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The Influence of a Trace Amount of Nitrobenzene on Racemization of $[Fe(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ in Aqueous Solution

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The racemization rates of tris(1,10-phenanthroline)iron(II), ($[Fe(phen)_3]^{2+}$), and -nickel(II), ($[Ni(phen)_3]^{2+}$), have been measured at 15 °C to 35 °C in aqueous solutions containing nitrobenzene below 0.015 mol·l⁻¹. The rate for $[Fe(phen)_3]^{2+}$ increases with increasing nitrobenzene content but that for $[Ni(phen)_3]^{2+}$ decreases, reflecting the difference between their racemization mechanisms. The association constants of the metal chelate ions with nitrobenzene in water were determined using the solubility of nitrobenzene in their aqueous solutions. The observed results were discussed in terms of preferential solvation of the metal chelate cations by nitrobenzene and donicity of water and nitrobenzene.

Introduction

The recent studies of racemization for phenanthroline complexes have shown that the racemization rate of the nickel-complex with an intermolecular mechanism is correlated with the donor number of solvent [1], and that of the iron-complex with an intramolecular mechanism is correlated with solvation of the aromatic phenanthroline ligands by solvents and the viscous resistance [2]. However, the detailed solvent effects on their racemization are still a matter for discussion, especially with respect to the different racemization mechanisms.

A trace amount of second solvent in a mixed solvent influences markedly for some times and the role of solvents can become clear. For example, the existence of a trace amount of water in dichloroethane accelerates the racemization rate of $[Ni(phen)_3]^{2+}$, showing S_N2 reaction through an intermediate containing a water molecule [1].

We have shown that the metal chelate electrolyte, $[Fe(phen)_3]Br_2$, strongly salts-in nitrobenzene in water, resulting from association of $[Fe(phen)_3]^{2+}$ with nitrobenzene by ion–dipole and van der Waals interactions through a hydrophobic interaction between them [3]. This phenomenon led us to inquire the influence of nitrobenzene on the racemization rate of $[Ni(phen)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ in water. The solvent, water, of a high dielectric constant which reduces counter anion effects is rather active in connection with coordination ability while the added solvent, nitrobenzene, is inactive. This system is in contrast with the above water–dichloroethane system.

Experimental

The optically active complexes, Δ-(+)$_{589}$- and Λ-(–)$_{589}$-$[Fe(phen)_3](ClO_4)_2$ and Δ-(–)$_{589}$- and Λ-(+)$_{589}$-$[Ni(phen)_3](ClO_4)_2$, were prepared and resolved using antimonyl-(+)-tartrate by the method of Dwyer and Gyarfas [4]. Nitrobenzene (Wako chemicals) was purified by shaking with sodium hydroxide solution, sulfuric acid and distilled water, successively, and then by distillation under reduced pressure after drying over calcium chloride.

Measurements of optical rotation (α) were made at 436 nm for $[Ni(phen)_3]^{2+}$ and at 578 nm for $[Fe(phen)_3]^{2+}$ with a Perkin Elmer Model 141 polarimeter using a Hg lamp and a 1-dm cell.

Solutions of approximately 5×10^{-5} *M* concentration of optically active $[Fe(phen)_3](ClO_4)_2$ and 1×10^{-4} *M* concentration of $[Ni(phen)_3](ClO_4)_2$ were prepared by adding the each salt to the aqueous solution containing a trace amount of nitrobenzene solutions. Because of the rapid racemization of $[Fe(phen)_3]^{2+}$, this solution was immediately poured into a 1-dm polarimeter tube equipped with a water jacket and maintained at constant temperature (20.0° ± 0.1, 25.0° ± 0.1, 30.0° ± 0.2 °C) with circulating water. The optical rotations were read at 1 or 2 minute intervals as soon as the equilibrium temperature was reached. The solutions of $[Ni(phen)_3](ClO_4)_2$ were immersed in a thermostatted bath (25.0° ± 0.05, 29.7° ± 0.07, and 35.0° ± 0.1 °C) and the portion was poured into the polarimeter tube. The measurements were made at 1-hour intervals. A plot of log α *vs.* time data yielded a straight line and apparent racemization constants k_{ap} were obtained from the slope, $-2k_{ap}/2.303$.

