Accelerating Effect of Donor Solvents on Racemization of the Tris(1,10-phenanthroline)iron(II) Cation

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Rates of racemization of the tris(1,10-phenanthroline)iron(II) cation, $[Fe(phen)_3]^{2+}$, have been measured at 7.5 °C to 17.5 °C in 1,2-dichloroethane, *o*-dichlorobenzene, nitrobenzene, and nitromethane, and in 1,2-dichloroethane solutions containing dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), methanol (MeOH), acetone (Ac), and acetonitrile (AN). In the four pure solvents, the observed racemization rates are markedly smaller than those calculated by the Van Meter and Neumann equation, which relates the racemization rate to the solvation energy of the phen ligands and viscous resistance. Addition of donor solvents to 1,2-dichloroethane solutions of the iron complex enhances the racemization rates. The degree of enhancement increases in the order AN < Ac < MeOH < DMF < DMSO and the activation energy decreases in the same order. This sequence lies in the order of increasing Gutmann donor number of the solvents, indicating a nucleophilic interaction of the solvents with the iron metal in the transition state. These obsevations may be interpreted in terms of Kepert's model for solvent-assisted racemization of tris-chelated complexes and the molecular structure of a solvate complex determined previously, and allow us to modify the Van Meter and Neumann equation.

The kinetics of racemization of the tris-chelated complexes of 1,10-phenanthroline (phen) with iron(II), nickel(II), and cobalt(III), $[Fe(phen)_3]^{2+}$, $[Ni(phen)_3]^{2+}$, and $[Co(phen)_3]^{3+}$, have been studied extensively,[1] and it was concluded that these three complexes racemize through different mechanisms: twist,[2] dissociative,[3,4] and electron exchange,[5] respectively. Solvent effects on the racemization reactions have been examined in organic solvents or in aqueous-organic solvent mixtures during recent decades.[6] In aqueous solutions, we have shown that a different solvent effect appears to reflect a difference between their racemization mechanisms.[7]

In our previous studies of racemization of the nickel complex in several solvents[8] and in 1,2-dichloroethane solutions containing various amounts of donor solvents,[9] the racemization rates were found to decrease with decreasing donicity of the solvents (Gutmann donor number[10]), indicating that attack of the donor on the central metal may be important for the racemization.[11] On the other hand, the racemization reaction of the iron complex has been thought to provide one of interesting examples of unimolecular reactions involving no formal separation of charge but the role of solvent in the racemization has not been obvious and is still a matter for discussion, especially with respect to the mechanism. In a study of the rates of dissociation and racemization of $[Fe(phen)_3]^{2+}$ in various solvents,[12] Van Meter and Neumann reported that solvent variation affects the rates of racemimization k_r, and derived empirically the equation,

$$\log k_r = c_i - (0.26\Delta G_L/2.303RT) - 0.48\log(\eta V_m), \quad (1)$$

where c_i, ΔG_L, η, and V_m are a constant, the free energy of solvation of the phen ligand, the solvent viscosity, and the molar volume of the solvent, respectively. Recently, the polarizability of solvents and added salts in aqueous solutions was suggested to be one of important factors which facilitate the racemization of the iron complex.[13] On the other hand, we noted that the racemization rates in aprotic solvents decrease with the solvent in the order, *N,N*-dimethylformamide > acetonitrile > nitrobenzene, despite the fact that the three solvents are very similar in ΔG_L; this sequence lies in the order of decreasing donicity of the solvents, implying that the donicity play a significant role on the racemization even in the case of the $[Fe(phen)_3]^{2+}$ complex,[14] as well as in the case of the $[Ni(phen)_3]^{2+}$ complex.[8,9]

