Kinetics and Mechanisms of Dissociation of Metal Chelates. Part 3.[1] Effects of Ions on the Acid Hydrolysis of Tris(1,10-phenanthroline)iron(II) Perchlorate †

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The rate of acid hydrolysis of the title complex cation, $[Fe(phen)_3]^{2+}$, has been investigated in the presence of varying concentrations of HCl, LiCl, NaCl, KCl, $[NH_4]Cl$, NaBr, KBr, $[NH_4]Br$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, and $MgBr_2$. In each system, the pseudo-first-order rate constant, k_{H_2O}, decreases linearly with increasing molality, *m*, of the added electrolyte. The degree of retardation is measured by the *retardation constant*, $k_r = \varepsilon/k_0$, where ε is the slope of the mean straight line obtained by least squares from plots of k_{H_2O} *vs.* *m* of the added salt, and k_0 is k_{H_2O} for $m = 0$. The constant k_r is linearly related to enthalpies and entropies of hydration, crystallographic radii of the added cations, reorientation times of water molecules around the ions, *etc.* It was concluded, as expected, that the degree of retardation of the rate of hydrolysis is related to the degree of formation of the ' structure of liquid water ' induced by the added ions. Ion-pair formation and nucleophilic action as well as charge–radius effects are suggested as contributing to the effects of anions.

THE water-assisted dissociation and racemization of the complex cations tris(1,10-phenanthroline)- and tris(2,2′-bipyridine)- iron(II), $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ respectively, and related complexes, have been extensively studied over the last 30 years.[2-7] Since early times,[8-10] the influence of added ions on the rate of hydrolysis of these complexes was recognized. Krumholz[11] pointed out that the correct interpretation of rate measurements in mixtures of electrolytes is made difficult by the fact that the activity coefficients depend not only on the total ionic strength but also on the qualitative composition of the solutions, due to specific ionic interactions. Recently, the effects of added cations on the kinetics of dissociation of $[Fe(bipy)_3]^{2+}$ in water[5] and of tris(5-nitro-1,10-phenanthroline)iron(II) in aqueous binary mixtures[7] were attributed to the ability of the cations to alter the ' structure ' of liquid water.

In this note a study of the effects of alkali- and alkaline-earth-metal chlorides and bromides, ammonium chloride and bromide, and hydrogen chloride on the rate of hydrolysis of $[Fe(phen)_3]^{2+}$ is presented. The results were published in part in a previous communication.[12]

EXPERIMENTAL

Tris(1,10-phenanthroline)iron(II) perchlorate was prepared and purified according to the literature.[8,13]

Kinetic measurements were carried out in aqueous solutions of HCl, LiCl, NaCl, KCl, $[NH_4]Cl$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, NaBr, KBr, $[NH_4]Br$, and $MgBr_2$ of varying molality. Some HCl was always added to make the solutions 0.05 mol dm^{-3}, thus inhibiting reformation of the complex. The concentration of the complex was *ca.* 10^{-5} mol dm^{-3}. The rate of hydrolysis was followed photometrically at 510 nm using a PM2D Carl Zeiss spectrophotometer. Kinetic runs were carried out at 25.00, 30.00, and 35.00 ± 0.03 °C. The reactions were followed for at least two half-lives. The rate constants were obtained in the usual way and refined by a least-squares treatment. Duplicate runs were reproducible to within ±1%.

RESULTS AND DISCUSSION

The rate of acid hydrolysis of $[Fe(phen)_3]^{2+}$ is first order in complex.[8] Plots of the rate constant, k_{H_2O}, *versus* molal concentrations of added chlorides and bromides of alkali-, alkaline-earth metals, and ammonium, and HCl, are shown in Figure 1. The rate constant, k_{H_2O}, is related to the molal concentrations of the added salts, *m*, by equation (1), where k_0 is the rate constant in the absence of electrolytes and ε is the absolute value of the slope of the mean straight line

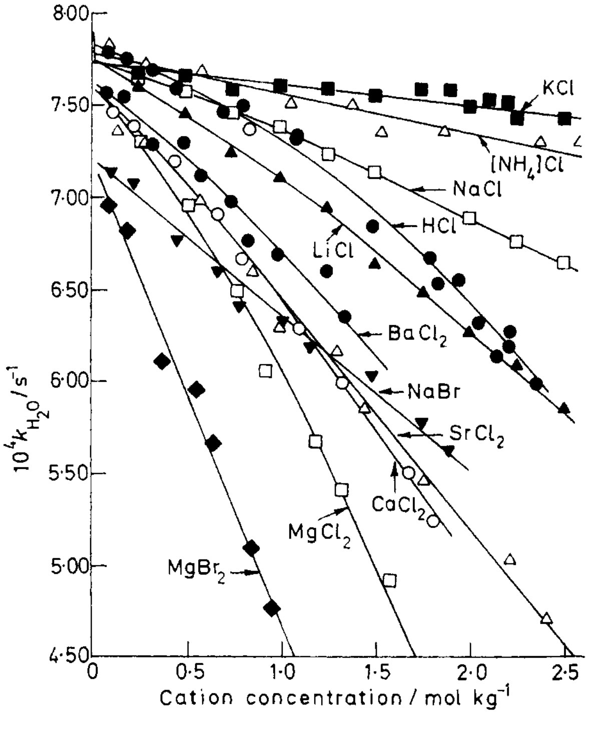

FIGURE 1 Plots of the rate constants of acid hydrolysis of $[Fe(phen)_3]^{2+}$, k_{H_2O}, against molal concentrations, *m*, of added electrolytes. Temperature = 25.00 °C; $[H^+] = 0.048$ mol dm^{-3} (HCl)

