Acid Solvolysis of Some Low-spin Tris(α,α′-di-imine)iron(II) Complexes in Dimethyl Sulphoxide: Kinetic Evidence for Competitive Ion-pair Formation

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The kinetics of acid solvolysis of some low-spin complexes of the type [Fe(L–L)$_3$]$^{2+}$ [L–L = 1,10-phenanthroline (phen), 5NO$_2$-phen, or 2,2′-bipyridyl (bipy)] have been examined in dimethyl sulphoxide (dmso). The rates of solvolysis in this solvent are about an order of magnitude faster than in water, and, unlike the behaviour in aqueous solution, the dependence of $k_{\mathrm{obs.}}$ on [acid] is similar for the three complexes studied. It is concluded that species containing unidentate protonated bipy are not formed to a significant extent during the acid solvolysis of [Fe(bipy)$_3$]$^{2+}$ in dmso. Addition of chloride ion to solutions of [Fe(phen)$_3$]$^{2+}$ containing H$_2$SO$_4$ dramatically enhances the rate of solvolysis of the complex. This effect is less marked at higher acid concentrations, and these observations are interpreted in terms of a mechanism involving competitive ion-pair formation between the complex and Cl$^-$ and [HSO$_4$]$^-$.

THE kinetics of aquation of low-spin iron(II) complexes of the type [Fe(L–L)$_3$]$^{2+}$ (L–L = α,α′-di-imine) have been studied extensively, and recently these reactions have been used to examine solvent effects in aqueous-organic solvent mixtures.[1–4] Ion-pair formation between cationic complexes and anions can become significant in media of reduced dielectric constant and indeed solvent extraction of these complexes as ion pairs is used in the spectrophotometric determination of iron.[5–8]

In connection with our work on substitution reactions of phthalocyaninatoiron(II) in dimethyl sulphoxide (dmso),[9] we were interested in reactions involving iron–nitrogen bond breaking, and we have studied the solvolysis of some [Fe(L–L)$_3$]$^{2+}$ complexes in dmso. The results described here provide information about the role of ion pairs in these reactions.

EXPERIMENTAL

Kinetics.—Reactions were monitored by following absorbance changes in the visible region at a wavelength characteristic of the [Fe(L–L)$_3$]$^{2+}$ complex concerned (L–L = phen, 510; NO$_2$-phen, 510; bipy, 525 nm).[‡] These $\lambda_{\mathrm{max.}}$ values in dmso are very similar to those in water. The concentration of the [Fe(L–L)$_3$]$^{2+}$ complex was *ca.* 10^{-4} mol dm^{-3} at the start of each reaction.

(*a*) *Slow reactions*. A Beckman DB spectrophotometer equipped with a thermostatted cell holder was used for studying the slow reactions. Temperature variations in a cell, at a set temperature, were less than 0.1 °C. Each kinetic run was started by adding 0.1 cm^3 of a concentrated dmso solution of the complex to a previous thermostatted quartz cell containing a known volume of a dmso solution made up from appropriate amounts of sulphuric acid, salts, and solvent. After mixing, changes in transmittance were recorded on a Servoscribe pen recorder. The final absorbance of these solutions was zero, and plots of log(absorbance) against time were linear for at least five half-lives.

(*b*) *Fast reactions*. An all-glass stopped-flow apparatus was used to follow the kinetics of the faster reactions. Our instrument is based on a recently published [10] design with drive syringes modified such that they are vertical, instead of horizontal, so bubbles in the system rise into the reactant reservoirs. Output was displayed on a storage oscilloscope. Since the absorbance changes were small (<0.01), the observed transmission changes are proportional to changes in absorbance and rate constants were obtained from plots of log $(T_\infty - T)$ against time, which were linear for at least three half-lives.

Preparation of Salts and Solutions.—Dimethyl sulphoxide (B.D.H., reagent grade) was dried over calcium hydride and distilled under a reduced pressure of pure nitrogen (40 °C, 1.5 mmHg) [§] before use. Solutions of sulphuric acid in dmso were prepared by slowly adding this acid (AnalaR 98%) to the solvent in a volumetric flask (100 cm^3) which was cooled in ice. The solution was then made up to the mark with solvent. The final acid concentration was determined by titrating aliquots, diluted with water, against standard aqueous sodium hydroxide with phenolphthalein as indicator.

The iron(II) complexes were isolated as their perchlorate salts, prepared by adding an excess of the ligand concerned, dissolved in a small volume of acetone, to a freshly prepared solution of iron(II) sulphate (AnalaR) in boiled-out water. After stirring, an excess of almost saturated sodium perchlorate solution was slowly added and the resulting precipitate filtered off and washed several times with water. Elemental analysis indicated that recrystallisation from acetone gave the desired solvent-free product.

