# EFFECT OF ADDED SALTS ON THE RATES OF DISSOCIATION AND RACEMIZATION OF TRIS(1,10-PHENANTHROLINE)IRON(II) ION IN AQUEOUS METHANOL SOLUTIONS

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Abstract—The kinetics of dissociation and racemization of  $[Fe(phen)_3]^{2^+}$  have been studied in aqueous methanol solutions containing perchlorate, chloride, and thiocyanate ions. The racemization rate was decreased by  $ClO_4^-$  and increased by  $SCN^-$ , while the dissociation rate was decreased by  $ClO_4^-$  and increased slightly by  $Cl^-$  and remarkably by  $SCN^-$ . The effect of anions on the reaction rates became remarkable with the increase in methanol content of the solutions. The results were reasonably explained in terms of ion association. The dissociation rate of the complex ion in the ion-pair increased in the order,  $ClO_4^- < Cl^- < SCN^-$ , of associated anions, suggesting the ion-pair interchange mechanism for the dissociation. The ion-association constants were determined to be  $11 \pm 4$ ,  $18 \pm 4$ , and  $25 \pm 15$  (I = 0.1,  $25^{\circ}C$ ) for  $ClO_4^-$ ,  $Cl^-$ , and  $SCN^-$ , respectively, in 0.64 mole-fraction (0.8 volume-fraction) aqueous methanol.

## INTRODUCTION

The kinetics of dissociation of  $[Fe(phen)_3]^{2+}$  and  $[Fe(bpy)_3]^{2+}$  have been studied extensively, and the effect of added salts on the reaction rates has been discussed in terms of ion-pair formation in aqueous<sup>1</sup> and non-aqueous<sup>2,3</sup> solutions. Blandamer *et al.*<sup>4</sup> studied the kinetics of the reactions of  $[Fe(bpy)_3]^{2+}$  with cyanide and hydroxide ions in binary aqueous solvent mixtures. On the standpoint of associative mechanism they have concluded that the chemical potential changes of anions with the change in solvent composition were dominant in determining reactivities in their reaction with  $[Fe(bpy)_3]^{2+}$ .

We previously studied the effect of various inorganic anions on the rates of dissociation and racemization of  $[Fe(phen)_3]^{2+}$  in aqueous solutions.<sup>1</sup> We analyzed the experimental results considering the ion-pair formation of the complex ion with an anion, and found the following trends. (1) The dissociation rate constant of the complex existing in the ion-pair increases with the increase in proton affinity (basicity) of the anion:  $I^- < Br^ < Cl^{-} < NO_{2}^{-} < OCN^{-} < N_{3}^{-} < F^{-} < OH^{-} \approx CN^{-}$ . (2) The intramolecular racemization rate constant, given by apparent racemization rate constant minus dissociation rate constant, increases with the increase in polarizability (softness) of the anion:  $OH^- \simeq CN^- \simeq F^- \simeq Cl^- < Br^- \simeq$  $NO_2^- < OCN^- < I^- < N_3^-$ . We thought it desirable to extend the study to include the systems containing perchlorate, which is one of the hardest, least basic anions, and thiocyanate, which is a very soft anion. However, the effects of these anions were difficult to measure in aqueous solution because of the low solubility of  $[Fe(phen)_3]^{2+}$  in the presence of these anions; only the effect of the thiocyanate ions on the racemization rate were measured in supersaturated solutions.

In the present study, the effects of perchlorate and thiocyanate ions on the dissociation and racemization of  $[Fe(phen)_s]^{2+}$  were investigated in aqueous methanol solutions. It was also our object to study the solvent effect on the rates of dissociation and to see whether or not the reactions in aqueous methanol solutions can be explained by the same mechanism as in aqueous solutions.

#### **EXPERIMENTAL**

The dissociation and racemization rates were obtained respectively from the changes in absorbance (510 nm) and optical rotation (546 nm) of the solution containing  $5 \times 10^{-5}$  mol dm<sup>-</sup>  $[Fe(phen)_3]$  (ClO<sub>4</sub>)<sub>2</sub> in a thermostated (±0.1°C) quartz cell. In measuring the dissociation rate of the complex,  $3.1 \times 10^{-4}$  mol dm<sup>-3</sup> nickel(II) perchlorate was added to the sample solution except for the cases where the concentration of the nickel(II) salt or perchloric acid is explicitly described; nickel(II) and hydrogen ions are effective as scavengers of liberated phenanthroline molecules.<sup>1</sup> The absorbances at 510 nm of the complex-salt solutions containing nickel(II) or hydrogen ions became negligible after a sufficient time, indicating that the complex ions completely dissociated to give solvated iron(II) ions. All the reactions were followed for four half-lives, and were found to be first order in the metal complex concentration in the time range studied. The dissociation and racemization rates obtained were reproducible within  $\pm 2$  and  $\pm 5\%$ , respectively. Methanol, a guaranteed reagent of Wako Pure Chemical Indistries, Ltd., was purified by fractional distillation. Mixed solvents were prepared by mixing appropriate volumes of the methanol and water; 0.6 and 0.8 volume fractions of methanol corresponds to 0.40 and 0.64 mole fractions (m.f.), respectively. The racemization and dissociation experiments were carried out mainly in 0.40 and 0.64 m.f. aqueous methanol solutions, respectively. Solutions of higher methanol concentrations are not suited for investigating the effect of SCN<sup>-</sup> ions on the rates because the reactions