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† Taken in part from the Ph.D. Thesis of M. Tubino.

Retardation constant, k_r, for $[Fe(phen)_3]^{2+}$, thermodynamic functions, $\Delta H^{\ominus}_{hydr.}$ and $T\Delta S^{\ominus}_{hydr.}$, for added cations (anions), and reorientation times of water molecules around the ions of added salts (temperature = 25 °C)

Electrolyte	$10^2 k_r$/ kg mol^{-1}	$\Delta H^{\ominus}_{hydr.}$/ kJ mol^{-1}	$T\Delta S^{\ominus}_{hydr.}$/ kJ mol^{-1}	10^{11} $\tau^{\pm c}$/ s
HCl	9.1	1 111.9 [a] (344.0) [a]	38.6 [a] (22.5) [a]	
LiCl	8.8	552.2 [b] (339.8) [b]	41.7 [a,b] (22.5) [a]	3.0
NaCl	5.6	443.1 [b] (339.8) [b]	32.6 [a,b] (22.5) [a]	2.1
KCl	0.9	358.6 [b] (339.8) [b]	21.7 [a,b] (22.5) [a]	1.4
$[NH_4]Cl$	2.1	(339.8) [b]	(22.5) [a]	
NaBr	13.5	443.1 [b] (310.6) [b]	32.6 [a,b] (18.4) [a]	2.0
KBr	8.7	358.6 [b] (310.6) [b]	21.7 [a,b] (18.4) [a]	1.3
$[NH_4]Br$	9.9	(310.6) [b]	(18.4) [a]	
$MgCl_2$	22.1	1 996.4 [b] (339.8) [b]	92.4 [b] (23.0) [b]	5.6
$CaCl_2$	17.9	1 667.4 [b] (339.8) [b]	75.2 [b] (23.0) [b]	4.2
$SiCl_2$	16.1	1 519.4 [b] (339.8) [b]	73.6 [b] (23.0) [b]	3.9
$BaCl_2$	13.0	1 377.3 [b] (339.8) [b]	60.2 [b] (23.0) [b]	3.6
$MgBr_2$	32.8	1 996.4 [b] (310.6) [b]	92.4 [b] (22.6) [b]	5.4

[a] Taken from ref. 14. [b] Taken from ref. 15. [c] Calculated for M_xA_y salt from $\tau^{\pm} = x\tau^+ + y\tau^-$. Values of τ^+ and τ^- from ref. 16.

obtained by least squares. Equation (1) can be transformed into (2), where $k = k_{H_2O}/k_0$ and $k_r = \varepsilon k_0$. The

$$k_{H_2O} = k_0 - \varepsilon m \qquad (1)$$

$$k = 1 - k_r m \qquad (2)$$

retardation constant, k_r, measures the effectiveness of the added salt in retarding the hydrolysis process. In general k_r should be temperature dependent but is apparent that, in this system, within experimental error, this is not true.

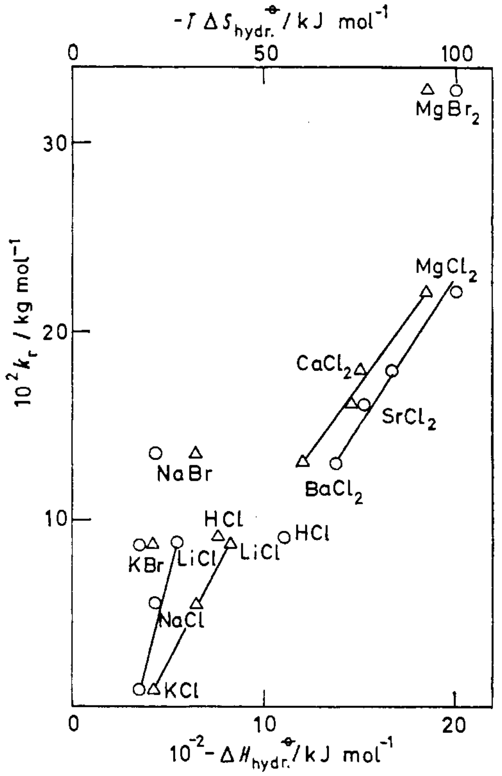

FIGURE 2 Plots of the retardation constant, k_r, against $-\Delta H^{\ominus}_{hydr.}$ (O) and $-T\Delta S^{\ominus}_{hydr.}$ (Δ) of added cations. Temperature = 25.00 °C