Benzyltriethylammonium chloride. This salt was prepared by heating benzyl chloride and triethylamine (1 : 1 mol ratio) under reflux in tetrahydrofuran, with continuous stirring. After 20 min, white crystals of the chloride began to separate and after 3 h these were filtered off. Reflux of the filtrate for another 8 h produced a second crop of crystals. The product was washed with dry diethyl ether and hexane, then dried *in vacuo* (Found: C, 69.0; H, 9.7; Cl, 15.0; N, 6.4. Calc. for $C_{13}H_{22}ClN$: C, 68.6; H, 9.7; Cl, 15.6; N, 6.15%). Benzyltriethylammonium perchlorate was precipitated by mixing equimolar portions of benzyltriethylammonium chloride and sodium perchlorate in aqueous solution. The product was filtered off, washed with water, and dried *in vacuo* over P_4O_{10} (Found: C, 53.2; H, 7.5; N, 5.2. $C_{13}H_{22}ClNO_4$ requires C, 53.5; H, 7.6; N, 4.8%). This salt dissolves freely in dmso.

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[‡] phen = 1,10-Phenanthroline, NO$_2$-phen = 5-nitro-1,10-phenanthroline, and bipy = 2,2′-bipyridyl.

[§] Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 cal = 4.184 J.

Lithium chloride was obtained from B.D.H. as ' not less than 98.5% pure ', and dried at 120 °C before use.

RESULTS AND DISCUSSION

Acid Solvolysis in Water and dmso.—As in water,[11,12] the three low-spin iron(II) complexes examined dissociate in dmso in the presence of excess of acid at easily measured rates that are first order in complex concentration [equation (1); L–L = bipy, phen, or NO_2-phen]. These reactions are about ten times faster

$$[Fe(L\text{–}L)_3]^{2+} + 3H^+ \longrightarrow Fe^{2+}(sol) + 3\,[HL\text{–}L]^+ \quad (1)$$

in dmso than in water, and Figure 1 shows the variation of $k_{obs.}$ for reaction of $[Fe(phen)_3]^{2+}$ in dmso–water solvent mixtures at constant $[H_2SO_4]$. The major increase in $k_{obs.}$ occurs in solutions containing >50% (w/w) of organic solvent, and it is noteworthy that there is no sudden variation in the value of $k_{obs.}$ at *ca.* 67% dmso, the region of maximum viscosity of dmso–water mixtures.[13] Activation parameters for these reactions calculated from rate constants obtained in dmso at a number of temperatures (Table 1) are compared in Table 2 with those for the corresponding reactions in water. Smaller enthalpies of activation are responsible for the enhanced reactivity in dmso. The entropies of activation are similar in both solvents for L–L = bipy and NO_2-phen, but more favourable in water than in dmso with phen.

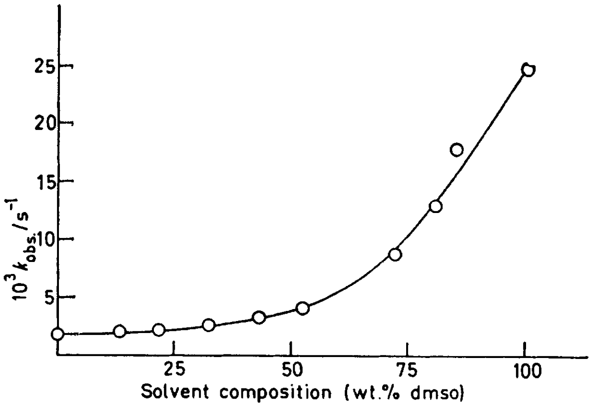


FIGURE 1 Solvolysis of $[Fe(phen)_3]^{2+}$ in dmso–water mixtures containing H_2SO_4 (0.61 mol dm^{-3}) at 30.0 °C

TABLE 2

Rate constants and activation parameters for acid solvolysis of $[Fe(phen)_3]^{2+}$, $[Fe(bipy)_3]^{2+}$, and $[Fe(NO_2\text{-}phen)_3]^{2+}$ in water and dmso

	$[Fe(phen)_3]^{2+}$		$[Fe(bipy)_3]^{2+}$		$[Fe(NO_2\text{-}phen)_3]^{2+}$	
	H_2O [a]	dmso [b]	H_2O [c]	dmso [b]	H_2O [a]	dmso [d]
$10^4k_{25}/s^{-1}$	0.7	10.7	2.0	12.7	4.9	15.6
$\Delta H^‡$/kcal mol^{-1} [e]	29.31 ± 0.20	26.60 ± 0.20	27.19 ± 0.60	26.26 ± 0.39	28.00 ± 0.17	25.68 ± 0.24
$\Delta S^‡$/cal K^{-1} mol^{-1} [e]	20.8 ± 0.7	17.1 ± 0.7	15.7 ± 1.9	16.3 ± 1.2	20.2 ± 0.6	19.3 ± 0.8

[a] $[H_2SO_4]$ = 0.54 mol dm^{-3}; results calculated from data given in ref. 11, and J. Bugess, Ph.D. Thesis, Cambridge, 1963. [b] $[H_2SO_4]$ = 0.16 mol dm^{-3}. [c] Refers to $k_1k_2/(k_{-1} + k_2)$ (see Scheme 2) to enable direct comparison with $[Fe(phen)_3]^{2+}$ and $[Fe(NO_2\text{-}phen)_3]^{2+}$. Values calculated from results for the reaction with CN^- (J. Burgess, *J.C.S. Dalton*, 1972, 1061). Values relating to k_1 are $\Delta H^‡$ = 26.10 ± 0.09 kcal mol^{-1}, $\Delta S^‡$ = 14.8 ± 0.3 cal K^{-1} mol^{-1} (M. V. Twigg, *Inorg. Chim. Acta*, 1974, **10**, 17). [d] $[H_2SO_4]$ = 0.61 mol dm^{-3}. [e] All the quoted errors are standard deviations corrected for the appropriate number of degrees of freedom such that doubling them produces 95% confidence limits.