In order to explore this possibility, first, we present further examples of solvents such as nitrobenzene in which the observed rate of the racemization is markedly smaller than that calculated by Eq. 1. Here, the contribution to the solvation energy, ΔG_L, for the $[Fe(phen)_3]^{2+}$ cations arising from ligand-solvent interactions was calculated from the solubility data for naphthalene by the method of Van Meter and Neumann.[15] Second, measurements of the racemization rates in 1,2-dichloroethane solutions with varying concentration of the donor solvents, dimethyl sulfoxide, *N,N*-dimethylformamide, methanol, acetone, and acetonitrile, were made over a temperature range. The results may be interpreted based on Kepert's model for solvent-assisted racemization of tris-chelated complexes.[16] Support for this is furnished by the X-ray structure of the nitrobenzene solvate, $[Fe(phen)_3]I_2 \cdot NB \cdot 2H_2O$, reported already.[17]

Experimental

Materials. The preparation of the optically active complex, $(+)\text{-}[Fe(phen)_3](ClO_4)_2 \cdot 3H_2O$, was performed according to the method of Dwyer and Gyarfas involving diastereoisomer resolution with antimonyl (+)-tartrate.[18]

Reagent-grade non-aqueous solvents were further purified before experimental use as follows. Nitrobenzene (NB), *o*-

dichlorobenzene (DCB), and 1,2-dichloroethane (DCE) were purified according to the procedures described in our previous papers[7,19,20] and nitromethane (NM) according to the method of Unni et al.[21]

Dimethyl sulfoxide (DMSO) was refluxed with potassium hydroxide for 3 h at 125 °C, and then fractionally distilled twice at 95 °C under reduced pressure with a nitrogen bleed. The middle fraction was collected each time. *N,N*-Dimethylformamide (DMF) was distilled fractionally under a pressure of a few millimeters. The middle cut was taken and, after being dried over 4-A Molecular Sieves for one week, distilled once more under vacuum at 65 °C with a nitrogen bleed. The middle fraction was collected. Methanol (MeOH), to which 6 M (1 M=1 mol dm^{-3}) sulfuric acid (25 cm^3 per liter) was added, was refluxed for several hours and distilled. The product was treated with 20 g of potassium hydroxide and 10 g of silver nitrate per liter, the mixture being refluxed and distilled. The distillate was dried over 3-A Molecular Sieves for 1 d, and then distilled fractionally from magnesium over nitrogen. Acetone (Ac) was dried over 4-A Molecular Sieves, filtered, and distilled. Acetonitrile (AN) was intermittently shaken or stirred (magnetic stirrer) with calcium hydride (10 g per liter) for 2 d, decanted, and then fractionally distilled from phosphorus pentaoxide (5 g per liter). The product was refluxed over calcium hydride (5 g per liter) for several hours, then fractionally distilled very slowly. The middle fraction was collected. All solvents have densities identical with or close to literature values: Observed densities for DCE, DCB, NB, and NM are given in Table 1; DMSO, 1.09525 (1.0958); DMF, 0.94401 (0.94397); MeOH, 0.78653 (0.78664); Ac, 0.78447 (0.78440); AN, 0.77662 (0.7766). Values in parentheses are from the literature.[22] Water contents in the solvents were measured coulometrically by using a Hiranuma AQ-3 aquacounter to be less than 0.01 M. Naphthalene was recrystallized three times from methanol. The melting point was 80.7 °C (lit,[23] 80.5 °C).

Rates of Racemization. The rates of racemization of (+)-$[\text{Fe(phen)}_3](\text{ClO}_4)_2$ in various solutions were determined over a temperature range by the method described in our previous work.[7] The optical rotations of the chelate were measured at 365 nm in DCE and DCB solutions and at 589 nm in NB and NM solutions by using a Perkin-Elmer Model 141 polarimeter with Hg and Na lamps, respectively. About 10^{-4} M solutions of the chelate were prepared by its dissolution in the appropriate solution. This solution was immediatedly poured into a 1-dm, water-jacketed, polarimeter tube and maintained at constant temperature (±0.1° C) by circulating water.

The values of the observed rotation, α, were plotted in the usual fashion, log α vs. time, and the slope of the straight line obtained is equal to $-k_r/2.303$ where k_r is the rate constant in s^{-1} for the racemization.

