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The Role of Solvento-cations on the Acid Hydrolysis of Tris(*o*-phenanthroline)iron(II)- and Tris(bipyridine)iron(II)-Perchlorates

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In spite of the great amount of investigation on the kinetics of dissociation of the complex cations tris(*o*-phenanthroline)iron(II), $Fe(phen)_3^{2+}$ and tris(bipyridine)iron(II), $Fe(bipy)_3^{2+}$, comparatively little attention has been devoted to the effects of added salts on the acid hydrolysis of these and related complexes. Krumholz [1] noted a quantitative difference in the kinetics of the acid dissociation, in aqueous solution, of $Fe(bipy)_3^{2+}$ when changing from the HCl–KCl system to HCl–LiCl mixtures. Recently a study of the effect of NO_3^-, SO_4^{2-} and Cl^- salts in different acid media (HCl, H_2SO_4, $HClO_4$) [2] showed that, for a given acid, the dissociation constant increases or decreases depending on the concentration of the anion. Basolo *et al.* [3] studied the effect of salts of alkaline metals and of HCl on the dissociation constant of $Fe(phen)_3^{2+}$ and found the following order of "effectiveness on retarding" the rate of dissociation of the complex: $HSO_4^- > Cl^- \sim NO_3^-$ and $H^+ > Li^+ > K^+$. Here we report the acid hydrolysis of $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ in the presence of a series of alkaline and alkaline earth chlorides.

Thermodynamically both $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ are very stable towards dissociation in aqueous solution, which occurs by two different mechanisms. The rate determining step of dissociation of $Fe(bipy)_3^{2+}$ is the rupture of one of the iron–nitrogen bonds leading to a half-bonded stationary intermediate [4], which either reforms the chelate ring or dissociates the first ligand molecule completely. Hydrogen ions catalyze the dissociation as a result of protonation of the free nitrogen atom in the half-bonded intermediate. For $Fe(phen)_3^{2+}$, where the ligand molecule is rigid, the rate determining step of dissociation is the simultaneous rupture of the two iron–nitrogen bonds of one of the ligands [4]. No

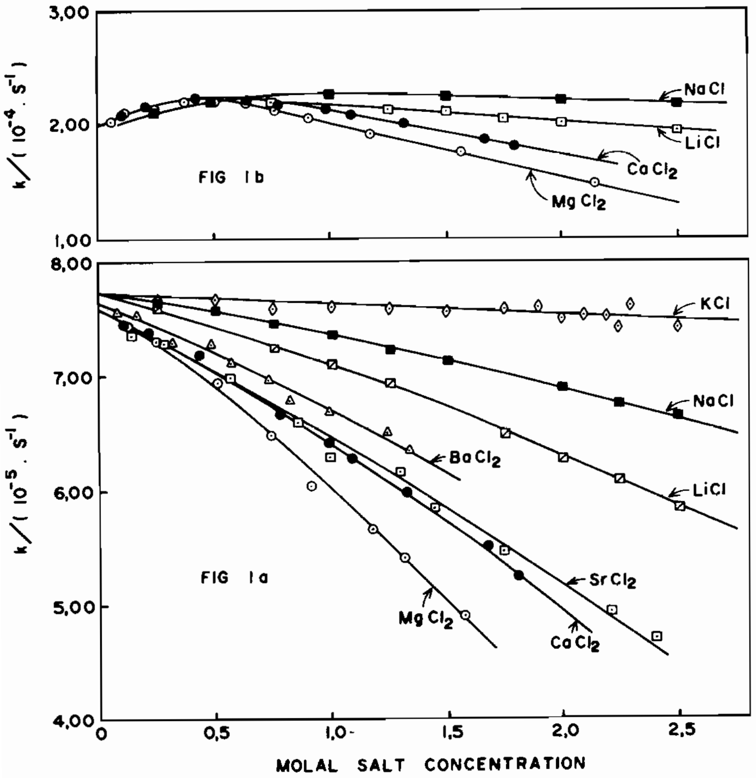

Figure 1. Plots of observed pseudo first order rate constants for the acid hydrolysis of (a) $Fe(phen)_3^{2+}$ and (b) $Fe(bipy)_3^{2+}$ against molal concentration of alkaline and alkaline earth chlorides at 25 °C. [HCl] = 0.05 mol dm^{-3}.

