	0.01032	4.13	0.98
0.80 Mole-Fraction Acetone at 11.56°C (K_{IP} = 1161)				
0.033	0.0003	0.034	31.0	0.98
0.121	0.0003	0.122	29.2	0.99
0.850	0.0003	0.851	20.8	1.00

Table X. Values of the Arrhenius Parameters for Racemization

X	E_a, kcal	Log (A) sec^{-1}	X	E_a, kcal	Log (A) sec^{-1}
Methanol–Water					
0	28.3	17.54	0.600	24.1	15.68
0.100	27.6	17.28	0.700	23.4	15.32
0.200	26.9	17.05	0.800	22.8	14.99
0.300	26.2	16.73	0.900	22.0	14.51
0.400	25.5	16.38	1.000	21.4	13.93
0.500	24.8	16.06			
Acetone–Water					
0	28.3	17.54	0.600	22.3	14.6
0.115	26.2	16.6	0.699	22.4	14.9
0.199	24.1	15.4	0.802	23.3	15.3
0.301	22.2	14.3	0.900	23.5	16.0
0.401	22.4	14.2	1.000	21.6	15.6
0.501	22.8	14.4			
N,N-Dimethylformamide–Water					
0	28.3	17.54	0.500	23.1	15.4
0.100	26.4	17.9	0.600	22.0	14.7
0.200	26.4	17.2	0.800	21.2	14.2
0.300	26.0	17.2	1.000	23.2	15.8
0.400	25.0	16.6			
Ethylene Glycol–Water					
0	28.3	17.54	0.745	26.0	16.25
0.248	27.0	16.9	0.993	27.7	17.45
0.496	26.7	16.75			
Glycerol–Water					
0	28.3	17.54			
0.100	28.0	17.35			
0.835	33.5	20.6			

dissociation. In methanol, acetone, formamide, *N,N*-dimethylformamide, acetonitrile, and acetic acid, the predominance of the intramolecular process increases even further over the dissociative process.

In attempting to correlate the rate behavior in the various solvents, several solvent parameters were examined. Among the parameters examined were: η, the coefficient of viscosity; $1/D$, where D is the dielectric constant; the Winstein Y value;[15] the Kosower Z value;[16] and the Hildebrand solubility parameter δ.[17]

No one parameter provides any satisfactory correlation. Even if glycerol and ethylene glycol are omitted from consideration, since their viscosities affect the rate, no correlation is observed. It was this lack of correlation which led us to attempt to evaluate the ligand solvation energy, ΔG_{ligand}, of the complex in each solvent.[11]

Effect of ΔG_{ligand} on Racemization. The expectation of a correlation with ΔG_{ligand} can be rationalized by a consideration of certain features of the transition state. The arguments will, in general, apply to any of the three twisting mechanisms which have been suggested for the intramolecular racemization of octahedral complexes. These mechanisms and their relation to one another have been reviewed recently.[18] Inspection of Fisher-Hirshfelder models shows that a significant expansion of the complex (lengthening of the Fe-N bonds) is necessary to satisfy the steric requirements for any of the three mechanisms. At least one of the ligands will have moved away from the central Fe atom. In any mechanism, the pockets in the complex structure will become more open, exposing the ligand to more solvent molecules. The solvation of the ligands in the transition state should then be greater (i.e., ΔG_{ligand} more negative) than in the ground state of the complex. The increased solvation of the ligands leads to a lower net free energy of activation, and thus to an increased racemization rate.

The change in dielectric solvation on activation of the $Fe(phen)_3^{2+}$ ion appears to be unimportant in determining the activation energy for racemization. This result is reasonable since the increase in the effective ionic radius on activation is probably small. Increased solvation of the phenanthroline ligands must then be the important factor in lowering the free energy of activation for racemization. The nature of the interaction of the solvent with the ligands is expected to be similar in the ground and transition states. Since the structural parameters for the complex ion should be nearly independent of the solvent for both ground and transition states, it is reasonable to assume that ΔG_{ligand} in the transition state, indicated by the symbol ΔG^*_{ligand}, will be proportional to ΔG_{ligand} in the ground state, i.e., $\Delta G^*_{ligand} = p\Delta G_{ligand}$, where $p > 1$. If the only effect of the solvent were its effect on ΔG^*_{ligand} it should then follow that the rate constants in various solvents should increase as ΔG_{ligand} becomes more negative.