Table 1. Solubilities and Apparent Molar Volumes of Naphthalene and Densities of Solvents at 25 °C

Solvent	S_{naphth}	V_{m}	d_0	
	M	$\text{cm}^3\,\text{mol}^{-1}$	obsd.	lit.
DCE	3.418±0.002	125.528±0.003	1.24574	1.2458[a)]
DCB	2.724±0.004	125.70 ±0.01	1.30036	1.30033[a)]
NB	2.747±0.002	125.75 ±0.03	1.19820	1.1983[b)]
NM	1.400±0.002	126.77 ±0.06	1.13111	1.13124[c)]

a) Data from Ref. 22. b) Data from Ref. 19. c) Data from Ref. 21.

Solubility of Naphthalene. The procedure of solubility measurement was similar to that for $[\text{Fe(phen)}_3](\text{ClO}_4)_2$[24] except that the solubility of naphthalene, S_{naphth}, was determined from density measurements by using the equation,

$$S_{\text{naphth}} = 1000(d_0 - d)/(V_{\text{m}}d_0 - M_{\text{W}}), \qquad (2)$$

where d_0 and d are the densities of a pure solvent and its solution containing naphthalene, respectively, and M_{w} is the molecular weight of naphthalene (M_{w}=128.175). The apparent molar volumes, V_{m}, of naphthalene, which are given in Table 1, were determined from density measurements by using the Eq. 2 for DCE, DCB, NB, and NM solutions with varying concentration of naphthalene prior to the solubility measurements. The densities of the sample solutions were measured by using a digital densimeter (Anton Paar Precision Density Meter, Model DMA 02D) with an internal measuring cell which is water jacketed with a water-circulating thermostat at 25.00±0.005 °C.

Results

Rates of Racemization. The rate constants in the various pure solvents are given in Tables 2 and 3. The errors are the standard derivations estimated from the residuals of the least-squares line for each run. The reproducibility of the measurements can be evaluated from the data obtained in duplicate under the same reaction conditions. There is no dependence of the racemization rate on the complex concentration in each solvent as given in Table 2. The activation parameters, E_{a} and log A for the rates were calculated from the Arrhenius plot of log k_r vs. $1/T$. The rate constants for DCE, DCB, NB, and NM at 25 °C were extrapolated from the Arrhenius plots. Table 4 gives the results and includes the data for AN, MeOH, Ac, and DMF[12] for comparison, indicating that the racem-

Table 2. Concentration Dependence of the Rate Constant for Racemization on $[\text{Fe(phen)}_3](\text{ClO}_4)_2$ in Various Pure Solvents at 15.0 °C

Solvent	$10^4\,C_{\text{c}}$[a)]	$10^4 k_r$
	M	s^{-1}
DCE	0.128	7.56±0.07
	0.580	7.65±0.03
	1.18	7.75±0.01
	1.44	7.63±0.05
DCB	0.45	8.15±0.11
	0.51	8.38±0.16
	0.56	7.72±0.17
NB	0.554	6.99±0.11
	0.817	6.70±0.06
	1.38	7.02±0.23
	2.52	6.69±0.06
NM	1.17	5.45±0.06
	2.31	5.53±0.07
	2.32	5.48±0.10
	3.21	5.51±0.13

a) C_{c} is the concentration of $[\text{Fe(phen)}_3](\text{ClO}_4)_2$.

Table 3. Rate Constants for Racemization of [Fe(phen)$_3$](ClO$_4$)$_2$ in Various Pure Solvents

Solvent	$10^4k_r/s^{-1}$				
	7.5 °C	10.0 °C	12.5 °C	17.5 °C	
DCE	2.20±0.02 2.02±0.02	3.35±0.01 3.40±0.01	5.00±0.02 5.08±0.02	11.54±0.05 11.59±0.05	
DCB	—	3.87±0.06 4.06±0.02	5.55±0.04 5.45±0.04	13.93±0.06 13.81±0.12	
NB	2.03±0.02 2.14±0.02	3.03±0.01 3.06±0.02	4.78±0.08 4.85±0.04	10.06±0.13 9.90±0.10	
NM	1.66±0.01 1.68±0.01	2.54±0.02 2.58±0.03	3.90±0.02 3.86±0.02	8.17±0.04 8.50±0.08	13.0[a]

a) Data (at 20.1 °C) from Ref. 13.