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proceed too fast. Other reagents and techniques were the same as those described in our previous paper.<sup>1</sup>

# **RESULTS AND DISCUSSION**

As shown in Table 1, both the dissociation and intramolecular racemization rates increased in the presence of SCN<sup>-</sup>, and they are decreased by ClO<sub>4</sub><sup>-</sup> in 0.40 m.f. aqueous methanol solutions. The results extend the previous findings in aqueous solutions that the intramolecular racemization rate increased with the increase in the polarizability of the anion, while the dissociation rate increased with increasing basicity of the anion.<sup>1</sup> The same order of the effect of the added anions was also observed in 0.64 m.f. aqueous methanol and in pure methanol (Tables 2 and 3). The retarding effect of ClO<sub>4</sub><sup>-</sup> on the racemization rate were also reported in several solvent systems by Van Meter and Neumann.<sup>5</sup>

For the analysis of the experimental results, the following reaction processes were assumed:

$$[\text{Fe(phen)}_3]^{2+} + X^- \stackrel{\kappa_{(x)}^{IP}}{\rightleftharpoons} [\text{Fe(phen)}_3]^{2+} \cdot X^-$$
(1)

$$[Fe(phen)_3]^{2+} \xrightarrow{k_d} [Fe(phen)_2]^{2+} + phen$$

$$\xrightarrow{fast} \rightarrow Fe^{2+} + 3phen \qquad (2)$$

 $[\text{Fe}(\text{phen})_3]^{2+} \cdot X^- \rightarrow [\text{Fe}(\text{phen})_2]^{2+} \cdot X^- + \text{phen}$ 

$$\stackrel{\text{fast}}{\rightarrow} \text{Fe}^{2+} + 3\text{phen} + X^-. \tag{3}$$

Then the thermodynamic ion-association constant for reaction (1),  $K_{(\infty)}^{IP}$ , and the dissociation rate constant,  $k_{d}^{obsd}$ , are given by:

$$K_{(\mathbf{X})}^{\mathbf{IP}} = \frac{[\text{Fe}(\text{phen}_{3}^{2^{+}} \cdot \mathbf{X}^{-}]}{[\text{Fe}(\text{phen}_{3}^{2^{+}}][\mathbf{X}^{-}]}\frac{1}{f_{2}}.$$
 (4)

$$k_d^{\text{obsd}} = \frac{k_d + k_{d(\Sigma)}^{\text{IP}} K_{(\Sigma)}^{\text{IP}} f_2[X^-]}{1 + K_{(\Sigma)}^{\text{IP}} f_2[X^-]}$$
(5)

Table 1. Dissociation and racemization rate constants of [Fe(phen)<sub>3</sub>]<sup>2+</sup> in 0.40 m.f. aqueous methanol at 20.0°C

Added Salts mol dm <sup>-3</sup>		$\frac{k_{d}^{obsd}}{10^{-3} s^{-1}}$	$\frac{k_r^{obsd}}{10^{-3} s^{-1}}$	$\frac{k_{\rm r}^{\rm i}}{10^{-3}  {\rm s}^{-1}}$
None		0.0797	2.75	2.67
NaClO4	0.51	0.0482	1.95	1.90
KSCN	0.51	0.608	5.32	4.71

\* Intramolecular racemization rate constant  $(k_r^{obsd} - k_d^{obsd})$ .

Table 2. Dissociation rate constants of [Fe(phen)<sub>3</sub>]<sup>2+</sup> in 0.64 m.f. aqueous methanol at 25.0°C

Added Salts/mol dm <sup>-3</sup>		$k_d^{obsd}/10^{-3} s^{-1}$	$k_{\rm d}^{\rm calcd*}/10^{-3}  {\rm s}^{-1}$	
Ni(C104)2	0.00019	0.243	0.246	
4 2	0.00032	0.243	0.245	
	0.00039	0.243	0.244	
	0.00075	0.245	0.242	
	0.00226	0.236	0.235	
	0.00298	0.236	0.232	
	0.00353	0.232	0.231	
	0.0119	0.214	0.214	
HC10	0.0160	0.212	0.214	
4	0.160	0.166	0.166	
NiCl <sub>2</sub>	0.00075	0.263	0.261	
2	0.0050	0.288	0.292	
	0.101	0.385	0.380	
	0.496	0.428	0.431	
KSCN	0.0005	0.335	0.393	
	0.0042	1.30	1.04	
	0.0693	2.82	2.79	
	0.804	3.98	4.06	

\* Calculated with the values given in Table 4.