Viscous Effect on Racemization.[19] The general effect, which is expected on the basis of the previous arguments, and which is observed in fact (see Figure 3), is that in water-organic mixtures there is an increasing rate of racemization as the mole fraction of water decreases. The system ethylene glycol-water deviates somewhat from this pattern and glycerol-water deviates markedly. (See Figure 2). It is reasonable to relate the deviations in these systems to their large viscosities. The complex, $Fe(phen)_3^{2+}$, is distinctly nonspherical and has three pockets capable of being occupied by solvent molecules. In an internal rearrangement from one antipode to the other these pockets and their attendant solvent molecules will be reorganized. If the solvent has molecular interactions that lead to a high viscosity

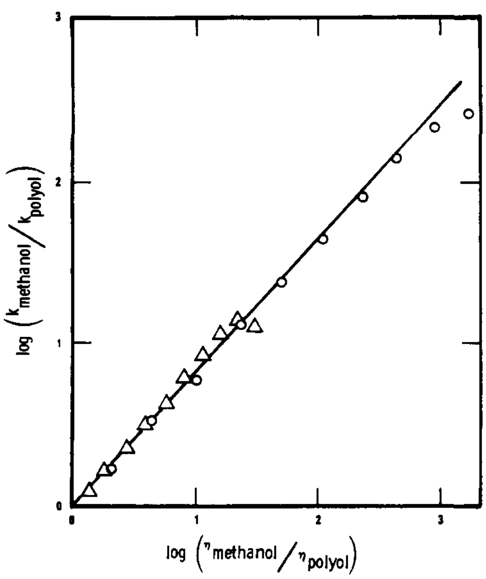

Figure 4. Correlation between rates of racemization and viscosity in water-alcohol mixtures: ethylene glycol, △; glycerol, ○.

as measured in flow experiments, similar interactions between solvent molecules associated with the pockets and the surrounding solvent structure will oppose the rearrangement. We shall call this simply the viscous effect.

Since the overall rate should be dependent on both a solvating effect and a viscous effect, it would be desirable to sort out the two effects. Ideally, the viscous effect should be evaluated using different solutions having the same solvating effect, i.e., same value of ΔG_{ligand}. Since our data are not extensive enough to do this, we assume that solutions of ethylene glycol and glycerol have solvating effects sufficiently like those of solutions of methanol of the same mole fraction for this purpose. If such is the case, k_{methanol}/k_x should be a smooth function of $\eta_{\text{methanol}}/\eta_x$, where x is ethylene glycol or glycerol. Figure 4 shows a plot of log $(k_{\text{methanol}}/k_x)$ vs. log $(\eta_x/\eta_{\text{methanol}})$. The fact that the data for both solvents fall along a single curve suggests the validity of the approach.

Supporting evidence of the importance of the viscous effect is the close relationship that appears to exist between the activation energy for racemization and the activation energy for viscous flow in these solvents. The activation energy for racemization in ethylene glycol is 27.7 kcal and in methanol is 21.4 kcal, a difference of 6.3 kcal. The corresponding difference in activation energies for viscous flow is 5.5 kcal. Comparison of 0.835 mole fraction glycerol with pure methanol gives differences of 12.1 kcal for racemization and 11.4 kcal for viscous flow. The viscous effect on rate thus seems established beyond doubt.

Free-Energy Relationships. We assume that the free energy of activation is composed of an intrinsic part, a part due to ligand solvation, and a part due to viscous effects.

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}_{\text{int}} + \Delta G^{\ddagger}_{\text{ligand}} + \Delta G^{\ddagger}_{\text{visc}}$$