TABLE I. Rate Constants of Racemization and Association Constants, with Nitrobenzene, of $[Fe(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ in Aqueous Solutions.

$[Fe(phen)_3]^{2+}$			$[Ni(phen)_3]^{2+}$		
10^2 k_f (min^{-1})	20 °C	0.861 ± 0.004 0.86[a]	10^4 k_f (min^{-1})	25 °C	3.35 ± 0.01 3.3[a] 3.0[d]
	25 °C	1.96 ± 0.01 2.0[a]		29.7 °C	6.40 ± 0.03
	30 °C	4.41 ± 0.03 4.4[a]		35 °C	12.7 ± 0.05
10^2 k_s (min^{-1})	20 °C	2.07 ± 0.12	10^4 k_s (min^{-1})	25 °C	2.11 ± 0.08 0.34[b]
	25 °C	4.79 ± 0.09 5.6[b]		29.7 °C	4.18 ± 0.16 0.69[b]
	30 °C	10.5 ± 0.3		35 °C	7.86 ± 0.42 1.38[b]
K_a	20 °C	14.5 ± 0.1	K_a	25 °C	15.2 ± 0.8
	25 °C	14.9 ± 0.3 14.1[c]		29.7 °C	15.9 ± 0.7
	30 °C	15.3 ± 0.4		35 °C	16.7 ± 0.9

[a] From ref. [5]. [b] Values in nitrobenzene from ref. [9]. [c] From ref. [17]. [d] From ref. [6].

Nitrobenzene solubility in the metal chelate electrolyte solutions were determined as follows. A metal chelate salt solution was saturated with nitrobenzene by vigorously agitating the solutions with an excess of nitrobenzene for at least 15 h in a constant temperature bath. The saturated solution was left in the bath for another several hours to attain complete phase separation of the excess nitrobenzene. Ten ml of the saturated solution was pipetted out and diluted to 500 ml with distilled water. Ten ml of this diluted solution was then shaken with 25 ml of cyclohexane for 10 min, which was confirmed to be enough for complete extraction of nitrobenzene into cyclohexane. The sample of cyclohexane phase was then analyzed for nitrobenzene at 252 nm with a Hitachi Model 139 spectrophotometer. At each run, the cyclohexane solution, which was prepared by agitating with the metal chelate salt solution free from nitrobenzene of the same concentration as that containing nitrobenzene, was used in the reference cell.

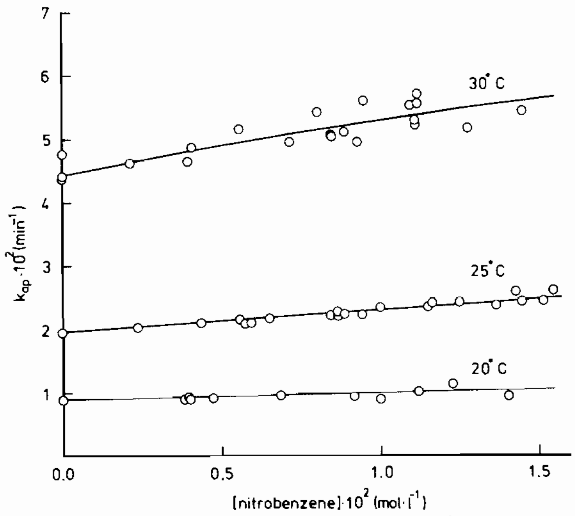

Fig. 1. Dependence of k_{ap} for $[Fe(phen)_3]^{2+}$ on nitrobenzene concentration. Solid lines are the curves calculated from eqn. 1 using the values in Table I.

