Inorganica Chimica Acta, 25 (1977) L75–L76
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Acid Solvolysis of Tris-(1,10-phenanthroline)iron(II) in Dimethylsulphoxide. Chloride Ion Catalysis, via Ion-pair Formation

D. J. FARRINGTON, J. G. JONES
New University of Ulster, Coleraine, Northern Ireland
M. V. TWIGG*
University Chemical Laboratory, Lensfield Road, Cambridge, U.K.

Received September 26, 1977

Currently there is considerable interest in reactions of low-spin iron(II) complexes of α,α'-diimine ligands (typified by 1,10-phenanthroline) with nucleophiles such as OH^- and CN^- that involve important second order reaction paths. Since the now conventional dissociative conjugate base mechanism [1] cannot operate due to the absence of ionizable proton, it has been suggested that the dependence of the rate of reaction on the incoming nucleophile is a result of bimolecular attack at the metal centre [2], or a mechanism involving initial attack on the ligand [3]. Here we report that acid solvolysis of $Fe(phen)_3]^{2+}$ in dimethylsulphoxide (dmso) is markedly catalysed by the relatively poor nucleophile chloride ion, and that this can be quantitatively accounted for by a process involving the formation of a reactive ion-pair.

Thermodynamically $[Fe(phen)_3]^{2+}$ is very stable towards dissociation (in water $\beta_3 \sim 10^{21}$), but in the presence of acid free ligand is protonated, and the complex dissociates in an attempt to restore equilibrium conditions. Values of stability constants, and pK_a of the ligand, are such that in the presence of dilute mineral acid complexes of this type completely dissociate at concentrations convenient for spectrophotometric studies. Kinetics of the acid (H_2SO_4) solvolysis of $[Fe(phen)_3]^{2+}$ in dmso was followed by monitoring the decrease of absorbance at 510 nm ($\log\epsilon$ = 4.0) using conventional spectrophotometers or a stopped-flow apparatus for the faster reactions. All reactions were accurately first order in complex with loss of the first ligand being rate determining [4]. Like the behaviour in aqueous acid the rate of solvolysis in dmso is almost independent of H_2SO_4 concentration. However, the observed rate constant at 25 °C (1.07×10^3 s^{-1}) is an order of magnitude larger than in water. The determined activation parameters ($\Delta H^{\neq}$ = 26.60 ± 0.20 kcal mol^{-1}, $\Delta S^{\neq}$ = 17.1 ± 0.7 cal K^{-1} mol^{-1} show that this enhanced reactivity is solely due to a decrease in enthalpy of activation ($\Delta H^{\neq}$ = 29.31 ± 0.20 kcal mol^{-1}, $\Delta S^{\neq}$ = 20.7 ± 0.7 cal K^{-1} mol^{-1}, ref. 6). Addition of chloride ion in the form of LiCl or $PhCH_2NEt_3Cl$ produced a dramatic increase in the rate of solvolysis *e.g.* with $[H_2SO_4]$ = 0.1 mol l^{-1} addition of 0.05 mol l^{-1} LiCl increased the observed rate constant by a factor of about 50. With conventional techniques the maximum chloride ion concentration was ~ 0.1 mol l^{-1} because above this value the reaction was too fast to follow. In this region the reaction was first order in both complex and chloride ion ($PhCH_2NEt_3Cl$ and LiCl produced identical results), and it was thought possible that chloride ion was involved in a bimolecular reaction at the ligand or metal centre. However, with stopped-flow techniques and higher chloride ion concentrations the resulting extended plot of k_{obs} against [LiCl] was not linear, and moreover increasing the concentration of acid (sulphuric) at constant chloride ion concentration caused a decrease in the value of the observed rate constant (see Figure). These observations can be

