

Kinetics and Mechanisms of Dissociation of Tris(2,2'-bipyridine)iron(II) Complex in Aqueous Salts Solutions

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Abstract

The pseudo first order rate of acid hydrolysis of the complex cation $\text{Fe}(\text{bipy})_3^{2+}$, has been determined in aqueous solutions of varying concentrations of LiCl , NaCl , KCl , NH_4Cl , NaBr , KBr , NH_4Br , MgCl_2 , CaCl_2 , SrCl_2 , BaCl_2 and MgBr_2 at 20.0, 25.0, and 30.0 °C in the presence of 0.012 mol kg^{-1} HCl, to avoid reformation of the complex. The rate rises with the salt concentration, reaching a maximum at *ca.* 0.5 to 1 mol kg^{-1} in chloride and *ca.* 0.3 mol kg^{-1} for bromide. Afterwards a linear decrease occurs with different slopes, which depends on the cation and anion involved. These trends are ascribed to the removal of water molecules from the bulk solvent by incorporation in the hydration shells of the cations of the salts and to ion-pair formation.

Introduction

The water-assisted dissociation of the complex cation tris(1,10-phenanthroline) and tris(2,2'-bipyridine)iron(II), $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Fe}(\text{bipy})_3^{2+}$ respectively, and related diimine complexes have been the subject of many investigations over the last four decades [1–5]. Since early times the influence of added ions on the rate of hydrolysis of these complexes has been observed [6–8] but relatively little attention has been given to this subject.

Krumholz pointed out that the correct interpretation of rate measurements in aqueous solutions of electrolytes is not obvious depending not only on the total ionic strength but also on the qualitative composition of the solutions [9].

Earlier studies on the effect of added ions upon the rates of dissociation of $\text{Fe}(\text{phen})_3^{2+}$ [10] showed that the rate constant decreases as the salt concentration increases, but no simple dependence on the activity of water was found. The effects of added cations on the kinetics of dissociation of $\text{Fe}(\text{bipy})_3^{2+}$ in water [11] and of tris(5-nitro-1,10-phenanthroline)iron(II) in aqueous binary mixtures [12] were attributed to the ability of the cation to modify the 'structure of liquid water'.

A more detailed study on the ability of salts to alter the rate constant of the acid dissociation of $\text{Fe}(\text{phen})_3^{2+}$ indicated an almost linear decrease in the rates *versus* an increase in salt concentration and a correlation between this effect and the intrinsic properties of the cations, such as crystallographic radii, enthalpy and entropy of hydration, etc. Deviation from linearity in plots of the rate constants against the added salt concentration are ascribed to ion pair formation and to nucleophilic action of anions [13–15].

In this work, we have studied the effect of added salts on the acid dissociation of $\text{Fe}(\text{bipy})_3^{2+}$ in an attempt to show that decreasing action of the cations coexists with the formation of ion-pairs between the anions and the complex. The results were published in part in previous communications [13, 16, 17].

Experimental

Tris(2,2'-bipyridine)iron(II) perchlorate was prepared under nitrogen atmosphere in a water-methanol solution of 0.38 g (1.3 mmol) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, by adding 0.51 g (3.3 mmol) of bipyridine and precipitating with a solution of sodium perchlorate. The crude product was recrystallized from water-methanol.

All chemicals were analytical grade (Merck, Fluka, Carlo Erba) products and were utilized without further purification.

Kinetic runs were done in aqueous solutions of LiCl , NaCl , KCl , NH_4Cl , MgCl_2 , CaCl_2 , SrCl_2 , BaCl_2 , NaBr , KBr , NH_4Br , and MgBr_2 of varying molality from 0 to 2.5. HCl was always added to form 0.012 mol dm^{-3} solutions in order to inhibit complex reformation. The concentration of the complex was *ca.* 10^{-5} mol dm^{-3} . The hydrolysis was monitored photometrically at 525 nm in a PM2D Carl Zeiss spectrophotometer, at 20.00, 25.00 and 30.00 ± 0.03 °C for at least two half-lives. Rate constants values were obtained from gradients of plots of $\ln A$ against time by a least-squares treatment. Duplicate or triplicate runs were reproducible to within ±1%.