Table 4. Arrhenius Parameters and Rate Constants for Racemization and Dissociation of [Fe(phen)$_3$](ClO$_4$)$_2$ in Various Pure Solvents at 25 °C

Solvent	Racemization			Dissociation
	E_a	log A	log k_r	log k_d
	kJ mol^{-1}	s^{-1}	s^{-1}	s^{-1}
DCE	114±2	17.6±0.3	−2.42	−6.84
DCB	112±7	17.2±1.2	−2.39	−5.61
NB	107±2	16.3±0.3	−2.51 −2.73[a]	−7.57
NM	109±2	16.5±0.3	−2.59	−8.58
AN[b]	—	—	−1.83	−5.69
MeOH[b]	90	13.93	−1.73	−4.40
DMF[b]	97	15.8	−1.16	−3.62
Ac[b]	90	15.6	−0.70	−5.22

a) Data from Ref. 2. b) Data from Ref. 12.

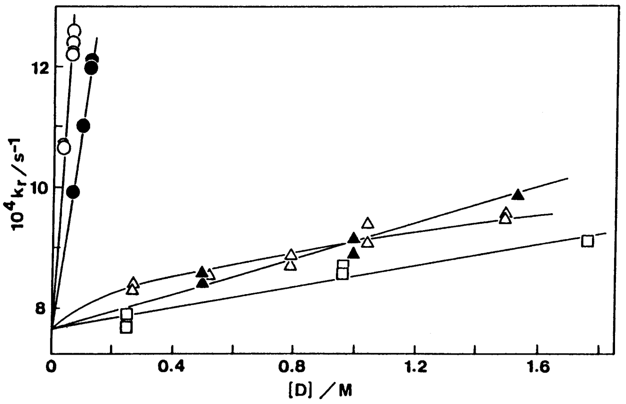

Fig. 1. Dependence of rate constant (k_r) for racemization of [Fe(phen)$_3$]$^{2+}$ on the concentration of donor solvent, [D], in DCE solution at 15.0 °C: (○), DMSO; (●), DMF; (△), MeOH; (▲), Ac; (□), AN.

ization occurs more slowly in DCE, DCB, NB, and NM.

Table 5 gives the rate constants in the DCE solutions with varying concentration of the various donor solvents and the typical results are illustrated in Fig. 1, where the data are plotted as k_r vs. donor solvent concentration, [D]. Figure 1 shows that the plots were good straight lines, except for MeOH. By a weighted least-squares procedure, the results were fitted to the equation,

$$k_r = k_0 + k_s[D], \tag{3}$$

where k_0 and k_s are the intercept and the slope of the plot, respectively. The values of k_0 were in agreement with the corresponding rate constants in the pure DCE solvent within error. Table 6 gives the k_s values with the activation parameters determined by the Arrhenius plots for k_s.

For MeOH, on the other hand, the plot shows a curve (Fig. 1). Similar rate behavior was observed for the racemization of [Ni(phen)$_3$]$^{2+}$ in the analogus solvent system.[9] The decrease of the accelerating effect is due to loss of MeOH activity[25] which is caused by self association of MeOH in DCE as reported for water and alcohols in relatively inert solvents.[26] Assuming dimerization of MeOH, we estimated an equilibrium constant of 0.49±0.20 M^{-1} for the formation of a dimer of MeOH and a k_s value of (2.28±0.43)$\times10^4$ s^{-1} M^{-1} (Table 6).