Table 3. Dissociation rate constants of  $[Fe(phen)_3]^{2+}$  in absolute methanol at 25.0°C.

Added Salt	s/mol dm <sup>-3</sup>	$k_{\rm d}^{\rm obsd}/10^{-3} {\rm s}^{-1}$
Ni(ClO <sub>4</sub> ) <sub>2</sub>	0.0005	0.036
	0.0021	0.036
	0.0111	0.038
KSCN	0.0081	8.00
	0.072	13.0

where  $k_d$  and  $k_{d(X)}^{IP}$  are the rate constants for reactions (2) and (3), respectively. The activity coefficient,  $f_z$ , of an ion with a charge of  $\pm z$  was estimated by using the extended Debye-Hückel equation:

$$\log f_z = -\frac{Az^2 \sqrt{I}}{1 + Ba\sqrt{I}} + bI \tag{6}$$

where A = 0.2174 ( $e^2/\epsilon kT$ ) $\sqrt{(8\pi N e^2/1000\epsilon kT)}$  and  $B = \sqrt{(8\pi N e^2/1000\epsilon kT)}$  with usual meanings of the notations.<sup>6</sup> The values of  $a = (7-10) \times 10^{-8}$  cm and  $b = 0.1z^2$  were assumed in the calculation, together with  $\epsilon = 78.5$  for water and  $\epsilon = 44.0$  for 0.64 m.f. aqueous methanol.

We first examine the effect of ion association on the concentration of free  $anion([X^-])$  and the ionic strength (I). The concentration of the complex salt was much lower than those of the added salt, and therefore it suffice to consider the effect of ion association only between added ions:

$$\mathbf{M}^{n+} + \mathbf{X}^{-} \rightleftharpoons \mathbf{M}^{n+} \cdot \mathbf{X}^{-} \tag{7}$$

where  $M^{n+}$  (n = 1 or 2) and  $X^{-}$  represent the cation and anion of the added salt. The association constant, K, is given by:

$$K = \frac{[M^{n+} \cdot X^{-}]}{[M^{n+}][X^{-}]} \frac{f_{n-1}}{f_n f_1} = \frac{x}{(c-x)(nc-x)} \frac{f_{n-1}}{f_n f_1}$$
(8)

where c is the total concentration of the added salt, and x the concentration of the ion-pair at equilibrium. With the knowledge of the values of K and  $f_z$ , the net concentration of the free anion, nc - x, can be obtained from eqn (8). In the absence of the experimental ion-association constants for such systems, K values for dipositive and mononegative ions and for monopositive and mononegative ions were calculated theoretically' using various values  $((3-6) \times 10^{-8} \text{ cm})$  of the closest distance of approach between ions. The approximate  $f_z$  values were obtained from eqn (6) by assuming the value of a to be  $(3-6) \times 10^{-8}$  cm, and with the first approximation of I = n(n+1)c/2. Then, the value of x was calculated from eqn (8). The  $f_z$  were recalculated with I =n(n+1)c/2 - nx to give a better x value as the second step of approximation. Further repetition of the procedure reproduced the x value within the limits of experimental error. The net concentration of the free anion and the ionic strength of the medium were calculated by the use of the x value thus obtained.

With the  $[X^-]$  and I values obtained, the  $K_{(\infty)}^{IP}$  and  $k_{d(\infty)}^{IP}$  values were determined to give the best fit between the observed kinetic data and the calculated curve according to eqn (5). In obtaining the  $K_{(\infty)}^{IP}$  and  $k_{d(\infty)}^{IP}$  values for  $X = CI^-$  and SCN<sup>-</sup>, we disregarded the effect of

perchlorate ions, contained in a low concentration  $(7.2 \times 10^{-4} \text{ mol dm}^{-3})$  as counter ions of the complex cations and the added nickel(II) ions. The  $K_{(\infty)}^{IP}$  values were transformed to the concentration ion-association constant,  $K_{(\infty)}^{IP}$ , at I = 0.1 by means of eqn (6).