Results and Discussion

The rate constants of racemization in water are in good agreement with those of the literatures [5, 6] as shown in Table I. The dependence of apparent racemization rate constants on the nitrobenzene concentration is shown in Fig. 1 for $[Fe(phen)_3]^{2+}$ and in Fig. 2 for $[Ni(phen)_3]^{2+}$. The

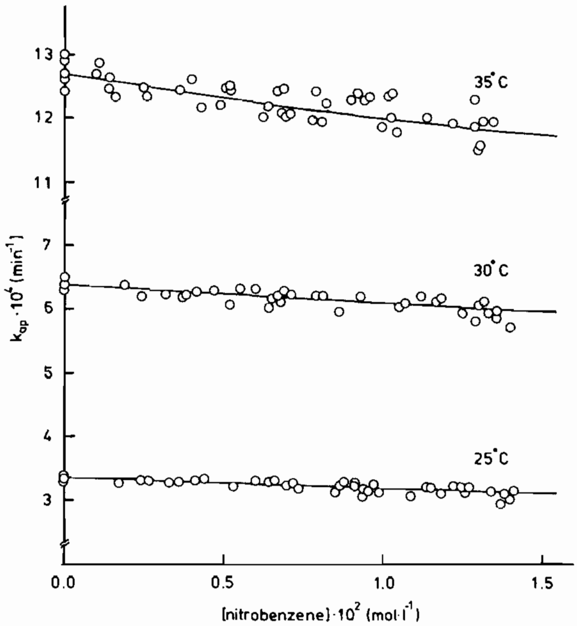

Fig. 2. Dependence of k_{ap} for $[Ni(phen)_3]^{2+}$ on nitrobenzene concentration. Solid lines are the curves calculated from eqn. 1 using the values in Table I.

presence of nitrobenzene in water clearly increases the rate of racemization of the $[Fe(phen)_3]^{2+}$ ion whereas decreases that of the $[Ni(phen)_3]^{2+}$ ion, and at higher temperature the phenomena are more marked. Since the $[Fe(phen)_3]^{2+}$ ion [6] was found to racemize mainly by an intramolecular process while the $[Ni(phen)_3]^{2+}$ ion [7] by an intermolecular process, the marked opposit influences of nitrobenzene are considered to reflect the difference between the two types of mechanism.

The metal chelate electrolytes of phenanthroline are almost dissociated in water [8] and the mole fraction of nitrobenzene (below 2.7×10^{-4}) is too low to change the bulky properties such as dielectric constant of water. Therefore the dielectric contribution of nitrobenzene to the racemization rates of the $[Fe(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ ions is unimportant in determining the activation energy of racemization. Thus, the accelerating or retarding effect of nitrobenzene suggests strong specific interactions between the metal chelate cations and nitrobenzene in the aqueous solution due to preferential solvation by nitrobenzene or structural change of water.

We have already shown that the rate of racemization of $[Ni(phen)_3]^{2+}$ increases with increasing the donor number of solvent, suggesting that a dissociation mechanism for the racemization involves formation of a seven-coordinated intermediate in the transition state [1]. In methanol–water, however, methanol retards the rate of racemization of $[Ni(phen)_3]^{2+}$ below 0.1 of the mole fraction [9], although the donor number (19.0) of methanol is comparable with that (18.0) of water [10]. This retarding effect of methanol could be attributed to the structural change of water. The addition of relatively small quantities of methanol to water actually enhances the three-dimensional structure of water [11]. This decreases the efficiency of donicity of water, leading to higher activation free energy. For nitrobenzene such a structural effect is unlikely since the hydrophilic nitro-group [12] weakens the water-structure making property of the benzene ring [13]. Furthermore, in the view of a lower donor number (4.4) of nitrobenzene, the preferential solvation of the metal chelate ion by nitrobenzene reasonably explains the influence of nitrobenzene as discussed in the following.