These results could suggest that solvation effects are important, but the possible participation of ion pairs [dielectric constant of dmso *ca.* 45 (ref. 14)] should not be overlooked (see below).

TABLE 1

Observed first-order rate constants for the solvolysis of $[Fe(phen)_3]^{2+}$, $[Fe(bipy)_3]^{2+}$, and $[Fe(NO_2\text{-}phen)_3]^{2+}$ in dmso containing sulphuric acid

θ_c/°C	$k_{obs.}/s^{-1}$		
	$[Fe(phen)_3]^{2+}$ [a]	$[Fe(bipy)_3]^{2+}$ [a]	$[Fe(NO_2\text{-}phen)_3]^{2+}$ [b]
20.0	4.92×10^{-4}	5.40×10^{-4}	7.17×10^{-3}
	4.83×10^{-4}	5.43×10^{-4}	7.26×10^{-3}
	4.77×10^{-4}		
25.0	1.15×10^{-3}	1.30×10^{-3}	1.57×10^{-2}
	1.06×10^{-3}	1.36×10^{-3}	1.59×10^{-2}
	1.10×10^{-3}		
	1.07×10^{-3}		
30.0	2.31×10^{-3}	2.80×10^{-3}	3.25×10^{-2}
		2.82×10^{-3}	3.29×10^{-2}
			3.24×10^{-2}
			3.28×10^{-2}
35.0	4.73×10^{-3}	5.67×10^{-3}	6.60×10^{-2}
		5.75×10^{-3}	6.35×10^{-2}
40.0	9.29×10^{-3}	1.07×10^{-2}	
	9.51×10^{-3}	1.16×10^{-2}	
45.0	1.90×10^{-2}	2.17×10^{-2}	
	2.03×10^{-2}	1.98×10^{-2}	
		2.22×10^{-2}	

[a] $[H_2SO_4]$ = 0.16 mol dm^{-3}. [b] $[H_2SO_4]$ = 0.61 mol dm^{-3}.

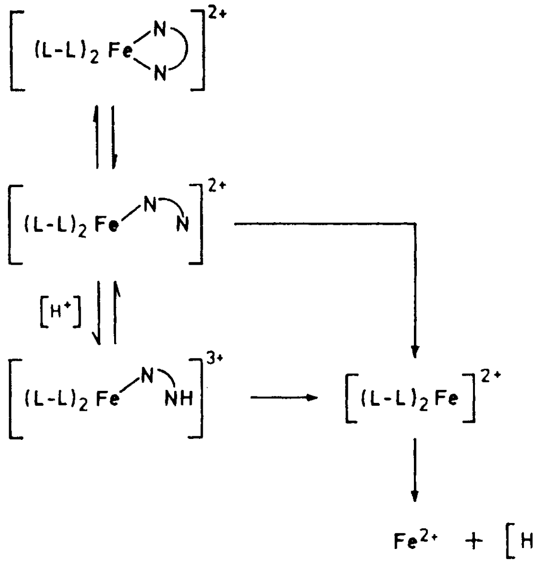
Effect of acid concentration. The rate of aquation of $[Fe(phen)_3]^{2+}$ shows only a slight negative dependence on acid concentration, whereas the rate of aquation of $[Fe(bipy)_3]^{2+}$ increases with increasing acid concentration until a limiting rate is reached at $[H^+] \sim 2$ mol dm^{-3}.[15] This behaviour has been interpreted in terms of a reaction scheme involving species containing protonated unidentate bipy that can be formed by virtue of the flexible nature of this ligand.[16] Such species containing the rigid phen ligand are not likely to be formed, and the rate of the acid-catalysed aquation of $[Fe(phen)_3]^{2+}$ does not show any marked acid dependence, until formal acidities approaching 18 mol dm^{-3} are reached.[17]

The effect of $[H^+]$ on the aquation of $[Fe(NO_2\text{-}phen)_3]^{2+}$ has not been reported. We therefore measured the rate of aquation of $[Fe(NO_2\text{-}phen)_3]^{2+}$ in several aqueous sulphuric acid solutions (Table 3), and found that the rate, like that of $[Fe(phen)_3]^{2+}$, decreases slightly as the acid concentration is increased. Enhanced reactivity of $[Fe(NO_2\text{-}phen)_3]^{2+}$ towards acid aquation over that of the unsubstituted phen complex has been interpreted[11] in terms of weakening of the iron–nitrogen σ bond by the electron-withdrawing substituent. As expected, this complex undergoes acid solvolysis in dmso faster than $[Fe(phen)_3]^{2+}$ (Figure 2); the ratio of the observed rate constants at 30 °C is *ca.* 7 : 1 in water and 13 : 1 in dmso ($[H^+]$ 0.2—0.8 mol dm^{-3}), *i.e.* the relative reactivity of $[Fe(NO_2\text{-}phen)_3]^{2+}$ is enhanced in dmso. This result is not surprising since it appears this derivative is the most sensitive to solvent effects.[1-4] In contrast to the behaviour observed in water, the rates of acid solvolysis of $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ are similar in dmso, *both* being almost independent of the acid concentration (Figure 2). This suggests that, in dmso, protonation of the complex containing unidentate bipy does not occur to any significant extent, or that the protonated complex has a reactivity similar to that of the unprotonated complex containing five co-ordinated nitrogen atoms. It seems likely that the apparent basicity of the unco-ordinated nitrogen atom, rather than the reactivity of the protonated complex, is reduced since nitrogen bases generally appear significantly less basic in dmso than in water.[18]