Salt solutions of molal concentration were prepared, when possible, directly by weight. In other cases, LiCl for example, the prepared solution was titrated potentiometrically with a silver electrode in a METROHM E520 potentiometer, the molal concentration being calculated through density measurements.

About 650 kinetic runs were performed and most of the values plotted are mean values obtained from, at least, two different experiments. The activation energies of Arrhenius were calculated in the usual way and the values have a mean deviation of about $\pm 2 \text{ kJ mol}^{-1}$.

Results

The linear plots of the natural logarithm of absorbance *versus* time, over five half-lives indicate that acid hydrolysis of $\text{Fe}(\text{bipy})_3^{2+}$ is first order in the complex up to 2.5 mol kg^{-1} salt solutions.

Tables I to III show the rate constants in the various solutions of salts at 20.00, 25.00 and 30.00 °C and the activation energies of Arrhenius. Figure 1 represents the plots of the rate constants *versus* the molal concentration of cations at 25.0 °C.

The rates of reactions *versus* salt concentration increase up to a maximum at *ca.* 0.5 to 1 mol kg^{-1} in chloride and *ca.* 0.3 mol kg^{-1} for bromide in almost all the series of salts solutions. Afterwards a linear decrease is observed. The maximum rate constant is not exactly the same for all salts but follows approximately the order alkaline chlorides > alkaline-earth chlorides > bromides. The decreasing effect observed after the maximum is quasi linear with respect to the salt (or cation) concentration.

Based on the retardation constant, k_r , (see Table IV) we can say that the order of the effectiveness in retarding the reaction is about the same as that observed for the acid hydrolysis of $\text{Fe}(\text{phen})_3^{2+}$ [13–15], *i.e.*, $\text{MgBr}_2 > \text{MgCl}_2 > \text{CaCl}_2 > \text{SrCl}_2 > \text{NaBr} > \text{BaCl}_2 > \text{NH}_4\text{Br} \approx \text{KBr} > \text{LiCl} > \text{NaCl} > \text{KCl} > \text{NH}_4\text{Cl}$, except in the case of KCl and NH_4Cl where we have an apparent inversion of position. The deviations of the values of the retardation constants are very expressive and we must be very careful when the difference between two k_r values is small. The retardation constant is defined as $k_r = \epsilon/k_0$ where ϵ is the absolute value of the slope of the mean straight line, after the maximum-values of k (see Fig. 1), obtained by least squares, and k_0 is the rate constant in the absence of salt.

It is very difficult to decide about the trend of the Arrhenius activation energy because of the small variations compared with the deviation of $\pm 2 \text{ kJ mol}^{-1}$. Nevertheless, we can observe that the trend of the activation energy is decreasing in going from pure water to the salt solution.

TABLE I. Observed First Order Rate Constants (k) for the Acid Hydrolysis of $\text{Fe}(\text{bipy})_3^{2+}$ in the Presence of Various Concentrations of LiCl, NaCl, KCl and NH_4Cl at 20.00 \pm 0.03, 25.00 \pm 0.03 and 30.00 \pm 0.03 °C and the Arrhenius Activation Energies. $[\text{H}^+] = 0.012 \text{ mol dm}^{-3}$ (HCl)

