

Equilibria in N-Heterocyclic Complexes. Part XXVII*: Decomposition of Tris(1,10-phenanthroline)iron(II) Salts in Dimethylsulphoxide: a Comment

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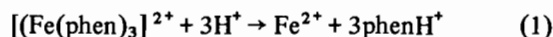
The loss of the red colour of tris-1,10-phenanthrolineiron(II) salts in DMSO in the presence of chloride is accompanied by the growth of absorption at around 600 nm, due to the formation of cis-dichlorobisphenanthrolineiron(II), $[\text{Fe}(\text{phen})_2\text{Cl}_2]$. A recent discussion of the rate loss of the red colour, in the presence of chloride and sulphuric acid, as being due to acid solvolysis of the tris-species, is criticized.

Low-spin complex ions of iron(II) with three 1,2-di-imine ligands (like 1,10-phenanthroline) are well-known and important for many reasons, not least their apparent simplicity as mechanistic models. They undergo many intriguing reactions. Some have been extensively studied: acid solvolysis [1] is one such. The mechanisms of their solvolyses in water are controversial, some believing that the second order terms (first order in hydroxide) arise [2] from direct attack at the iron centre, and others that these and similar terms stem [3] in these and related systems in protic media from pre-equilibria involving attachment of the nucleophile (OH^- being the most prominent example of a class including CN^- , OR^- , and carbanions) to the quasi-quaternized N-heterocyclic ligand.

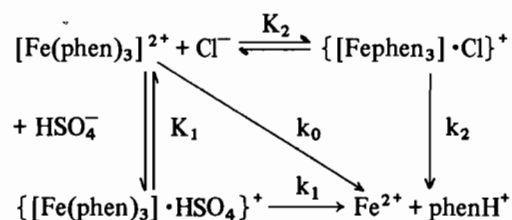
A recent study [1] by Farrington, Jones and Twigg of the acid solvolysis of tris-1,10-phenanthroline-iron(II) by sulphuric acid in dimethylsulphoxide drew attention to an increase in the rate of disappearance of the red colour in the presence of chloride ion, and analysed this in terms of formation of reactive ion-pairs, going on to suggest "the possibility of an ion pair mechanism being responsible for the apparent second order behaviour of this, and related complexes, with anions in other solvents....".

The purpose of this note is to indicate why the results, although undoubtedly correct, and incomplete and therefore naively interpreted, and why, in any case, the whole study (including the quoted conclusion) is irrelevant to reactions in water.

First, the reaction studied (in DMSO, containing complex, and varying amounts of H_2SO_4 and chloride ion, in the form of its lithium salts, or its benzyltriethylammonium salt) is allegedly the acid solvolysis of the tris-complex:



The observed rates were said to refer to the rate-determining loss of the first ligand, and were interpreted in detail in terms of Scheme 1:



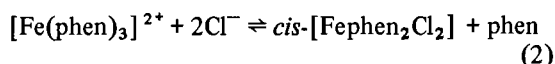
Scheme 1 (from ref. 1)

However, while under the conditions indicated, the reaction in DMSO with sulphuric acid in the absence of chloride may well be as indicated, the Scheme is not adequate in the presence of chloride. Other reactions intervene, and their effect (large, in DMSO) should be included.

In DMSO, tris-phenanthrolineiron(II) reacts rapidly with chloride, in the absence of acid. This is clear from the figure in reference [1]. There, at 0.10 molar LiCl, the rate at 25 °C increases as the sulphuric acid concentration decreases, and, although no value of k_{obs} is recorded for zero acid concentration, that rate is clearly greater still. In my new experiments here at 20 °C, the rate of disappearance of the red colour (monitored, as in the earlier study [1] at 510 nm) of $[\text{Fe}(\text{phen})_3](\text{BF}_4)_2$ dissolved in DMSO on adding lithium chloride (in concentrations up to 0.25 M) is indeed extremely fast. That is, quite independent of any acid solvolysis, there is a rapid reaction leading to the disappearance of $[\text{Fe}(\text{phen})_3]^{2+}$, as monitored by its absorption at 510 nm.