In the phenanthroline complexes metals are surrounded by the three large aromatic ligands, resulting in its non-spherical shape of large pockets and in a large size. It follows that the charge effect, of electrostriction, on the water structure is shielded to some extent by the ligands, leading to a hydrophobic property of the ions. The negative temperature dependence of the viscosity of $[Fe(phen)_3]^{2+}$ in water provides evidence of a hydrophobic character of the ion [14]. Therefore if a non-electrolyte, rather hydrophobic, coexists with the metal chelate ions in water, association between them could be induced by hydrophobic interactions. This aspect reasonably explains the abnormally large salting-in of nitrobenzene (the salting coefficient, $k_s = -4.71$ in l$\cdot$mol^{-1}) [3], *o*-dinitrobenzene ($k_s = -7.62$) [3], and tris(acetylacetonato)cobalt(III) $[Co(acac)_3]$ ($k = -2.47$) [15] by the $[Fe(phen)_3]^{2+}$ ion, and the crystallization of the nitrobenzene solvate, $[Fe(phen)_3]I_2 \cdot 2H_2O \cdot C_6H_5NO_2$ [16] from nitrobenzene–saturated water. The solubility of nitrobenzene was measured at 20 to 35 °C in the $[Fe(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ aqueous solutions to get the association constant (K_a) of the complex ions with nitrobenzene. The solubilities are tabulated in Table II. The increasing solubilities comparing with those in pure water were exclusively attributed to association [17], $M^{2+} + NB \rightarrow M^{2+} \cdot NB$, where M^{2+} is the metal chelate ions and NB nitrobenzene. It is noteworthy that the association constants obtained (Table I) are larger than the ionic association constant (*ca.* 7) [8] of $[Fe(phen)_3]^{2+}$ with Cl^- at 25 °C in water and that the positive temperature dependences of the association constants are not inconsistent with association due to ion–dipole [18] and hydrophobic interactions [15]. Recently (Δ)-$(-)_{589}$-$[Ni(phen)_3]^{2+}$ was found to salt-in selectively the (Δ)-$(+)_{589}$-$Co(acac)_3$ [19]. This shows the face to face contact between the ligand planes of both the complexes by hydrophobic and van der Waals interactions coming close to each other along their three

TABLE II. Solubilities of Nitrobenzene in Aqueous Solutions of $[Fe(phen)_3]Br_2$ and $[Ni(phen)_3]Br_2$.

$[Fe(phen)_3]Br_2$			$[Ni(phen)_3]Br_2$		
t °C	C (mol·l^{-1})^a × 10^2	S (mol·l^{-1})^b × 10^2	t °C	C (mol·l^{-1}) × 10^2	S (mol·l^{-1}) × 10^2
20 °C	0	1.46	25 °C	0	1.56
	1.03	1.64		0.52	1.65
	1.55	1.73		1.04	1.75
	2.06	1.82		1.56	1.88
				2.08	1.99
25 °C^c	0	1.56			
	1.03	1.75	29.7 °C	0	1.62
	1.25	1.79		0.624	1.74
	1.29	1.80		1.04	1.82
	2.13	1.95		1.56	1.96
	2.48	2.04		2.08	2.07
	3.28	2.21			
			30 °C	0	1.70
30 °C	0	1.62		0.52	1.80
	0.800	1.77		1.04	1.94
	1.24	1.87		1.55	2.05
	1.25	1.86		2.07	2.19
	1.53	1.93			
	2.22	2.09			

[a] Concentrations of metal chelate electrolytes. [b] Solubilities of nitrobenzene. [c] From ref. [3].

fold axes. The larger salting-in of nitrobenzene than that of $Co(acac)_3$ indicates that the associated nitrobenzene molecule would permeate one of the large pockets between the phenanthroline ligands.

