Hydrolysis of Tris(1,10-phenanthroline)iron(II) Complex in 1,4-Dioxane–Water Mixtures

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Thermodynamic and kinetic parameters have been obtained for the hydrolysis of tris(1,10-phenanthroline)iron(II) in several 1,4-dioxane–water mixtures. A linear relationship was found between ln k and the solvent-polarity parameter E_T. This relationship is interpreted and discussed in terms of the thermodynamic excess properties of the mixtures.

The dioxane–water system is very interesting due to the controversy surrounding the role of the dioxane in the breaking or forming[1,2] of the water structure. The hydrolysis of tris(1,10-phenanthroline)iron(II), $[Fe(phen)_3]^{2+}$, in several aqueous mixtures has been studied by Blandamer, Burgess and co-workers[3–5] but the available kinetic data in 1,4-dioxane–water mixtures is limited to three compositions (20, 40, and 60% v/v dioxane) and only at 35 °C.[5] A first-order kinetic law has been found for these reactions in which the rate-determining step is the loss of the first ligand. Burgess *et al.*[5] found an increase in the rate constant with increasing dioxane content of the mixture. According to these authors, the explanation for this behaviour is the disruption of the water structure when adding dioxane if the mechanism is associative or by solvation of the initial and transition states if the mechanism is dissociative.

Several workers[6,7] have found that $[Fe(phen)_3]^{2+}$ and related ions are stabilised on going from water to binary aqueous mixtures, suggesting that solvation of this complex ion is not mainly due to acid–base interaction of the ion but to hydrophobic interaction of the co-ordinated ligand.

The main objective of this work is to find a relationship between the rate constant for the hydrolysis of this ion and the relevant properties of the solvent mixtures.

Experimental

Materials.—A 1.10×10^{-4} mol dm^{-3} aqueous solution of tris(1,10-phenanthroline)iron(II) was prepared according to the usual procedure.[8] 1,4-Dioxane (Aldrich Chemical Co.) was purified following a standard procedure, which was carried out before each of the kinetic runs in order to prevent peroxide formation. 1.0 N Sulphuric acid (Harleco, p.a.) was used to adjust to 0.1 N the formal acid concentration in the dioxane–water mixtures used in the kinetic measurements.

2,6-Diphenyl-4-(2′,4′,6′-triphenyl-1′-pyridinio)phenolate, kindly supplied by Professor C. Reichardt, was used as received. The preparation of solutions of the mixed solvents was done from appropriate quantities of the components (dioxane–water) using a Precision Sampling syringe (2 cm^3).

Kinetics Measurements.—Aliquots (3 cm^3) of the solvent mixture were introduced into 1-cm quartz cells (Hellma 110 QS) and placed in the thermostatted cell-holder of a Perkin-Elmer Lambda-3 spectrophotometer. After thermal equilibration, 2 μl of the tris(1,10-phenanthroline)iron(II) stock solution were injected into the cell. The reaction was followed by monitoring the decrease in absorbance at 510 nm with time; all the reactions were followed for a little more than three half-lives, the plots of log (absorbance) *versus* time always remaining linear. First-order rate constants ($k_{obs.}$) were obtained in all cases. All the kinetic runs were performed in duplicate, and plots giving correlation coefficients worse than 0.999 were discarded. All the reactions were irreversible, the absorbance at 'infinite' time being zero.

Data Treatment.—A program for a Commodore computer was used for the calculation of rate constants and activation parameters using the Arrhenius and Eyring equations.

Results and Discussion

The observed rate constants for the hydrolysis reaction of $[Fe(phen)_3]^{2+}$ are shown in Table 1. The rate constant increased with decreasing water content over the whole composition range, even in a region of extremely low water content (*i.e.* 97% dioxane).

In order to study the dependence of the rate constant on the acid concentration, a solvent mixture 70% v/v in dioxane was chosen because at this composition the most prominent increase in the rate constant was observed (Figure). The overall effect of the sulphuric acid concentration on the rate constant

Table 1. First-order rate constant (s^{-1}) for the hydrolysis of $[Fe(phen)_3]^{2+}$ at the indicated temperatures (K)

Dioxane (% v/v)	$10^4 k_{obs.}$				
	298.1	302.2	308.3	313.3	E_T^N
0	0.77	1.8	4.4	10.3	1.000
10	0.80	2.1	4.5	10.7	0.840[b]
22	0.83[a]	2.1	5.1	11.4	0.756
33	1.0[a]	2.6	6.0	13.2	0.731
55	1.4[a]	3.7	7.9	20.1	0.701
77	2.2[a]	6.3	13.0	30.0	0.559
88	2.9	8.1	17.1	39.7	0.552
90	3.8	9.5	20.4	42.9	0.472
93	4.3	9.6	22.0	—	0.432
95	4.5	10.2	24.0	44.0	0.395
97	4.8	10.5	24.9	52.2	0.339

[a] Interpolated value from constants at slightly different compositions.
[b] Calculated using Langhals equation.