From the previous assumption that

$$\Delta G^{*}_{\text{ligand}} = p\Delta G_{\text{ligand}}$$

it follows that

$$\Delta G^{\ddagger}_{\text{ligand}} = (p-1)\Delta G_{\text{ligand}}$$

It is not immediately obvious how the quantity $\Delta G^{\ddagger}_{\text{visc}}$ is to be related to measured properties of the solvent. Since in the Eyring theory of viscosity,[20] the equation

$$\eta V_{\text{m}} = Nhe^{\,\Delta G^{\ddagger}_{\text{flow}}/RT}$$

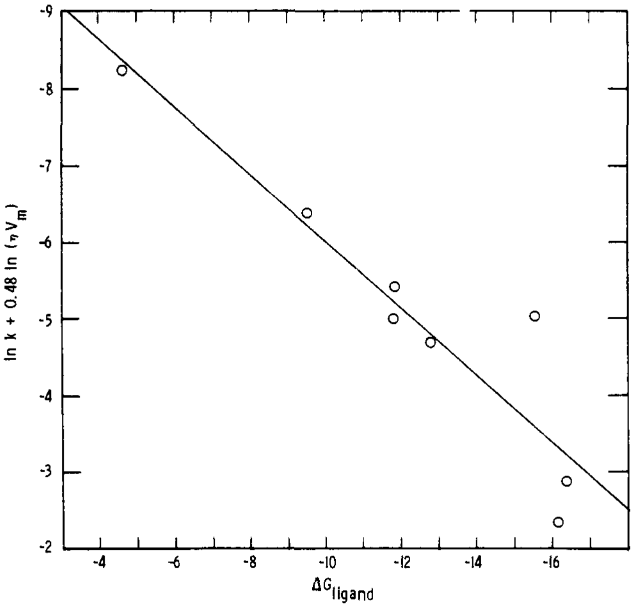

Figure 5. Correlation between rate of racemization, viscosity, and ΔG_{ligand}.

(where η is the coefficient of viscosity, and V_{m} is the molar volume) appears in an analogous position to the equation

$$k = \frac{RT}{Nh}e^{-\Delta G^{\ddagger}/RT}$$

in the theory of chemical reaction rate, we will take

$$\Delta G^{\ddagger}_{\text{flow}} = RT\ln(\eta V_{\text{m}}) - RT\ln(Nh)$$

We then assume

$$\Delta G^{\ddagger}_{\text{visc}} = q\Delta G^{\ddagger}_{\text{flow}}$$

where it is expected that $q \leq 1$.

Similarly, we will take

$$\Delta G^{\ddagger} = RT\ln\frac{RT}{Nh} - RT\ln k$$

Appropriate combination of equations leads to

$$\ln k + q\ln(\eta V_{\text{m}}) = C - \frac{(p-1)\Delta G_{\text{ligand}}}{RT}$$

where

$$C = \ln\frac{RT}{Nh} + q\ln(Nh) - \frac{\Delta G^{\ddagger}_{\text{int}}}{RT}$$

A plot of $[\ln k + q\ln(\eta V_{\text{m}})]$ vs. ΔG_{ligand} should then be linear if a correct value of q can be chosen. Linear regression gives a best value of 0.48 for q. Figure 5 shows the appropriate plot for the pure solvents. The value of $(p-1)$ as determined from the slope is 0.26. The correlation of the experimental data with the derived equation indicates that the assumptions made in the derivation of the equations are good approximations. A value of 0.26 for $(p-1)$ is very reasonable; it implies that in the transition state the solvation energy is 26% larger than in the ground state of the complex in solution. The value of $\Delta G^{\ddagger}_{\text{int}}$ is 22.0 kcal.

Rate of Dissociation. Although the transition state for the dissociation process will not be the same as that for the racemization process, solvation energies should show parallel behavior because in both transition states the ligand is increasingly exposed to solvent. Organic solvents should then lower the free energy of activation for dissociation by solvating the leaving phenanthroline ligands in a manner similar to the solvation of the ligands during racemization.

Comparison of Figures 1 and 3 shows that this expectation is borne out in solutions with high water content.

A second effect is necessary to explain the sharp decrease in rate on approaching pure solvent (Figure 1) in systems like methanol-water and acetone-water. This decrease had previously been observed with methanol-water mixtures,[7] and explained in terms of the lower coordinating ability of methanol molecules. The results in Figure 1 are consistent with this view. The order of dissociation rates in pure solvent is: *N,N*-dimethylformamide > formamide > water > methanol > acetone > acetonitrile > acetic acid. For dimethylformamide, formamide, methanol, and acetone, the rates are in the same order as the solvent's ability to act as a ligand, the latter ability being judged on the basis of stability constants of complexes where the solvents act as ligands. For instance, the amides act as ligands in methanol solution.[21]

The qualitative conclusion reached is that organic solvents act to lower the activation barrier to dissociation of a phenanthroline ligand, but a strongly coordinating ligand must be present to replace the dissociated ligand. Thus, in mixed solvents, a maximum in the rate occurs when there is water to fill the vacated coordination positions and an organic solvent to solvate the leaving ligand.