In our previous study of the racemization of [Ni(phen)$_3$]$^{2+}$ in DCE solutions containing various amount of water,[8] it was found that the rate increases dramatically with increasing water content. However, the analogous increase in rate for [Fe(phen)$_3$]$^{2+}$ is very small: The k_r value at 15.0 °C is (8.19±0.06)$\times10^{-4}$ s^{-1}

Table 5. Observed Rate Constants for Racemization of [Fe(phen)$_3$](ClO$_4$)$_2$ in DCE Solutions Containing Various Donor Solvents

		$10^4k_r/\mathrm{s}^{-1}$						
Temp	[DMSO]		[DMF]		[Ac]		[AN]	
°C	M		M		M		M	
7.5	0.0813	4.56±0.03						
		4.54±0.01						
	0.1240	5.75±0.02						
		5.70±0.03						
	0.1647	6.69±0.03						
		6.69±0.02						
	0.1965	7.46±0.04						
10.0	0.0186	4.13±0.02	0.0319	4.10±0.01	0.385	3.79±0.01	0.982	3.72±0.02
		4.17±0.01		4.03±0.01		3.70±0.01		3.68±0.01
	0.0275	4.71±0.04	0.0682	4.77±0.01	0.789	4.13±0.02	1.373	3.86±0.01
		4.72±0.02		4.88±0.01		4.03±0.01		3.94±0.01
	0.0537	5.56±0.02	0.1017	5.52±0.04	1.171	4.23±0.01	1.945	3.95±0.01
		5.54±0.01		5.36±0.02		4.27±0.01		4.01±0.01
	0.0736	6.48±0.04	0.1418	6.23±0.04	1.625	4.58±0.02	2.230	4.14±0.02
		6.23±0.01		6.08±0.02		4.57±0.01		4.18±0.01
	0.1060	8.04±0.06	0.1768	6.54±0.03				
		7.86±0.03		6.80±0.02				
	0.1371	8.97±0.06						
		8.78±0.02						
	0.1496	9.47±0.01						
		9.73±0.03						
12.5	0.0488	8.30±0.10	0.0268	6.04±0.04	0.394	5.67±0.03	0.475	5.49±0.03
		8.05±0.04		5.96±0.04		5.56±0.03		5.52±0.03
	0.0732	8.88±0.03	0.0586	6.67±0.03	0.808	6.01±0.03	0.972	5.56±0.03
		9.10±0.03		6.64±0.03		6.01±0.03		5.61±0.02
	0.0983	10.78±0.03	0.0885	7.40±0.04	1.630	7.14±0.02	1.482	5.84±0.03
		10.56±0.07		7.32±0.04				5.84±0.03
	0.1208	11.73±0.10	0.1203	8.48±0.06	1.985	7.55±0.04	1.957	6.01±0.02
		11.71±0.05		8.17±0.03				6.04±0.02
			0.1478	8.83±0.05			2.435	6.34±0.04
				8.74±0.05				6.10±0.03
15.0	0.0316	10.65±0.04	0.0617	9.91±0.04	0.493	8.60±0.06	0.251	7.87±0.03
		10.71±0.04		9.91±0.03		8.46±0.02		7.68±0.03
	0.0594	12.17±0.04	0.0940	10.99±0.09	0.994	8.89±0.03	0.960	8.71±0.04
		12.26±0.13				9.15±0.04		8.57±0.03
	0.0612	12.61±0.06	0.1215	11.94±0.03	1.530	9.81±0.02	1.760	9.12±0.05
		12.39±0.14		12.10±0.03		9.87±0.03		9.13±0.03
	0.0832	14.59±0.06	0.1575	13.51±0.06	2.010	10.95±0.04	2.470	9.20±0.03
		14.41±0.11		13.61±0.04		10.69±0.02		9.24±0.02
	0.0994	15.44±0.08	0.1835	15.01±0.05	2.530	11.48±0.04	5.003	11.44±0.07
		14.97±0.09		14.59±0.10		11.78±0.04		11.66±0.09
					3.010	12.30±0.04		
						12.30±0.04		