Table 2. Dependence of the first-order rate constant for the hydrolysis of $[Fe(phen)_3]^{2+}$ on the sulphuric acid concentration for a mixture (70% v/v) in dioxane at 308.3 K

Normality of H_2SO_4	$10^4 k_{obs.}$/s^{-1}
0.05	10.6
0.10	10.0
0.20	9.5
0.50	6.1
0.80	4.7
1.80	3.0

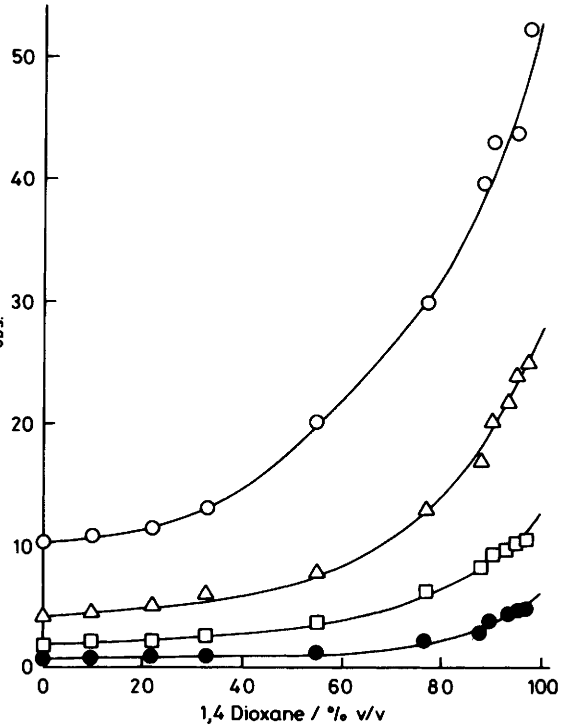

Figure. Dependence of the rate constant for the hydrolysis of $[Fe(phen)_3]^{2+}$ on the composition of the solvent mixture: ●, 298.1; □, 302.2; △, 308.3; ○, 313.3 K

at 35.2 °C is shown in Table 2. Although the effect is significant we can exclude the participation of solvated H^+ ions in the rate-determining step of the reaction. Burgess *et al.*[5] found the same effect at higher water contents (20, 40, and 60% v/v). The large inhibiting effect of added sulphuric acid (Table 2) was interpreted[5] as the result of two opposite effects. On the one hand, the ion-pair formation between the complex cation $[Fe(phen)_3]^{2+}$ and the HSO_4^- anion should produce an increase in the substitution rate of the former. On the other hand, the activity of water will decrease as the acid concentration increases. These authors[5] gave no explanation for the fact that H_2SO_4 and $HClO_4$ decrease the value of k, whereas H_3PO_4, HCl, and CCl_3CO_2H increase it.

Recently Tachiyashiki and Yamatera[9] investigated the dissociation of $[Fe(phen)_3]^{2+}$ in aqueous methanol solutions containing ClO_4^-, Cl^-, and SCN^- ions. The results were explained in terms of ion association and the dissociation rate constant of the complex existing as the ion pair increases with increasing basicity of the anion. This result is in reasonable agreement with the data reported by Burgess *et al.*[5] concerning the dissociation rate of the complex in 1,4-dioxane–water mixtures. For a given acid concentration they found the following sequence for k: $H_3PO_4 > HCl > CCl_3CO_2H \gg H_2SO_4 > HClO_4$. With the exception of HCl this sequence is the same as that for the decreasing basicity in water of the conjugate anion.[10]

Taking into account that the concentration of H_2SO_4 is far greater than the concentration of complex and that the thermodynamic ion-association constant for the reaction (1) is

$$[Fe(phen)_3]^{2+} + X^- \rightleftharpoons [Fe(phen)_3]^{2+}{\cdot}X^- \qquad (1)$$

probably greater in dioxane–water than in methanol–water mixtures, an increasing concentration of acid does not imply a significant increase in the concentration of ion pairs. The inhibiting effect of added sulphuric acid can be explained in terms of the decrease in activity of water upon solvation of the HSO_4^- anion through hydrogen bonding.

Table 3. Parameters a and b for the equation $\ln k = a + bE_T^N$ at four temperatures

a	b	r^a	n^b	T/K
-6.38 ± 0.23	-3.50 ± 0.35	0.957	11	298.1
-5.55 ± 0.22	-3.36 ± 0.34	0.957	11	302.2
-4.77 ± 0.21	-3.32 ± 0.32	0.961	11	308.3
-4.18 ± 0.24	-3.00 ± 0.37	0.945	10	313.3

[a] Correlation coefficient. [b] Number of data points.