There has been considerable interest recently in the rates of aquation of complexes in mixed solvents. Of particular pertinence to this work, Burgess has measured the rate of aquation of $[Fe(phen)_3]^{2+}$, where phen has been various substituted 1,10-phenanthrolines, in aqueous mixtures with *tert*-butyl alcohol,[22a] ethanol,[22b] formic acid,[22b] acetonitrile,[22c] and dioxane.[22d] The emphasis in these studies was on solutions rich in water, with the mole fraction of the organic component less than 0.2. Correlation with the Grunwald-Winstein Y value[15] was applied with caution,[22b] recognizing that the Y value is most useful when the leaving ligand is an anion, which is not the case in the aquation of $[Fe(phen)_3]^{2+}$. Correlation with the Y value has been successful[23] in the aquation reactions of several transition metal complexes such as $[Co(NH_3)_5Cl]^{2+}$ and $[Co(en)_2Cl_2]^{+}$, where the leaving ligand is an anion. It is quite clear that the quantity ΔG_{ligand} is a more appropriate quantity for correlations in the aquation reaction of $[Fe(phen)_3]^{2+}$.

References and Notes

(1) Taken from the Ph.D. Thesis of F. M. Van Meter, Jr., Georgia Institute of Technology, 1969.

(2) Some of the conclusions of this work are summarized in "Inorganic Reaction Mechanisms. Part II", J. O. Edwards, Ed., Interscience, New York, N.Y., p 428.

(3) E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms", Academic, New York, N.Y., 1966.

(4) G. K. Schweitzer and J. M. Lee, *J. Phys. Chem.*, **56**, 195 (1952).

(5) N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 1325 (1954).

(6) G. K. Schweitzer and J. L. Rose, *J. Phys. Chem.*, **56**, 428 (1952); S. T. Spees and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962); A. L. Odell and D. Shooter, *J. Chem. Soc., Dalton Trans.*, 135 (1972); V. S. Sastri and C. H. Langford, *J. Phys. Chem.*, **74**, 3945 (1970).

(7) L. Seiden, F. Basolo, and H. M. Neumann, *J. Am. Chem. Soc.*, **81**, 3809 (1959).

(8) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **75**, 5102 (1953).

(9) R. G. Wilkins and M. J. G. Williams, *J. Chem. Soc.*, 1763 (1957).

(10) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 3807 (1954).

(11) F. M. Van Meter and H. M. Neumann, *J. Am. Chem. Soc.*, preceding paper in this issue.

(12) F. P. Dwyer and E. C. Gyarfas, *J. Proc. R. Soc. N.S.W.*, **83**, 263 (1950).

(13) P. Lauger, S. Fallab, and H. Erlenmeyer, *Helv. Chim. Acta*, **37**, 1050 (1954).

(14) H. Brintzinger, S. Fallab, and H. Erlenmeyer, *Helv. Chim. Acta*, **38**, 557 (1955).

(15) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

(16) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3267 (1958).

(17) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", 3rd ed, Reinhold, New York, N.Y., 1950, p 129.

(18) N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 408–412 (1972).

(19) Numerical values of viscosity coefficients in this section, and activation energies for viscous flow, were derived from data in J. Timmermans, "Physico-Chemical Constants of Binary Systems", Vol. 4, Interscience, New York, N.Y., 1960.

(20) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941, pp 480–484.

(21) C. K. Jorgensen, "Inorganic Complexes", Academic Press, New York, N.Y., 1963, pp 98, 104.

(22) (a) J. Burgess, *J. Chem. Soc. A*, 1085, 2728 (1968); (b) *ibid.*, 1899 (1969); (c) *ibid.*, 2351 (1970); (d) J. Burgess, F. M. Mekhail, and E. R. Gardner, *J. Chem. Soc., Dalton Trans.*, 1335 (1973).

(23) J. Burgess, *J. Chem. Soc. A*, 2703 (1970); J. Burgess and M. G. Price, *ibid.*, 3108 (1971).