The rate constant for the dissociation of the complex ion in the ion-pair (eqn (3)) increased in the order,  $ClO_4^- < Cl^- < SCN^-$ , of the associated anion in 0.64 m.f. aqueous methanol (Table 4). The sequence is consistent with those obtained in aqueous solutions;<sup>1</sup> i.e. the rate constant for the ion-pair increased with the increase in the pKa of the conjugate acid of the anion. This suggests that the mechanism of dissociation in this case is the same as that in aqueous solutions (ion-pair interchange mechanism<sup>1</sup>).

The dissociation rate constants of the complex in the presence of SCN<sup>-</sup> and of Cl<sup>-</sup> increased with the increase in methanol content, as can be seen from a comparison of the results given in Tables 1-3. Similar results were obtained for the dissociation of  $[Fe(bpy)_3]^{2+}$  by Seiden et  $al^{2}$  The increase in rate with the increase in methanol content is caused by the increase in the reactivity of the ion-pair as well as the increase in the association constant (see Table 4). The larger reactivity of the ion-pair in the solution of higher methanol content can be well understood by considering the influence of the dielectric constant of the medium. The free-energy difference between the polar ion-pair and the less polar activated complex is larger in a medium with a higher dielectric constant.<sup>8</sup> Thus, the activation energy becomes smaller with the decrease in the dielectric constant of a medium, or with the increase in methanol content. In this connection, it is interesting to note the fact that  $[Fe(phen)_3]Cl_2$  and  $[Fe(pbm)_3](SCN)_2$  are converted to [Fe(pbm)<sub>2</sub>(SCN)<sub>2</sub>]<sup>10</sup> [Fe(phen)<sub>2</sub>Cl<sub>2</sub>]<sup>9</sup> and in dichloromethane and chloroform, respectively, at rates much faster than the dissociation rates of the tris-complexes in aqueous solutions.

The dissociation rate of the free complex cation in 0.64 m.f. aqueous methanol was found to be considerably smaller than that in dimethyl sulfoxide (Table 4) reported by Farrington *et al.*,<sup>3</sup> in spite of the fact that the dielectric constants of the two solvents are almost the same. Similar but more pronounced tendencies were observed, when the complex cation was ion-paired with  $ClO_4^-$  and with  $Cl^-$ . This shows that the coordinating ability, in addition to the dielectric constant, of solvent molecules makes a significant contribution to the dissociation rate of the complex ion.

As shown in Table 4, the ion-association constants increased in the order of  $ClO_4 < Cl^- < SCN^-$  in 0.64 m.f. aqueous methanol; a consistent order was previously found in aqueous solution.<sup>1</sup> The  $K_{C(X)}^{IP}$  values for  $Cl^-$  and  $SCN^-$  were greater in 0.64 m.f. aqueous methanol than in water. This trend is consistent with the theoretical prediction (Table 4). Table 4 also lists the  $K_{C(X)}^{IP}$  values reported for  $ClO_4$  and  $Cl^-$  in dimethyl sulfoxide;<sup>3</sup> the values are much greater than those obtained in 0.64 m.f. aqueous methanol in the present study. However, the literature values cannot directly be compared with the present results, since the former were derived without allowance for the ion association of the added salt and for the change in ionic strength.

The effect of added salts on the rate of dissociation of  $[Fe(phen)_3]^{2+}$  in aqueous methanol solutions can reasonably be understood in terms of ion association of the complex with anions.

 $k_{d(X)}^{IP}/10^{-3} s^{-1}$  $\kappa_{C(X)}^{IP}$ /mol dm<sup>-3</sup> Counter water<sup><u>a</u>) 0.61 m.f.</sup> 0.61 m.f. dmso<sup>b)</sup> dmso<sup>b</sup>) Ion water MeOH MeOH 0.073 0.249±0.002 0.77 free ion C104 0.086±0.033 1.5 10.6± 3.6 39±10 1.5±0.8<sup>Ç)</sup> c1<sup>-</sup> 18.4± 4.1 53±27 0.452±0.022 580. 2.6±1.1<sup>C)</sup> 25.1±14.9 SCN 4.69 ±1.34 Theory<sup>d)</sup> a= 5 Å 2.6 13.0 13.0 1.3 5.2 5.2 a=10 Å

Table 4. Ion-association constants of [Fe(phen)<sub>3</sub>]<sup>2+</sup> with anions and dissociation rate constants of the complex in ion-pairs at 25.0°C and I = 0.1

<u>a</u>) Data in 0.1 mol dm<sup>-3</sup> HCl.

- b) Ref. 3. The K values were obtained without considering the effect of ionic strength.
- c) Ref. 1. The K values at 32.0°C.
- d) Ref. 6a. The symbol a (Å=10<sup>-10</sup> m) represents the closest

distance of approach between ions.

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