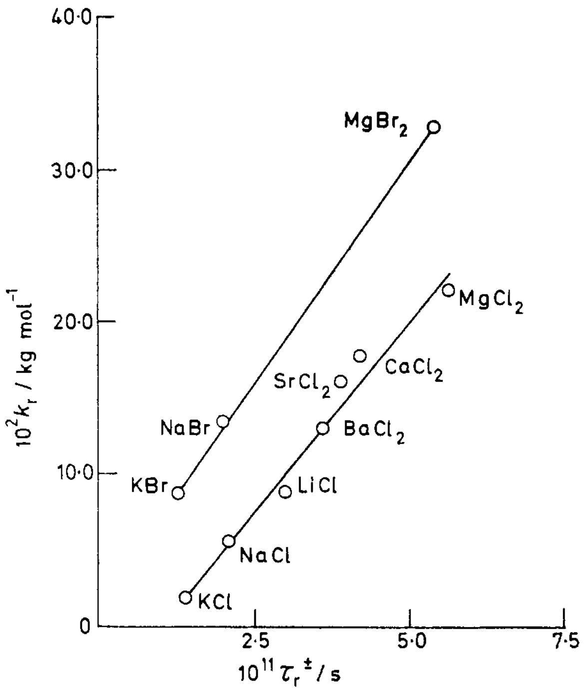

FIGURE 3 Plots of the retardation constants, k_r, against the sum, $\tau^{\pm}$, of the reorientation times of water molecules in the hydration shell of cations, τ^+, and anions, τ^-. $\tau^{\pm} = x\tau^+ + y\tau^-$ for M_xA_y. Temperature = 25.00 °C

The Table shows the values for k_r, ionic thermodynamic parameters ($\Delta H^{\ominus}_{hydr.}$ and $T\Delta S^{\ominus}_{hydr.}$),[14,15] and reorientation times of water molecules in the hydration shell of ions.[16] The constant k_r is linearly related to $\Delta H^{\ominus}_{hydr.}$ and to $T\Delta S^{\ominus}_{hydr.}$ as shown in Figure 2. The enthalpies of hydration are proportional to the square of charge and to the inverse of the effective ionic radius of the cations.[17] In a previous communication [12] we showed that k_r is linearly related to the hydration and crystal radii (r_+) of the added cations. The straight lines k_r *vs.* r_+ for alkali- and alkaline-earth-metal cations are parallel within experimental error, and can be expressed by equation (3), where z is the charge of the cation.

$$k_r = 0.15z - 0.12r_+ \qquad (3)$$

The proton and Li^+ show different $\Delta H^{\ominus}_{hydr.}$ values but similar $\Delta S^{\ominus}_{hydr.}$ values. The values of k_r are very close suggesting that they have similar 'kinetic radii' (related to entropy) in spite of the proton having a much smaller effective ionic radius. The constant k_r is also linearly related to the reorientation times of the water molecules in the hydration shell of the added ions, $\tau^{\pm}$, as shown in Figure 3. We assumed that $\tau^{\pm} = x\tau^+ + y\tau^-$ for a given M_xA_y salt. Qualitatively, the shorter the reorientation time, the less organized is the 'structure' of liquid water in the solution.[16] Linear correlations were also obtained between k_r and hydration numbers and ionic conductances at infinite dilution.

The results confirm for $[Fe(phen)_3]^{2+}$ that the retardation of the hydrolysis in salt solutions is a consequence of the organization of the 'structure' of liquid water, induced by the ions. Large and ' soft ' cations are ' water structure breakers ' and are expected to accelerate the hydrolysis. This was in fact observed in the aquation of tris(5-nitro-1,10-phenanthroline)-iron(II) in the presence of the tetra-n-butylammonium ion in binary aqueous solutions.[7]

Deviations from linearity in Figure 1 could be attributed to the effects of anions. As well as charge–radius effects, ion-pair formation [18,19] and nucleophilic action [20] have to be considered. Ion pairing could decrease the rate of hydrolysis since the ion-pair adduct is expected to be more stable than the ' free ' $[Fe(phen)_3]^{2+}$.[18,19] The higher values of k_r for the bromides compared with the corresponding chlorides (Cl^- is smaller than Br^-) could be explained on the basis of a more stable $[Fe(phen)_3]Br_n$ compound compared with $[Fe(phen)_3]Cl_n$. Extrapolation of k_{H_2O} *vs.* m, to $m = 0$, in Figure 1, shows lower values than the experimental ones, obtained in the absence of added salts. The difference is bigger for Br^- than for Cl^-. Acting as nucleophiles, anions are expected to increase the rate of hydrolysis. Evidence that the slight curvature of the ' straight lines ' at low concentrations of salt in Figure 1 is in part due to the nucleophilic action of the anions is being obtained for $[Fe(bipy)_3]^{2+}$,[21] where these effects are much more pronounced.[12]

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