TABLE 3

Aquation of $[Fe(NO_2\text{-}phen)_3]^{2+}$ in aqueous H_2SO_4 at 36 °C

$[H_2SO_4]$/mol dm^{-3}	$10^3k_{obs.}/s^{-1}$
0.14	3.06
0.26	2.93
0.43	2.84
0.50	2.77
0.75	2.58
1.07	2.17



SCHEME 1

On going from the ground state to the transition state during the dissociative solvolysis process, increased interaction of the bound ligand with the bulk solvent becomes possible. On the basis of the solubility of $[Fe(phen)_3][ClO_4]_2$ and naphthalene (a model for the hydrocarbon portion of the ligand) in a variety of solvents, Van Meter and Neumann[19] concluded that this interaction, as well as the availability of a donor to replace the dissociated ligand, is important in the solvolysis of $[Fe(phen)_3]^{2+}$. Using their solubility data for naphthalene in water and dmso, a value of −5.4 kcal mol^{-1} is obtained for the free energy of transfer of naphthalene in these solvents. The corresponding change in free energy of activation for solvolysis of $[Fe(phen)_3]^{2+}$ is −1.6 kcal mol^{-1}. Naively, this might be taken to indicate that the ligand is 30% dissociated in the transition state. Interestingly, on the basis of the volume of activation, other workers concluded that in water the Fe–N bonds are extended by 39% of the total necessary for complete dissociation in the transition state.[20]

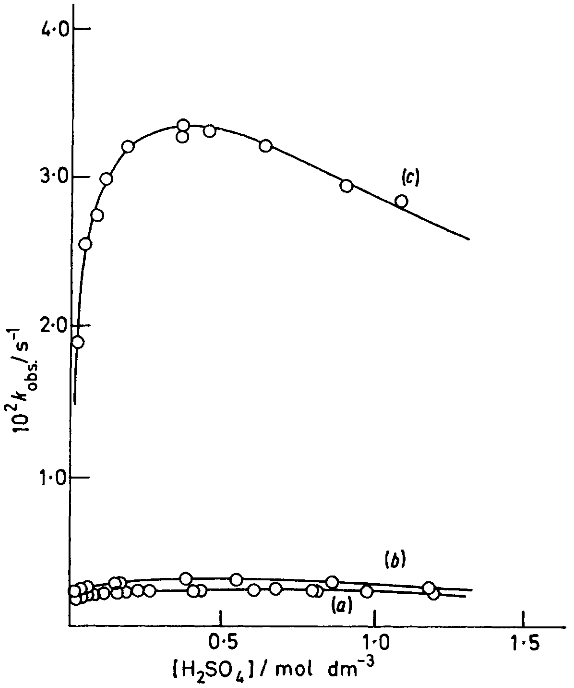


FIGURE 2 Variation of $k_{obs.}$ with $[H_2SO_4]$ for the solvolysis of (*a*) $[Fe(phen)_3]^{2+}$, (*b*) $[Fe(bipy)_3]^{2+}$, and (*c*) $[Fe(NO_2\text{-}phen)_3]^{2+}$ in dmso at 30.0 °C

Previously[21] it was shown that addition of salts to methanol solutions of $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ increased the rate of acid solvolysis of these complexes in this solvent, and it was suggested that this results from the formation of reactive ion pairs. The small dependence of $k_{obs.}$ on $[H_2SO_4]$ for the acid solvolysis of both these complexes in dmso is consistent with the formation of hydrogensulphate ion pairs with $[Fe(L\text{-}L)_3]^{2+}$ which are somewhat more reactive than $[Fe(L\text{-}L)_3]^{2+}$

$$\begin{tikzcd} {[Fe(L\text{-}L)_3]^{2+} + [HSO_4]^-} \arrow[r, shift left, "K_1"] \arrow[d, "k_0"] & {[Fe(L\text{-}L)_3]^{2+}.[HSO_4]^-} \arrow[l, shift left] \arrow[d, dash, "k_1"] \\ {Fe^{2+}(sol) + 3[HL\text{-}L]^+} & {} \arrow[l] \end{tikzcd}$$