This reaction is anation by chloride, leading to cis- $[\text{Fephen}_2\text{Cl}_2]$ (i.e. reaction 2):

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The product is a known compound, which is (when solid) blue. Consonant with this, in DMSO containing chloride but no acid, while the intense electronic absorption due to $[\text{Fephen}_3]^{2+}$ decreases, a much weaker absorption above 600 nm increases (as shown in Fig. 1, which records results obtained at 25 °C) due

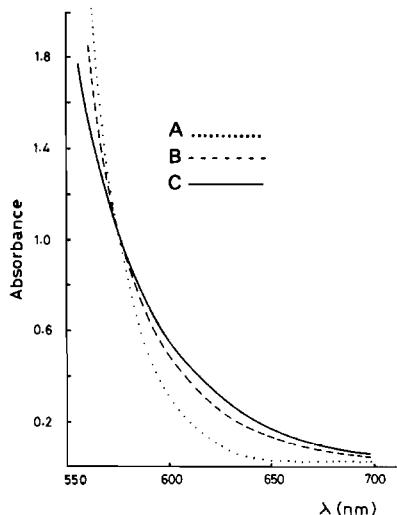


Fig. 1. Electronic spectra (taken after the establishment of equilibrium) on the longer wavelength edge of the absorption band of $[\text{Fe}(\text{phen})_3]^{2+}$ in DMSO, as a function of chloride ion concentration. Measurements are in 1-cm cells at 25 °C: A is $10^{-3} M$ $[\text{Fe}(\text{phen})_3](\text{BF}_4)_2$; B is the same in $0.133 M$ LiCl; C is the same in $0.4 M$ LiCl. These are initial concentrations.

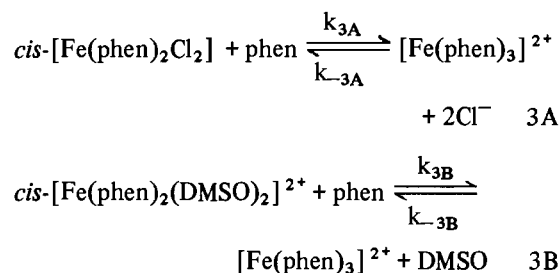
to the formation of high-spin *cis*- $[\text{Fephen}_2\text{Cl}_2]$ (λ 600 nm, 535 nm: these values are from reflectance spectra [4]). This product can also be observed spectroscopically (under some concentration conditions of reference [1]) in the presence of both chloride and sulphuric acid at intermediate stages of reactions. Indeed, where relatively little acid is present, the final solutions are often blue to the eye.

So, the rate of loss of absorbance at 510 nm (used in ref. 1 to obtain rate constants) refers not only (or even primarily) to the acid solvolysis (1) but also to the anation (2) (such would not be true in water: the anation there is of no significance). Discussion of the results in DMSO as if they related only to acid solvolysis of $[\text{Fephen}_3]^{2+}$ is clearly inadequate. Further reactions of the spin-free blue dichloro species $[\text{Fephen}_2\text{Cl}_2]$ with acid (in water or other protic media) are very rapid indeed.

The chief fallacy in the analysis in reference 1 (and, indeed, in some other studies in mixed solvent) is the comparison (often explicit) between aqueous solutions containing $[\text{Fe}(\text{phen})_3]^{2+}$ and those in

DMSO or like solvents. The value $\log \beta_3 \approx 21$ is given [1] as support for the statement that “thermodynamically, $[\text{Fe}(\text{phen})_3]^{2+}$ is very stable towards dissociation...”. However [5], 21 is the value appropriate to water, and *only to water*. There is no reason to suppose that the free energies of transfer of the species $[\text{Fe}^{2+}]$, $[\text{Fe}(\text{phen})_3]^{2+}$, Cl^- and so forth from water to DMSO would have the constant ratio necessary to preserve β_3 as $10^{21.2}$. There is every reason to suppose this to be impossible, and indeed the apparent stability constants in such systems are known to show a decrease on addition of a solvent with water. The gross distinctions in activity coefficients (and hence equilibrium constants) of species in water as against DMSO are well-known from such facts [6] as the monobasicity of H_2SO_4 in DMSO.

Further, in general, and in aprotic solvents in particular, K_3 for $[\text{Fe}(\text{phen})_3]^{2+}$ cannot be related to solvato-species alone. A more useful equilibrium expression for K_3 is based on the reactions shown as 3:



Treating the equilibrium shown as 3A further,

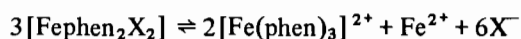
$$K_{3(A)} = \frac{\{[\text{Fe}(\text{phen})_3]^{2+}\} \{[\text{Cl}^-]\}^2}{\{[\text{Fe}(\text{phen})_2\text{Cl}_2]\} \{\text{phen}\}}$$

The value of this equilibrium constant *in water* is, of course, very large (because chloride ion and the charged cationic tris complex are well solvated). However, in DMSO, charged species are badly solvated, and the value of K_{3A} is small. An estimate from such values as those in Fig. 1, assuming that all absorption at 640 nm is due to $[\text{Fephen}_2\text{Cl}_2]$, is that $K_{3A} = 4.4 \times 10^{-3} \text{ mol dm}^{-3}$. In a similar way, Madeja, Wilke, and Schmidt found [7] that, in neat pyridine, the tris-complex began to be observable only in the presence of a gross excess of phenanthroline relative to $[\text{Fephen}_2\text{Cl}_2]$: however, in the presence of 5–10% water, the tris-complex was stable. Since reaction (2) is the reverse of (3A), $K_2 = (K_{3A})^{-1} = 227 \text{ mol}^{-1} \text{ dm}^3$, in DMSO.