c (mol kg^{-1})	LiCl			NaCl			KCl			NH_4Cl		
	$k \times 10^4$ (s^{-1})			E_a (kJ mol^{-1})			$k \times 10^4$ (s^{-1})			E_a (kJ mol^{-1})		
	20 °C	25 °C	30 °C	20 °C	25 °C	30 °C	20 °C	25 °C	30 °C	20 °C	25 °C	30 °C
0	0.563	1.27	2.96	122.6	122.6	122.6	0.563	1.27	2.96	122.6	122.6	122.6
0.075	0.619	1.40	3.09	118.8	118.8	118.8	0.616	1.36	3.12	119.8	118.2	119.5
0.112	—	1.42	—	—	—	—	—	—	—	—	—	119.9
0.175	0.633	1.37	3.18	119.2	119.2	120.4	0.629	1.38	3.21	120.4	117.4	118.9
0.250	0.650	1.43	3.20	117.8	117.8	120.6	0.629	1.42	3.22	120.6	117.6	120.1
0.500	0.655	1.46	3.23	117.9	117.9	121.1	0.643	1.46	3.31	121.1	116.8	119.9
0.750	0.658	1.44	3.24	117.8	117.8	120.5	0.640	1.45	3.27	120.5	117.5	119.8
1.00	0.646	1.45	3.22	118.7	118.7	119.0	0.649	1.47	3.25	119.0	116.6	119.7
1.25	0.640	1.42	3.16	118.0	118.0	118.6	0.647	1.46	3.22	118.6	116.6	118.8
1.50	0.619	1.38	3.12	119.5	119.5	119.4	0.635	1.46	3.32	117.3	117.3	118.6
1.75	0.614	1.38	3.08	119.2	119.2	119.4	0.630	1.44	3.31	117.4	116.1	118.6
2.00	0.594	1.35	3.06	121.1	121.1	118.8	0.623	1.41	3.11	118.8	117.4	118.6
2.25	0.583	1.34	2.99	120.8	120.8	118.9	0.620	1.40	3.10	118.9	119.0	118.6
2.50	0.580	1.32	2.96	120.4	120.4	118.8	0.613	1.38	3.06	118.8	118.8	118.8

TABLE IV. Retardation Constants (k_r) for $\text{Fe}(\text{bipy})_3^{2+}$

Salt	$10^2 \times k_r$ (kg mol^{-1})	Salt	$10^2 \times k_r$ (kg mol^{-1})	Salt	$10^2 \times k_r$ (kg mol^{-1})
LiCl	6.9	MgCl ₂	25.4	NaBr	13.0
NaCl	4.4	CaCl ₂	19.9	KBr	7.9
KCl	2.7	SrCl ₂	19.4	NH ₄ Br	7.9
NH ₄ Cl	0.8	BaCl ₂	12.5	MgBr ₂	32.1

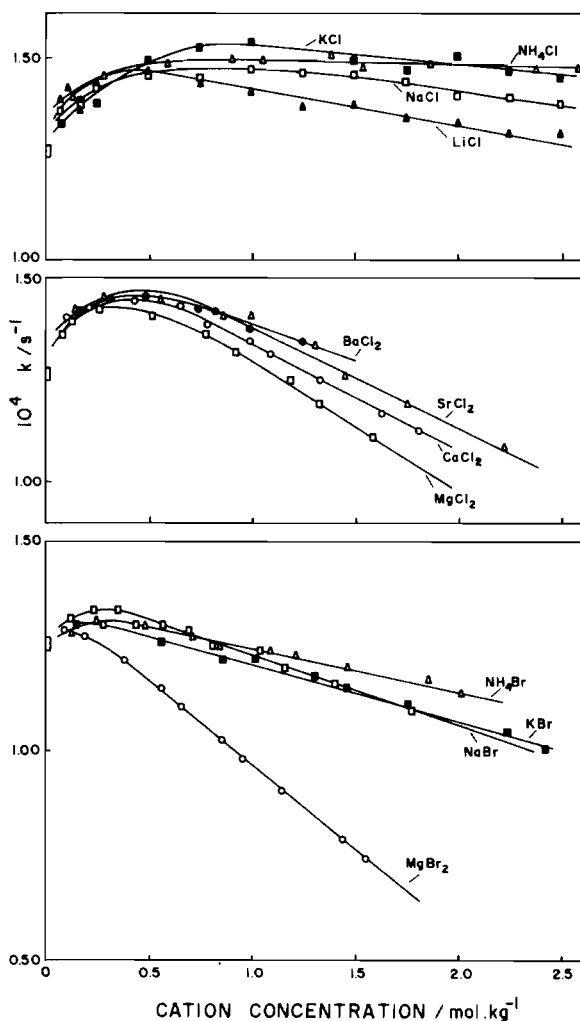


Fig. 1. Dependence of the acid hydrolysis first order rate constant, k , of $\text{Fe}(\text{bipy})_3^{2+}$ on the concentration of added salts, at $25.00 \pm 0.03^\circ\text{C}$. $[\text{H}^+] = 0.012 \text{ mol dm}^{-3}$ (HCl).