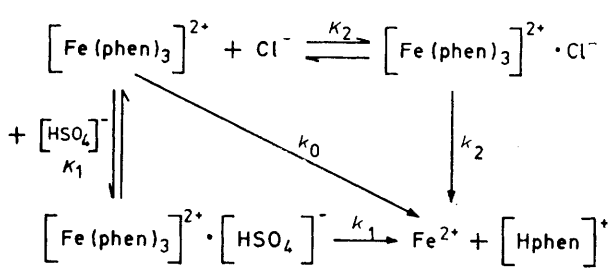
itself. The involvement of the $[HSO_4]^-$ ion rather than $[SO_4]^{2-}$ is postulated because H_2SO_4 behaves[22] as a monobasic acid in dmso. The concentration of ion pairs depends on $[HSO_4^-]$ and the value of the formation constant K_1. As $[HSO_4^-]$ increases, $k_{obs.}$ increases as more of the reactive ion pair is formed, until no free $[Fe(L\text{–}L)_3]^{2+}$ remains, and $k_{obs.}$ reaches the value for the rate of dissociation of the ion pair. However, addition of H_2SO_4 (*D ca.* 110) and the small amount of water contained in ' concentrated sulphuric acid ' increases the dielectric constant of the solvent, so reducing the ion-pair formation constant and hence $k_{obs.}$. It is also possible that the addition of $[HSO_4]^-$ might markedly affect solvent structure through hydrogen bonding. Ion pairs of the type described [23,24] are known to be formed between Cr(III) and Co(III) complexes with various anions in dmso, and further experimental support for their participation in these reactions is obtained from reactions involving added ions (see below). Under pseudo-first-order conditions, the observed rate constant for this reaction scheme is given by equation (2). If the ion pair is

$$k_{obs.} = \frac{k_0 + k_1K_1[HSO_4^-]}{1 + K_1[HSO_4^-]} \qquad (2)$$

more reactive than $[Fe(L\text{–}L)_3]^{2+}$, then $k_0 < k_1K_1\,[HSO_4^-]$ and, at all but very low concentrations of $[HSO_4]^-$, plots of $1/k_{obs.}$ against $1/[H_2SO_4]$ will be linear with an intercept equal to $1/k_1$ on the $1/k_{obs.}$ axis and a gradient equal to $1/k_1K_1$. This plot for the solvolysis of $[Fe(phen)_3]^{2+}$ in dmso–H_2SO_4 at 30 °C is not completely satisfactory because of the decrease of $k_{obs.}$ at the higher concentrations of H_2SO_4. However, from the results obtained at low $[H_2SO_4]$, an estimate of K_1 can be made. The value obtained * (220 ± 90 dm^3 mol^{-1}) is larger than expected for ion-pair formation between 2+ cations and 1− anions in dmso, but is in agreement with the results of experiments involving competitive ion pairing between $[HSO_4]^-$, Cl^-, and $[Fe(phen)_3]^{2+}$ (see below).

Effect of added salts. Preliminary experiments showed that the addition of $[NEt_3(CH_2Ph)]Cl$, a salt freely soluble in dmso, produces a dramatic increase in the rate of solvolysis of $[Fe(phen)_3]^{2+}$ in this solvent (*e.g.* at 25 °C with $[H_2SO_4] = 0.1$ mol dm^{-3}, addition of 5×10^{-2} mol dm^{-3} chloride salt increased $k_{obs.}$ by a factor of *ca.* 50). That this is caused by chloride ion, rather than by the organic cation, is shown by experiments with anhydrous lithium chloride: identical results were obtained with both these chloride salts. Lithium chloride has appreciable solubility in dmso [25] and it has been shown that LiCl does not itself form ion pairs in dmso to an extent that would cause complications in this study.[26] Recently, it has been found that tetra-alkylammonium bromides increase the rate of aquation of $[Fe(NO_2\text{-}phen)_3]^{2+}$, while alkali-metal bromides have the opposite effect.[27] In contrast to the present results obtained in dmso, it appears that enhanced rate of aquation is caused by interaction between the complex cation and the tetra-alkylammonium cation, rather than with the halide ion.

Although a plot of $k_{obs.}$ against $[Cl^-]$ for these preliminary results is linear, and therefore not conclusive evidence for the participation of ion pairs, it seems very likely that the highly reactive ion pair $[Fe(phen)_3]^{2+}\cdot Cl^-$ is involved and suggests the following competitive ion-pairing scheme (Scheme 2) with $k_2 \gg k_1 \gtrsim k_0$: Scheme 2 predicts that at a given chloride-ion concentration the observed rate constant will decrease as $[H_2SO_4]$ is increased, since relatively more of the less reactive $[Fe(phen)_3]^{2+}\cdot[HSO_4]^-$ ion pair is formed at the expense of the reactive chloride ion pair. The equation giving $k_{obs.}$ according to this reaction scheme is (3). This



SCHEME 2

$$k_{obs.} = \frac{k_0 + k_1K_1[HSO_4^-] + k_2K_2[Cl^-]}{1 + K_1[HSO_4^-] + K_2[Cl^-]} \qquad (3)$$

equation predicts that when $k_2K_2[Cl^-] > k_0 + k_1K_1[HSO_4^-]$ at constant $[Cl^-]$, the observed rate constant should decrease with increasing $[HSO_4^-]$ and a plot of $1/k_{obs.}$ against $[HSO_4^-]$ should be linear. Moreover, at constant $[HSO_4^-]$ the value of $k_{obs.}$ should increase with $[Cl^-]$ and reach a limiting value equal to k_2 when $1 + K_1[HSO_4^-] < K_2[Cl^-]$. At this point, all the iron complex exists as the chloride ion pair. To enable the considerably faster reactions to be monitored at higher chloride-ion concentration, it was necessary to use a stopped-flow instrument. The results obtained at 25 °C and constant $[H_2SO_4] = 0.05$ mol dm^{-3} are shown in Figure 3 in the form of a plot of $k_{obs.}$ against $[Cl^-]$, and clearly the relation is not linear, with $k_{obs.}$ approaching a limiting value at the higher chloride-ion concentrations. Another set of results was obtained in which $[HSO_4^-]$ was varied with $[Cl^-] = 0.10$ mol dm^{-3}. As predicted, $k_{obs.}$ decreased as $[HSO_4^-]$ increased (Figure 3), and a plot of $1/k_{obs.}$ against $[HSO_4^-]$ was linear.