		$10^4k_r/\mathrm{s}^{-1}$					
Temp	[MeOH]		Temp	[Ac]		[AN]	
°C	M		°C	M		M	
15.0	0.27	8.40±0.03	17.5	0.207	11.99±0.07	0.408	11.71±0.03
		8.27±0.02			12.17±0.08		11.96±0.04
	0.52	8.54±0.02		0.412	12.35±0.06	0.806	12.37±0.06
		8.51±0.03			12.39±0.11		12.31±0.06
	0.79	8.86±0.04		0.532	12.89±0.06	1.243	12.76±0.10
		8.68±0.03			12.87±0.07		13.00±0.04
	1.04	9.40±0.02		0.621	13.49±0.06	2.031	13.53±0.05
		9.12±0.02			12.97±0.07		
	1.49	9.59±0.04		0.732	13.30±0.07		
		9.50±0.03			13.15±0.06		
	1.94	9.73±0.02		0.927	13.63±0.07		
		9.83±0.02			13.79±0.10		
	2.93	10.76±0.04					
		10.45±0.04					

Table 6. Derived Rate Constants k_s and Arrhenius Parameters for the Racemization of $[Fe(phen)_3](ClO_4)_2$ in DCE Solutions Containing Various Donor Solvents

Temp	$10^4k_s/s^{-1}M^{-1}$				
°C	DMSO	DMF	MeOH	Ac	AN
7.5	27.5±0.6	—	—	—	—
10.0	41.0±0.7	18.7±0.5	—	0.717±0.038	0.339±0.021
12.5	55.0±1.8	25.2±0.8	—	1.25±0.03	0.449±0.035
15.0	77.3±2.2	38.2±0.7	2.28±0.43	1.55±0.03	0.761±0.032
17.5	—	—	—	2.38±0.15	1.026±0.052
			E_a/kJ mol^{-1}		
	91±4	96±8	—	104±12	106±9
			log A (in $s^{-1}M^{-1}$)		
	14.4±0.7	14.9±1.4	—	15.1±2.2	15.0±1.6

Table 7. Solvent Parameters and the c_i Values Calculated from Eq. 1$^{a)}$ at 25 °C

Solvent	ΔG_L / kJ mol^{-1}	log $(\eta V_m)^{b)}$ / P cm^3 mol^{-1} $^{c)}$	DN$^{d)}$	c_i/s^{-1}
DCE	−68.9	−0.207	0	−5.65
DCB	−67.9	0.175	$(2.3)^{e)}$	−5.40
NB	−67.9	0.270	4.4	−5.47
NM	−64.5	−0.483	2.7	−5.76
AN	$-65.0^{f)}$	−0.743	14.1	$-5.15^{g)}$
Water	$-19.4^{f)}$	−0.794	18.0	$-4.45^{g)}$
MeOH	$-53.6^{f)}$	−0.654	19.0	$-4.48^{g)}$
FA	$-49.5^{f)}$	0.120	$24.7^{h)}$	$-4.42^{g)}$
DMF	$-68.6^{f)}$	−0.207	26.6	$-4.38^{g)}$
Ac	$-67.5^{f)}$	−0.648	17.0	$-4.09^{g)}$

a) Values calculated by the equation, $c_i = \log k_r + (0.26\Delta G_L/2.303RT) + 0.48 \log(\eta V_m)$. b) Data of η from Ref. 22. c) 1P=0.1 Pa s. d) Data from Ref. 10. e) See Ref. 36. f) Data from Ref. 15. g) Data of k_r from Ref. 12. h) Data from M. S. Greenberg, R. L. Bodner, and A. I. Popov, *J. Phys. Chem.*, **77**, 2449 (1973).

in water-saturated DCE ($[H_2O]=0.094$ M) and is $7.65\times10^{-4}\,s^{-1}$ in pure DCE (Table 2).

Solubility of Naphthalene. Table 1 gives the solubilities of naphthalene in the various solvents. Each value of the solubilities is the mean of data obtained in triplicate and the error is a mean deviation. Van Meter and Neumann showed that the solvation energy is related to the solubility or the free energy of solvation of naphthalene, ΔG_{naphth}, by the equation,[15]

$$\Delta G_L = 2.053\,\Delta G_{naphth}, \qquad (4)$$

for which $\Delta G_{naphth} = -RT\ln S_{naphth} - \Delta G_{subl}$, where the free energy change, ΔG_{subl}, for the sublimation of naphthalene, is calculated, from the vaper pressure[27] of naphthalene at 25 °C, to be 30.57 kJ mol^{-1}. The Eq. 4 is valid especially for aprotic solvents, althouth some steric factors may become important in such a tris complex. The ΔG_L values calculated for DCE, DCB, NB, and NM are comparable to those for other aprotic solvents such as AN, Ac, DMF, etc. as given in Table 7.