Discussion

Despite the large amount of work on kinetics of substitution reactions of low-spin iron(II) diimine complexes, particularly of $\text{Fe}(\text{phen})_3^{2+}$, $\text{Fe}(\text{bipy})_3^{2+}$ and its derivatives, the mechanism of dissociation of

these complexes in water and aqueous solvents is not yet clearly determined. Two mechanisms have been proposed [18, 19]. Basolo's mechanism [18] for the dissociation of $\text{Fe}(\text{bipy})_3^{2+}$ considers the rotation of one pyridine ring about the 2,2'-bipyridine bond, producing a half bonded intermediate that is sequentially protonated. This idea was reinforced by the study of the acid dissociation of tris complexes of iron(II) with non-symmetrical diimines [20, 21]. Gillard's proposition [19] assumes the formation of covalent hydrates as intermediates for the dissociation of phen and bipy ferrous complexes. It seems that these mechanisms, if really operative, are not mutually exclusive. Probably they could be cooperative, representing different ways of reaction, *i.e.*, parallel or in series mechanisms. In the first hypothesis (parallel), the domination of one over the other path could occur depending on specific ligand, solvent, acid or base concentration, etc. Independently of the assumed mechanism, it seems to be clear that in aqueous dissociation, water is important in the process [10, 19, 22–28]. Experiments with deuterium oxide demonstrate this [23d, 28] although the entry of water to occupy a vacant site in the complex is considered unlikely according to results from high-pressure experiments [28]. The existence of a preequilibrium high-spin \rightleftharpoons low-spin occurring in reactions of iron(II) diimine complexes has been claimed [5, 28, 29]. Krumholz estimated at approximately 15 kcal mol^{-1} (63 kJ mol^{-1}) the difference between the enthalpies of formation of spin-paired and spin-free $\text{Fe}(\text{bipy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ [5].

The high-pressure acid aequation of $\text{Fe}(\text{bipy})_3^{2+}$ indicates, through the markedly positive activation volume values, a dissociative mechanism. An estimate of the contribution on the spin preequilibrium was made from the bond changes in tris(picolin-2-amine)-iron(II) occurring between low-spin (200 pm) and high-spin (220 pm) forms [28, 30]. The partial molar volume change of the order of $11 \text{ cm}^3 \text{ mol}^{-1}$ calculated using a simple spherical model is very close to the activation volume of aequation of $\text{Fe}(\text{bipy})_3^{2+}$ [28] and of $\text{Fe}(\text{phen})_3^{2+}$ and its derivatives [31] and can be certainly related to this. Despite this very good estimate we must not forget that such complexes are not completely filled spheres but have three major pockets between the three perpendicular ligand

planes [25] that can accommodate a total of six water molecules, the whole aggregate becoming quasi spherical. So, we have to suppose, that the estimate of the partial volume change referred to above includes the water molecules in the pockets. It is very difficult to decide whether such water molecules collaborate in the spin equilibrium or not. But it is not difficult to see that the high positive values of activation volume, in this case, cannot be assigned securely to the dissociative mechanism because the water molecules in the pockets can effectively act as nucleophiles. The proximity and orientation of these water molecules towards the iron atom could make possible a nucleophilic attack to the coordination sites vacated by the departure of the ligands [25]. According to Gillard's proposition [19] nucleophilic action is on the ligand. In both cases water molecules can assist the spin equilibrium. The two mechanisms are not mutually exclusive.