Rearrangement of (3), with the numerator dominated by the k_2 term, affords (4). From the intercept of the

$$1/k_{obs.} \sim \frac{1 + K_1[HSO_4^-]}{k_2K_2[Cl^-]} + 1/k_2 \qquad (4)$$

plot of $1/k_{obs.}$ against $1/[Cl^-]$ at constant $[HSO_4^-]$ a value of $k_2 = 0.58 \pm 0.02$ s^{-1} was obtained. The value of the gradient of this plot, together with that from the linear plot of $1/k_{obs.}$ against $[HSO_4^-]$ at constant $[Cl^-]$, enabled estimates of K_1 and K_2 to be made: $K_1 = 180 \pm 90$ dm^3 mol^{-1}, $K_2 = 53 \pm 27$ dm^3 mol^{-1}. By estimating values of k_0 and k_1 from results of previous experiments made in the absence of chloride ion, and inserting these, together with the other derived con-

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* Values for other complexes at 30 °C are: $[Fe(bipy)_3]^{2+}$, 230 ± 60; $[Fe(NO_2\text{-}phen)_3]^{2+}$, 110 ± 70 dm^3 mol^{-1}.

stants into (3), values of the rate of solvolysis under the various experimental conditions could be calculated. There is very good agreement between calculated and observed rate constants (Table 4). A computer program, written in Algol W and employing the Simplex method of minimisation, was also used to obtain estimates of unknown constants. This fitted all the experimental results to equation (3), so as to obtain the best fit between calculated and observed rate constants assuming a constant fractional error in each individual rate constant. Values of the parameters so derived were very similar to those obtained by the graphical technique, but instability problems arose as a result of the rather large errors associated with K_1 and K_2. However, such errors are common in studies of this type. The reasonable agreement between the value of K_1 derived from the results of the competitive ion-pair experiments and that obtained (at 30 °C) in the absence of Cl^- provides further support for the proposed competitive ion-pairing scheme ($K_1 = 220 \pm 90$ and 180 ± 90 dm^3 mol^{-1} in the absence and presence of Cl^- respectively).

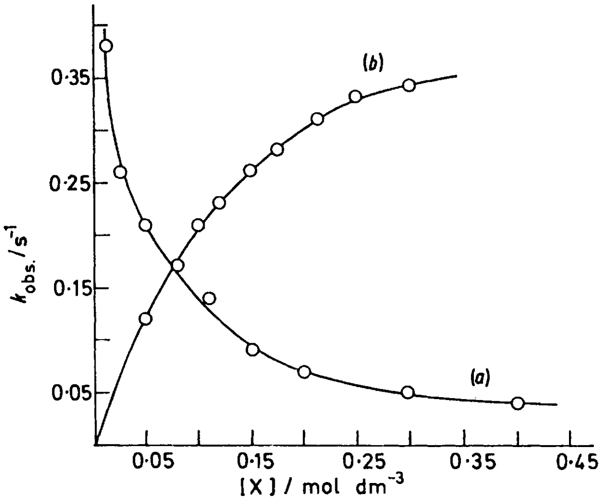


FIGURE 3 Plots of the observed pseudo-first-order rate constant against (a) the concentration of H_2SO_4 at $[NEt_3(CH_2Ph)Cl]$ = 0.10 mol dm^{-3} and (b) the concentration of $[NEt_3(CH_2Ph)]Cl$ at $[H_2SO_4]$ = 0.05 mol dm^{-3} and 25.0 °C

TABLE 4

Observed and calculated rate constants for the solvolysis of $[Fe(phen)_3]^{2+}$ in dmso in the presence of H_2SO_4 and $[NEt_3(CH_2Ph)]Cl$ at 25.0 °C

$[H_2SO_4]$	$[NEt_3(CH_2Ph)Cl]$		
mol dm^{-3}		$k_{obs.}$/s^{-1}	$k_{calc.}$*/s^{-1}
0.050	0.050	0.12	0.121
0.050	0.080	0.17	0.172
0.050	0.120	0.23	0.238
0.050	0.150	0.26	0.255
0.050	0.175	0.28	0.277
0.050	0.212	0.31	0.305
0.050	0.249	0.33	0.328
0.050	0.300	0.34	0.354
0.013	0.100	0.38	0.356
0.026	0.100	0.26	0.278
0.050	0.100	0.21	0.200
0.110	0.100	0.14	0.117
0.151	0.100	0.09	0.092
0.200	0.100	0.07	0.073
0.298	0.100	0.05	0.052
0.400	0.100	0.04	0.040

* Obtained from equation (3) using derived values of constants: $k_2 = 0.58$ s^{-1}, $K_1 = 183$, $K_2 = 53$ dm^3 mol^{-1}, with $k_0 = 0.77 \times 10^{-3}$ and $k_1 = 1.10 \times 10^{-3}$ s^{-1}.