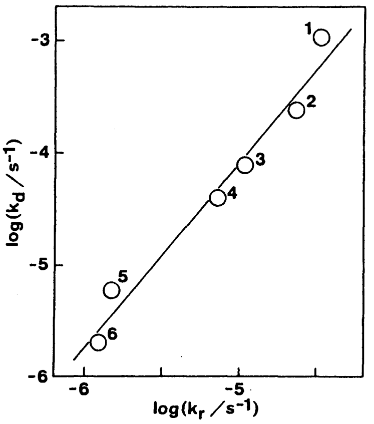

Fig. 2. Plot of log $k_d$$^{a)}$ for dissociation of $[Fe(phen)_3]^{2+}$ vs. log $k_r$$^{b)}$ for racemization of $[Ni(phen)_3]^{2+}$ at 25 °C in various solvents: (1), DMSO$^{c)}$; (2), DMF; (3), water; (4), MeOH; (5), Ac; (6), AN. a) Data from Ref. 12. b) Data from Ref. 8. c) Data of k_d from D. J. Farrington, J. G. Jones, and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, **1979**, 221.

Discussion

Since the racemization of $[Ni(phen)_3]^{2+}$ complex occurs mainly by a dissociative process,[4,28] measurements of the racemization rate, k_r, of the nickel complex allow us to estimate the dissociation rate, k_d, of the $[Fe(phen)_3]^{2+}$ complex as follows.[29] Figure 2 shows that a linear free-energy relationships[30] exists: A plot of log k_d for the iron complex against log k_r for the nickel complex in various solvents is linear, with slope 1.66±0.15 and intercept 4.21±0.77. The k_d values for DCE, DCB, NB, and NM can be extrapolated from this plot as the k_r values for the solvents are available from our data.[31] Table 4 gives the estimated k_d values with the values of k_r for the iron complex, indicating that racemization of the iron complex is extremely faster than dissociation in these solvents where the complex favors an intramolecular racemization process, as well as that in the other organic solvents, AN, Ac, DMF, etc. (more than 99.5% of the time).[1,12,32]

When the Van Meter and Neumann Eq. 1 is valid for a given solvent, the value of the constant, c_i, of an intrinsic part in the Eq. 1 should be −4.56.[33] Table 7 shows that this is the case for DMF and MeOH while the solvents, DCE, DCB, and NM, as well as NB,[14] have significantly lower c_i values: Despite similarities of ΔG_L and $\log(\eta V_m)$ between DMF and DCE, for example, the rate in DCE is smaller than that in DMF (Table 4). Furthermore, DCE or DCB is a solvent of lower dielectric constant compared to NM or NB and thus substantially all the complex cations are associated with the ClO_4^- ion into ion-pairs in the former solvent (about 10^{-4} M solutions of the complex used here)[34] while they are dissociated to a great extent in the latter.[35] However, the racemization rate or the c_i value in DCE or DCB is comparable to that in NM or NB. In addition, the racemization rates are independent of the complex concentrations in the solvents (Table 2). These results indicate that the ion pairing effect is negligibly small. DCE, DCB, NB, and NM have extremely low donicities[36] and so the c_i value appears to increase predominantly with increasing donor number of the solvents (Table 7). This implies that the c_i constant for the racemization should contain not only an intrinsic part but also a part due to a nucleophilic interaction with the iron metal.