The studies of Merbach [32] on the high pressure effects on the rates of fast solvent exchange reactions for divalent and trivalent high-spin first row hexa-solvated transition metal ions, show a gradual change from **1a** to **1d** behaviour, in going from vanadium to nickel, after the d^5 configuration. Consequently we are inclined to believe that the mechanism of dissociation of $\text{Fe}(\text{bipy})_3^{2+}$ in the high-spin form is, probably, **1d**. However we must not forget that the low-spin \rightleftharpoons high-spin equilibrium is probably favoured to the right by the nucleophilic assistance of the water molecules, in Basolo's [25] or Gillard's [19] mechanisms.

In this discussion we will consider the existence of this nucleophilic action without specifying the electrophilic site in which it occurs.

It became very clear after Gillard's observation, that $\text{Fe}(\text{bipy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ do not dissociate in 100% H_2SO_4 [19], that water or other nucleophiles are indispensable for the dissociation of these complexes.

Previously we reported [14] that the rate of acid dissociation of $\text{Fe}(\text{phen})_3^{2+}$ in aqueous salts solutions decreases with increasing salt concentration. No significant nucleophilic action, of the ions, was observed in this case. In contrast, the acid dissociation of $\text{Fe}(\text{bipy})_3^{2+}$ shows an increasing effect that can be attributed to the anions (Fig. 1).

The difference between the two complexes can be understood in terms of the pronounced rigidity of phen ligands compared with the possibility of rotation about the 2,2 carbon bond in bipy [18].

In $\text{Fe}(\text{phen})_3^{2+}$ the six water molecules positioned in the pockets [25] will certainly have difficulty in changing with molecules of the bulk solvent because of steric difficulties. Probably, for the more deeply embedded three water molecules, in this complex, the water exchange is extremely difficult. So, the anions present in solution will not show a marked nucleo-

philic action. This is in accordance with experimental observation [14]. On the other hand, for $\text{Fe}(\text{bipy})_3^{2+}$, a less compact complex, the rotation of half of the ligand will favor the changing of the water molecules of the pockets with other water molecules or anions from the bulk solvent leading to the observed nucleophilic effect of anions (Fig. 1).

The above mentioned nucleophilic action of anions can be coexistent with the formation of ion-pairs. This formation leads to a retarding effect. The existence of external sphere ion-pairs between $\text{Fe}(\text{bipy})_3^{2+}$, $\text{Fe}(\text{phen})_3^{2+}$ and Cl^- , Br^- , I^- , etc. is indicated by solubility studies [33]. The hypothesis that ion-pair formation leads to a retarding effect in these complexes has already been invoked by other authors [10, 25, 34]. The formation of ion-pairs between Fe^{2+} , Ru^{2+} , Cr^{2+} phen tris complexes with several ions has been well established [35, 36].

In Fig. 1 we can see that the bromides retard the rates more than the analogous chlorides. As for the phen complexes we can suppose that this could be due to ion-pair formation. The existence of such species is reinforced by the well known fact that certain ions like ClO_4^- , BF_4^- and I^- , easily precipitate with $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Fe}(\text{bipy})_3^{2+}$ forming stable entities. In a preceding study of the $\text{Fe}(\text{phen})_3^{2+}$ acid dissociation in salt solution, the formation of ion pairs is quite evident [14].

The different rates observed in function of the cation concentration is certainly related to its hydration. Based on the three pockets model of Basolo [25], the assumption that the presence of a high concentration of hydrated cations can decrease the population of the water molecules properly oriented for coordination, explains the decreasing observed effect. If the model of Gillard [19] is considered we would arrive at the same conclusion.

The very good correlations obtained between the retardation constant, k_r [13–15], and several parameters like, enthalpy and entropy of hydration, re-orientation times of water molecules in the hydration shell of ions, crystallographic radii, etc., reinforce the above exposed idea about the decrease in the population of properly oriented water molecules in the hydration sphere of the complex. In other words, the transfer of water molecules from bulk solvent to the hydration shells of the cation of the added salts [4] perturbs the water molecules into the pockets by a chain effect transmitted through hydrogen bonds.

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