While an analysis of results in DMSO in terms of the rate-determining back solvolysis (with rate constant k_{-3B}) is appropriate to acidified (e.g. H_2SO_4) systems, when anions are present (e.g. Cl^-) capable of complexation in DMSO competitive with that of the solvent, then the anation with rate constant k_{-3A} is important. Indeed, Farrington,

Jones, and Twigg actually point out [1] that, around their median conditions, the reaction was first-order in both complex and chloride ion (*cf.* k_{-3A}).

Indeed, in other aprotic solvents, this effect has been known for many years (*i.e.* that chloride, contrary to the statement [1] that it is a "relatively poor nucleophile" may be highly reactive toward charged ions). For example, (+)[Fephen₃]Cl₂, dissolved in chloroform, rapidly loses optical activity while the solution becomes blue, showing the spectrum of [Fephen₂Cl₂]. Indeed, this (using the racemic tris-chloride) is a favoured preparative method [7] for the dichloro-compound from the tris-chloride, which occurs with pyridine, picoline, DMF or acetonitrile. In a very similar way, while solutions of [Fephen₂X₂] (X being a halide or pseudo halide) disproportionate in water, they do not do so in such aprotic media as acetone. That is, writing the disproportionation as:



with

$$K = \frac{[\text{Fephen}_3]^{2+} [\text{Fe}^{2+}] [\text{X}^-]^6}{[\text{Fephen}_2\text{X}_2]^3},$$

K is large in water, but much smaller in aprotic solvents. The arguments presented here on sizes of equilibrium constants are qualitatively well-known [4, 7].

The misconception about general non-intervention by bis-phenanthrolineiron(II) species arises because of a long-standing loose usage of the phrase "ligand field stabilization" relating to [Fe(phen)₃]²⁺ and similar compounds which should actually be applied only to aqueous systems. In water, the commonly observed order $K_1 > K_2 > K_3$ (*cf.* for $\text{M}^{2+} + \text{phen}$: M = Mn, 4.1, 3.2, 3.1 and for Ni²⁺, 8.7, 8.2, 7.8) fails, and the values for Fe²⁺ and phen of log K₁ (5.8) and log β₃ (~21.0 in ref. 1, and 21.2 given by McBryde in his scholarly and useful recent survey [5]) lead to the conclusion that log K₂ + log K₃ > 2 log K₁. Clearly either K₂ or K₃ (or both) is greater than K₁ (Brisbin and McBryde give [8] reasons for refusing to accept proposed experimental values for K₂). Since the magnetic moment of the system changes from paramagnetic at phen:Fe = 2.1 to diamagnetic at phen:Fe

= 3:1, it is often assumed that $K_3 \gg K_2$ and this has been attributed to the "stability of the ligand field stabilized low-spin ferrous complex".

This is a hazy concept. The stability of tris-phenanthrolineiron(II) salts in water is a property of their polar environment, and not particularly of their electronic configuration. In non-protic solvents, K_{3A} is small, and the anation may occur through spin-free states. The mechanisms of such anations leading to change of spin state will indeed be fascinating. They seem not to have been deliberately studied, although it is clear that for reaction (2) the simple rate expression, Rate = k[Fephen₃][Cl⁻] applies, in DMSO.

The results analyzed in reference 1 refer to the complicated pattern of reaction made up of a mixture of chloride anation and acid solvolysis, and any attempt to derive 'unique' mechanisms, and particularly to use such mechanisms to make general comments on the aqueous reactivity of [Fephen₃]²⁺ and the like is wrong. A similar comment would also relate to a paper [9] entitled "Accelerating Effects on the Racemization of [Ni(phen)₃]²⁺ in H₂O-t-BuOH mixtures by Halide Anions." Basically, chloride ions have no effect on the rate in pure water (*cf.* equilibrium K_{3A} above) but the observed loss of optical rotation in solvents where the *mol fraction* of tBuOH is > 0.5 accelerates (*cf.* equilibrium K_{3B} above).

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