We found that k increases as the relative permittivity[11] (ε) of the mixture decreases but there is no linear relationship between $\log k$ and $1/\varepsilon$ or $(\varepsilon - 1)/(2\varepsilon + 1)$. We found that k is fitted by the relationship $\ln k = a + bE_T^N$ (Table 3), where E_T^N is the $E_T(30)$ solvent parameter normalised according to Reichardt and Harbusch-Görnert.[12] At the same time, the $E_T(30)$ values obtained from Langhals equation[13] are in good agreement with those we obtained experimentally.

The relationship found indicates that the reaction is accelerated by decreasing the solvent polarity. In other words, the transition state seems to be less polar than the initial state.[14] A relationship between $\ln k$ and E_T points to a transition state which is similarly solvated to that of the initial state. In other words, the solvation change takes place just after the transition state in the reaction co-ordinate for the rate-determining step.[15]

The reported thermodynamical data for dioxane aqueous solutions show clearly that at room temperature this system has a positive excess Gibbs free energy over the whole composition range.[16] Thus the system has a negative excess enthalpy in mixtures low in dioxane whereas it is zero when the mole fraction of dioxane is *ca.* 0.45. This means that the overall result of adding dioxane in this range is exothermic. This is exactly the same range where dioxane addition does not greatly influence the reaction rate (Figure). Upon increasing addition of dioxane to pure water the enthalpy of the mixture increases, because the added dioxane can be solvated with free water molecules[17] without a serious change in the water structure. Nevertheless, at dioxane mole fractions of $\geqslant 0.2$, further addition of dioxane causes the enthalpy of mixture to become steadily less negative, *i.e.* associated water molecules begin to be disrupted. When more dioxane is added to the mixture also a much greater influence on the rate constant is observed. Therefore, one can understand the effect of the addition of dioxane on the overall water structure in the mixture. The Figure shows the dependence of the rate constant on the composition of the solvent mixture. The enthalpy of the mixture at dioxane mole fractions in the range 0.45—1.0 is positive, which indicates that the water structure has already been strongly disrupted by the presence of dioxane molecules. An alternative explanation can be given in terms of the stabilisation of both the reactant and the transition state through free non-associated dioxane molecules in this region, the stabilisation of the transition state being greater.

In conclusion, the controversy concerning the behaviour of dioxane–water mixtures seems to be explained by the thermodynamical excess functions in relation to the rate constants of this reaction. In water-rich mixtures at dioxane mole fractions from 0 to 0.2, dioxane behaves as a water-structure-forming solvent; at greater dioxane contents, however, it behaves as a water-structure-breaking solvent.

The thermodynamic activation parameters, $\Delta H^‡$ and $\Delta S^‡$, for the reaction in the various dioxane–water mixtures at

Table 4. Thermodynamic parameters* for the hydrolysis of $[Fe(phen)_3]^{2+}$ in dioxane–water mixtures at 298 K

Dioxane (% v/v)	$\Delta H^‡$	$\Delta S^‡$	r
0	127 ± 5	104 ± 52	0.998
10	125 ± 10	96 ± 98	0.994
22	128 ± 7	108 ± 74	0.997
33	125 ± 9	100 ± 88	0.995
55	128 ± 10	111 ± 102	0.994
77	125 ± 13	105 ± 125	0.990
88	125 ± 12	109 ± 116	0.992
90	117 ± 9	84 ± 90	0.994
93	118 ± 11	89 ± 114	0.996
95	113 ± 7	70 ± 73	0.996
97	117 ± 4	86 ± 43	0.999

* $\Delta H^‡$ in kJ mol^{-1}, $\Delta S^‡$ in J K^{-1} mol^{-1}; the errors indicated are the standard errors.

25.0 °C are shown in Table 4. The $\Delta H^‡$ values are almost constant in the range from 0 to 88% v/v dioxane. A similar behaviour is observed in the range from 90 to 97% v/v dioxane. This trend takes place approximately in the range in which the maximum in the enthalpy of mixing for the dioxane–water system appears,[15] and indicates a smaller activation enthalpy for this reaction in water-poor mixtures, in the range in which the water structure is completely destroyed and the ions probably occur as ion pairs. When the relative permittivity of the medium decreases we would expect the counter ion of the $[Fe(phen)_3]^{2+}$ to exert a favourable effect on the activation enthalpy, neutralising more effectively the positive charge of the cation. The activation entropy shows the same trend as $\Delta H^‡$, in spite of the errors.

We conclude that the loss of the first phenanthroline ligand takes place not in a single step but in at least two steps, of which loss of a co-ordination site at the metal atom could be the first and the rate-determining one. The fact that this reaction does not occur in the absence of acid is perhaps due to a subsequent rapid protonation of the free end of the ligand.

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