Before discussing the values of the derived ion-pair formation constants and rate constants it is appropriate to consider complications that could arise from ion-pair formation involving protonated dmso. Although Kolthoff and Reddy concluded from their results of polarographic and indicator studies[22] that H_2SO_4 and HCl are fully ionised in dmso, Bolzan and Arvia[28] subsequently interpreted their electrical-conductance data for HCl in dmso in terms of the Fuoss theory for associated 1 : 1 electrolytes. At 25 °C they derived a value of 116 dm^3 mol^{-1} for K_{ip} (which probably has significant, unquoted, error limits) for equilibrium (5). However,

$$[Hdmso]^+ + Cl^- \overset{K_{ip}}{\rightleftharpoons} [Hdmso]^+ \cdot Cl^- \qquad (5)$$

association constants for the simple ions $[NMe_4]^+ \cdot I^-$ and $[NMe_4]^+ \cdot Br^-$ in this solvent have been estimated[29] to be only *ca.* 2 and 4 dm^3 mol^{-1} respectively, and virtually negligible for $[NEt_4]^+ \cdot I^-$ and $[NPr_4]^+ \cdot Cl^-$. Similarly, in spite of wide variation of the equivalent conductance of LiCl in dmso over a very wide concentration range, it was not necessary to invoke ion-pair formation to obtain a theoretical fit of the results.[26] If $[Hdmso]^+$ readily forms ion pairs with Cl^- there is no obvious reason why $[HSO_4]^-$ should not also form ion pairs with $[Hdmso]^+$. Since results of electrical-conductivity measurements are not available for H_2SO_4 in dmso, and in the light of results for other salts in this solvent, we have not included these ion pairs in the reaction scheme. Should they in fact be present, the numerical results of our calculations (see above) will be in error, but this is not evidence against the involvement of $[Fe(phen)_3]^{2+}$ ion pairs in these solvolysis reactions.

Using the well known Fuoss equation,[30] a value of 32 dm^3 mol^{-1} can be calculated for the ion-pair formation constant between a 2+ cation and a 1− anion assuming the closest distance of approach (a_0) is 5.7 Å {the shortest Cu–Cl distance in the $[Cu(phen)_3][ClO_4]_2$ crystal[31]}. However, the value obtained is very sensitive to a_0, and it has been suggested that a small ion could approach as close as 3 Å.[19] The corresponding ion-pair formation constant is *ca.* 240 dm^3 mol^{-1}. Values of K_1 and K_2 are therefore expected to be in the range 32—240 dm^3 mol^{-1} and indeed the derived values from the competitive ion-pair experiments, 183 and 53 dm^3 mol^{-1} respectively, are within these limits. Hydrogensulphate ion is larger than chloride ion, and on the basis of the Fuoss equation it is expected that the latter would have the larger ion-pair formation constant. The opposite is observed, and might reflect some specific effect such as hydrogen bonding, or differences in the energy needed to desolvate the anions on formation of solvated ion pairs. An alternative, tentative, explanation is that there is a low concentration of $[SO_4]^{2-}$. This, by virtue of the 2— charge, would form ion pairs with $[Fe(phen)_3]^{2+}$ some 100 times more strongly than $[HSO_4]^-$, and as a result the observed ion-pair formation constant would be increased.

The values of K_1 and K_2 are also within the range previously found for *cis*- and *trans*-$[M(en)_2X_2]^+{\cdot}X^-$ (M = Cr or Co, en = ethylenediamine) in dmso by conductance measurements. For instance, for *cis*-$[Cr(en)_2Cl_2]^+{\cdot}Cl^-$, $K = 290$ dm^3 mol^{-1}, and for the corresponding *trans* isomer $K = 25$ dm^3 mol^{-1}. The dipole moment of the *cis* isomer is expected to increase its ion-pair formation constant, but there is also n.m.r. evidence [32] indicating that there is some specific interaction of the type $N{-}H \cdots Cl^-$. The chemical shift of the 5,6-protons of $[Fe(phen)_3]^{2+}$ in acetone solution is sensitive to the concentration of $[ClO_4]^-$.[19] Increasing $[NaClO_4]$ to *ca.* 0.06 mol dm^{-3} produced a downfield shift of 3.2 Hz. Sinilarly, we recorded the ^1H n.m.r. spectrum of $[Fe(phen)_3][ClO_4]_2$ in dmso in the absence, and presence, of a large excess of $K[HSO_4]$ or $[NEt_3(CH_2Ph)][HSO_4]$. The observed spectrum was in accord with that previously reported by Miller and Prince,[33a] but showed a small change on addition of hydrogensulphate salts, the largest change being a 3—4 Hz downfield shift of the 5,6-proton resonances. These observations are in accord with ion-pair formation, but not necessarily with significant specific interactions.