In order to clarify the role of donor solvents in the racemization of the iron complex, the dependence of the rate on the concentration of added solvents was investigated in DCE solutions.[37] Figure 1 shows that addition of donor solvents to DCE solutions enhances the racemization rates and the correlation between them is linear. As presented for the $[Ni(phen)_3]^{2+}$ complex,[9] the rate behavior can be understood on the basis of the scheme,

$$(+)\text{-}[Fe(phen)_3]^{2+} + D \rightleftarrows (+)\text{-}[Fe(phen)_3]^{2+}\cdot D \rightarrow (-)\text{-}[Fe(phen)_3]^{2+} + D, \qquad (13)$$

which, provided that an outer-sphere complex in a rapid preequilibrium is weak, leads to a second-order rate law.[38] Since the sizes of the added solvents do not greatly differ or the solvents are similar in ΔG_L, it is reasonable that equilibrium constants for the formation of the outer-sphere complexes for the solvents are approximately equal. Thus it is quite likely that the kinetics are controlled by the interaction of the complex cation with the added donor solvent molecule in the process concerned in the rate-determining step.

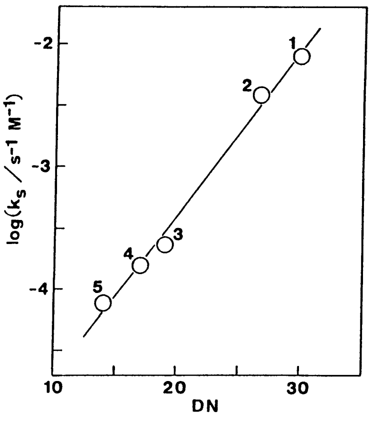

Fig. 3. Correlation of $\log k_s$ in DCE solutions containing donor solvents at 15 °C with Gutmann donor number DN of the solvents: (1), DMSO; (2), DMF; (3), MeOH; (4), Ac, (5), AN.

The k_s values derived by using Eq. 3 increase with added solvent in the order AN < Ac < MeOH < DMF < DMSO. This sequence lies in the order of increasing donicity of the solvents. A plot of $\log k_s$ against donor number shows a good linear correlation between them as shown in Fig. 3. Futher, Table 6 shows that a decrease in the activation energy, E_a, for the system, AN > Ac > DMF > DMSO, is consistent with the trend in $\log k_s$ as donor number of the solvent increases. This can be rationalized in terms of a mechanism involving expansion of a complex cation to a 7-coordinate transition state with one donor solvent as proposed for racemization of the $[Ni(phen)_3]^{2+}$ complex.[8,9,11] The trends in $\log k_s$ and E_a may be attributable to the ability of the solvents to stabilize the transition state by donation, which thus leads to a lower energy of activation for racemization.

Recently, we have reported the detailed structure of the nitrobenzene solvate, $[Fe(phen)_3]I_2\cdot NB\cdot 2H_2O$, as a result of the X-ray structure determination.[17] In the structure, the nitrobenzene molecule occupies one of the three major V-shaped pockets between the phen ligands. Thus, the above solvent-assisted racemization of the tris-chelated complexes can be explained by a double-opposed-initiated twist proposed by Kepert[39] if it is assumed that a donor solvent molecule is placed instead of the nitrobenzene molecule in the solvate (Fig. 1 of Ref. 17), although differences in coordination to the metal center may be also involved, as well as differences in solvation energy in the transition state. Moreover, it has been reported that for ion-pair formation of the iron complex and arenesulfonate ions the above major pockets are also important.[40]

In summary, it is concluded that the donor number of the solvent is one of the important factors in solvent effects on the racemization of $[Fe(phen)_3]^{2+}$. From this point of view, we can relate the c_i constant to donor number (Table 7)[41] and derive the equation,

$$c_i = -5.66 + 0.057\text{DN},$$

which may allow us to modify the Van Meter and Neumann Eq. 1. On the other hand, it is surprising that the racemization of the iron complex in Ac is extremely rapid (Table 4) while the accelerating effect of Ac on the racemization in DCE solutions is lower (Table 6). Langford and Tong have pointed out that changes in the bulk properties of the solvent beyond the contact solvation shell may influence reaction rates.[42] Further investigation is undertaken for clarifying bulk solvent effects on the racemization.

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