The above discussion leads to the following mechanism of racemization of the metal chelate ions in the presence of nitrobenzene,

$$\begin{tikzcd}
(\Delta)\text{-}M^{2+} \arrow[r, "NB"] \arrow[d, "k_f"] \arrow[dr, phantom, "K_a"] & (\Delta)\text{-}M^{2+}\cdot NB \arrow[d, "k_s"] \\
(\Lambda)\text{-}M^{2+} \arrow[r, "NB"'] & (\Lambda)\text{-}M^{2+}\cdot NB
\end{tikzcd}$$

and the relationship,

$$k_{ap} = k_f + \frac{(k_s - k_f)\cdot K_a \cdot [NB]}{1 + K_a \cdot [NB]} \qquad (1)$$

where k_{ap} is the observed rate constant, k_f the rate constant for the metal chelate ion in pure water, and k_s for the nitrobenzene-associated metal chelate ions. Using the values of k_f and K_a in Table I, k_s values were calculated at each concentration of nitrobenzene and the average values are given in Table I. The Arrhenius parameters, E_a(kcal) and logA (min^{-1}), for the racemization rates were evaluated plotting logk_f or logk_s against 1/T. The values are shown in Table III. The kinetic effect of nitrobenzene can be thus explained by the formation of nitrobenzene-associated species of which the racemization rate constants for $[Fe(phen)_3]^{2+}$ is larger than that in pure water and of which those for $[Ni(phen)_3]^{2+}$ is smaller.

TABLE III. The Arrhenius Parameters.

	$[Fe(phen)_3]^{2+}$		$[Ni(phen)_3]^{2+}$	
	E_a (kcal)	log A (min^{-1})	E_a (kcal)	log A (min^{-1})
k_f	28.7 ± 0.1	19.4 ± 0.1	24.3 ± 0.1	14.3 ± 0.1
k_s	28.5 ± 0.4	19.6 ± 0.3	24.0 ± 0.9	13.9 ± 0.7

The rate constant of the mono-nitrobenzene solvate of $[Fe(phen)_3]^{2+}$ in water amounts to about 85% magnitude of 5.6 × 10^{-2} sec^{-1} [9] in pure nitrobenzene. Van Meter and Neumann [2] have suggested that a solvent effect on the racemization rate for $[Fe(phen)_3]^{2+}$ is due mainly to the solvating effect consisting of ion–dipole and the van der Waals interactions between solvents and the metal chelate ion, or the aromatic ligands: for an intramolecular mechanism, the solvation of the ligands which move away from the central iron atom in the transition state should be greater than in the ground state of the complex, the activation free energy being decreased. Our result coincides with this view. Since the solvation of phenanthroline by nitrobenzene is stronger than by water, the mono-nitrobenzene solvate of [Fe-$(phen)_3]^{2+}$ racemizes more rapidly.

On the other hand, as mentioned earlier, for the racemization of $[Ni(phen)_3]^{2+}$ with a dissociation process a much more important factor is donicity of solvent molecules to be a seven-coordinate intermediate in the transition state [1, 20] where the solvent molecule attacks on the central metal and replace the dissociated ligand. The donor number (4.4) of nitrobenzene is smaller than that (18.0) of water. Therefore, for the mono-nitrobenzene solvate of the $[Ni(phen)_3]^{2+}$ ion the activation free energy should be larger than for the nitrobenzene-free complex ion which is attacked by water molecules only. It is a controversial subject to what extent the solvation of the leaving phenanthroline ligands in a manner similar to the solvation effect for an intramolecular mechanism contributes to the dissociation process. In absolute dichloroethane (with a donor number of 0.0) the $[Ni(phen)_3](ClO_4)_2$ complex does not racemize [1]. It racemizes when a trace quantity of water is added to the solvent. For the $[Ni(phen)_3]^{2+}$ ion, the solvation of ligand thus appears to affect hardly the racemization. Even if it does, its effect is overcome by the effect of the decrease in donicity of solvents in the coordination sphere.

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