Values of the ion-pair formation constants of $[Fe(phen)_3]^{2+}$ with $[HSO_4]^-$ and Cl^- could not be estimated with sufficient accuracy to enable their temperature coefficients to be derived with meaningful precision. However, values of the rate constant for reaction of the chloride ion pair (k_2) were derived from observed rate constants obtained in the presence of various amounts of Cl^- at constant $[HSO_4^-]$ over the range 25—45 °C and activation parameters were calculated (Table 5). While the entropy of activation is characteristic of a dissociative reaction,[33b] the enhanced reactivity of this ion pair results from a favourable decrease in enthalpy of activation (*ca.* 4 kcal mol^{-1}).

TABLE 5

Rate constants and derived activation parameters for the reaction of $[Fe(phen)_3]^{2+}{\cdot}Cl^-$ in dmso

θ_c/°C	k_2/s^{-1}	$k_{calc.}$*/s^{-1}
25.0	0.58 ± 0.02	0.58
30.0	1.14 ± 0.06	1.11
35.0	1.89 ± 0.11	2.07
40.0	3.92 ± 0.15	3.80
45.0	6.67 ± 0.47	6.84

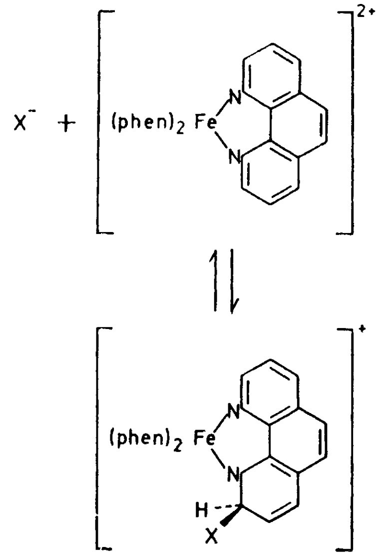
Derived activation parameters: $\Delta H^\ddagger = 22.65 \pm 0.59$ kcal mol^{-1}, $\Delta S^\ddagger = 16.3 \pm 1.9$ cal K^{-1} mol^{-1}.

* Calculated from derived activation parameters.

Addition of other salts. (*a*) *Halides.* Addition of NaBr to acid solutions of $[Fe(phen)_3]^{2+}$ in dmso increased the rate of solvolysis of the complex, and preliminary initial-rate studies indicated that $k_{obs.}$ increases with [NaBr], although to a smaller extent than with chloride ion (*e.g.* $[H_2SO_4] = 0.11$ mol dm^{-3} and [LiBr] = 0.37 mol dm^{-3} produced a six-fold increase in $k_{obs.}$). This reaction is, however, complicated by the appearance of free bromine and the removal of hydrogen ion brought about by the oxidation of bromide ion by the acidic dmso. Iodide ion is similarly oxidised, and in this case it was not possible to obtain even semiquantitative estimates of rate constants because of the large absorption of iodine in the visible region of the spectrum.

(*b*) *Perchlorate.* A small increase in the rate of solvolysis of $[Fe(phen)_3]^{2+}$ was brought about by the addition of perchlorate ion in the form of $[NEt_3(CH_2Ph)][ClO_4]$, *e.g.* a two-fold increase with 0.7 mol dm^{-3} salt ($[HSO_4^-] = 0.058$ mol dm^{-3}). Graphical analysis of the results obtained at 30 °C, together with the previously determined value of the ion-pair formation constant with $[HSO_4]^-$, afforded a value of 39 ± 10 dm^3 mol^{-1} for the ion-pair formation constant with $[ClO_4]^-$.

An Alternative Explanation.—An alternative way of explaining the results could use Gillard's [34] proposal of initial attack of a nucleophile on a co-ordinated heterocyclic ring. Instead of Scheme 2, there could be competition between Cl^- and $[HSO_4]^-$ for reversible attack on the 2- or 9-carbon atoms of the co-ordinated phenanthroline, break-up of the intermediate so formed being rate determining. The mathematical treatment of the results would remain unchanged, the ion-pair formation constant being replaced by the formation constant for the Gillardian intermediate.



In some systems there is evidence for Gillard's proposals where nucleophiles such as methoxide,[35] hydroxide,[36] and cyanide [37] are involved, where intermediates have been detected by extra-kinetic means (*cf.* refs. 35 and 36) and where there is a close parallel with organic examples.[38] However, wholehearted application to our systems meets the following difficulties. (*a*) Perchlorate and hydrogensulphate accelerate the rate of acid-catalysed decomposition; although these ions are not known to attack activated carbon atoms in organic molecules. (*b*) Where chloride is concerned the formation constant of the intermediate is large enough for the product of addition of chloride ion, to the phenanthroline ring to be observed by n.m.r. spectroscopy. Yet only small spectral differences have been observed when chloride is added to a solution of the iron(II) phenanthroline complex. There is no shift of one of the α proton lines to higher field as one might expect from a change in hybridisation on addition, with a simultaneous loss of ring current.[38]

Thus, in the systems discussed here the experimental results are quantitatively described by the ion-pair mechanism shown in Scheme 2. No direct evidence has been obtained for the participation of σ-bonded intermediates. If such species are formed from the complex ion pair they must be present in very low concentrations. Should the reaction sequence involve them, then the observed ion-pair formation constant will be the product of formation constants for the ion pair and σ-bonded species.

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