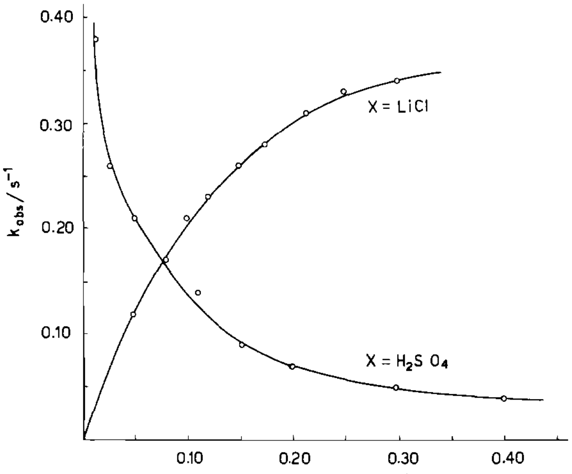
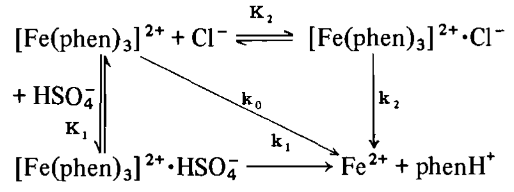


Figure. Plots of observed *pseudo* first order rate constant against concentration of H_2SO_4 with [LiCl] = 0.10 mol l^{-1} and concentration of LiCl with $[H_2SO_4]$ = 0.05 mol l^{-1} at 25.0 °C.



Scheme.

---

*Present address: ICI Ltd., Agricultural Division, Billingham, Cleveland.

Phen = 1,10-phenanthroline.

quantitatively interpreted in terms of competitive ion-pairing between Cl^-, HSO_4^- [7], and $[Fe(phen)_3]^{2+}$ as illustrated in the Scheme. Derived values of K_1 = 180 and K_2 = 50 are within the range calculated for ion-pairs of this type in dmso: similar results have been reported for related complexes in this solvent that were determined by static methods [8]. The substantial enhanced reactivity of the chloride ion-pair ($k = 0.5\ s^{-1}$) is likely to be a consequence of the delocalised and polarisable nature of the ligand. Polarisation by HSO_4^- is expected to be small, and accordingly the reactivity of this ion-pair is comparable to that of the free complex.

It has been demonstrated that $[Fe(phen)_3]^{2+}$ forms ion-pairs in water as well as other solvents [9], and the possibility of an ion-pair mechanism being responsible for the apparent second order behaviour of this, and related complexes, with anions in solvents other than dmso should not be overlooked.

References

1 "Inorganic Reaction Mechanisms", by M. L. Tobe, Nelson (1972) Ch. 7.

2 J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane and R. D. Wyvill, *J. Chem. Soc. A*, 44 (1971).

3 R. D. Gillard, *Coord. Chem. Rev., 16,* 67 (1975).

4 M. V. Twigg, *Inorg. Chim. Acta, 10,* 17 (1974).

5 J. E. Dickens, F. Bosolo, and H. M. Neumann, *J. Am. Chem. Soc., 79,* 1286 (1957).

6 J. Burgess and R. H. Prince, *J. Chem. Soc.*, 5752 (1963); J. Burgess, *Ph.D. Thesis,* Camrbidge (1963).

7 In dmso H_2SO_4 is monoacidic: I. M. Kolthoff and T. B. Ready, *Inorg. Chem., 1,* 189 (1962).

8 D. A. Palmer and D. W. Watts, *Inorg. Chim. Acta, 6,* 197 (1972) and previous publications.

9 E. Kubota and M. Yokoi, *Bull. Chem. Soc. Japan, 49,* 2674 (1976); A. Hulanicki and J. Nieniewska, *Talanta, 21,* 896 (1974); Y. Yamamoto, T. Tarumoto and Y. Hanamoto, *Bull. Chem. Soc. Japan, 42,* 268 (1969); Y. Yamamoto, T. Tarumoto and E. Iwamoto, *Anal. Letters, 2,* 1 (1969); E. Iwamoto, *J. Inorg. Nucl. Chem., 35,* 2001 (1973).