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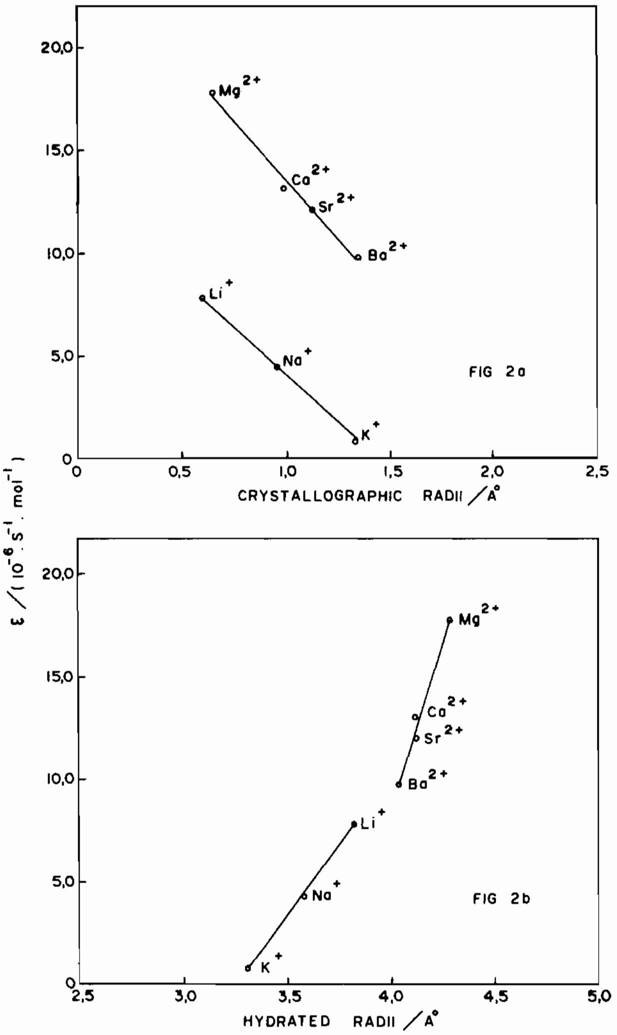

Figure 2. Plots of the angular coefficients, ϵ, of mean straight lines in Figure 1a against (a) crystallographic radii and (b) hydrated radii of the alkaline and alkaline earth cations.

hydrogen ion catalysis is observed, but protonation of the free ligand inhibits the reformation of the original complex. In both complexes the solvent has an important role in the dissociation process by attacking the metal atom as a nucleophile – the question of the mechanism being either S_N1 or S_N2 not yet being resolved.

The kinetics of the acid hydrolysis (HCl 0.05*M*) of $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ was studied at 25 °C in the presence of LiCl, NaCl, KCl and NH_4Cl, and $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$. The reactions were followed by monitoring the decrease of absorbance at the maximum of absorption of the complexes, using a conventional spectrophotometer. The $Fe(phen)_3^{2+}$ system showed a quasi-linear dependence of the pseudo-first order rate constants on the molal concentration of the salts, as shown in Figure 1a. The angular coefficient, ϵ, of the mean straight lines was used as a measure of the effectiveness in retarding the rate of dissociation for a given cation. A good correlation was found between ϵ and the crystallographic radii [5] of the cations, as shown in Figure 2a. In our view this result shows that the hydration of the cations is an important factor in retarding the dissociation of these complexes. This hypothesis is supported by the correlation of ϵ and the hydrated radii [6] of the cations, as shown in Figure 2b. The process of transferring one water molecule from the ionic atmosphere to one $Fe(phen)_3^{2+}$, in the rate determining step, is presently under investigation in our laboratory.

In the $Fe(bipy)_3^{2+}$ system the pseudo-first order rate constant increases with the salt molality up to 1*m* in Cl^- and decreases with further increasing in *m*, as shown in Figure 1b. The ascending part of the curve may be explained on the basis of a catalytic effect of the Cl^- ions which can attack the iron atom in the half bonded intermediate, helping the dissociation.

In both $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ systems we cannot overlook the role of ion pairing in the kinetics and mechanism of dissociation. Further experiments are being prepared to verify this point.

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