

**On the Acid Hydrolysis of Tris( $\alpha$ -diimine)iron (II) Complexes.  
Variable Pressure Studies of the Acid Hydrolysis of  
Tris(Pyridine-2-Carboxaldehyde-N-Alkylimine) Iron (II)  
Complexes**

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Estudou-se a dependência da pressão, de 0,1 a 100 MPa, da hidrólise ácida dos complexos tris(piridina-2-carboxaldeído-N-metilimina) de ferro(II), tris(piridina-2-carboxaldeído-N-etilimina) de ferro(II), tris(piridina-2-carboxaldeído-N-propilimina) de ferro(II), tris(piridina-2-carboxaldeído-N-butilimina) de ferro(II), à temperatura e força iônica constantes. Os volumes de ativação experimentais foram  $11,5 \pm 0,3 \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $14,2 \pm 0,3 \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $13,0 \pm 0,3 \text{ cm}^3 \cdot \text{mol}^{-1}$  e  $13,1 \pm 0,3 \text{ cm}^3 \cdot \text{mol}^{-1}$ , respectivamente. Estes resultados, juntamente com os volumes de ativação para  $\text{Fe}(\text{bipy})_3^{2+}$  e  $\text{Fe}(\text{phen})_3^{2+}$  e o mecanismo de Basolo estabelecido para a hidrólise ácida destes complexos, indicam claramente a importância da dissociação de ligações na reação (id).

The pressure dependence, from 0.1 to 100 MPa, of the acid hydrolysis of the complexes tris(pyridine-2-carboxaldehyde-N-methyl-imine)iron (II), tris(pyridine-2-carboxaldehyde-N-ethylimine)iron(II), tris(pyridine-2-carboxaldehyde-N-n-propylimine)iron(II), tris(pyridine-2-carboxaldehyde-N-n-butylimine)iron(II) was studied at constant temperature and ionic strength. The experimental activation volumes were, respectively,  $11.5 \pm 0.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $14.2 \pm 0.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $13.0 \pm 0.3 \text{ cm}^3 \cdot \text{mol}^{-1}$  and  $13.1 \pm 0.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ . These results, taken together with the activation volumes of  $\text{Fe}(\text{bipy})_3^{2+}$  and  $\text{Fe}(\text{phen})_3^{2+}$  and with the Basolo's mechanism established for the acid hydrolysis of these complexes, indicated clearly the importance of bond dissociation in the reaction (Id)

**Key words:** diimines; complexes; iron II; hydrolysis.

## Introduction

The beginning of the study of the acid hydrolysis of iron(II)- $\alpha$ -diimines complexes can be attributed to the work of Lee, Kolthoff and Leussing<sup>1</sup>, who studied the acid aqueous dissociation of tris (1,10-phenanthroline)iron(II),  $\text{Fe}(\text{phen})_3^{2+}$ . This process is almost acid independent. Baxendale and George<sup>2</sup> and Krumholz<sup>3</sup> were the first to examine the acid hydrolysis of tris(2,2'-bipyridine)iron(II),  $\text{Fe}(\text{bipy})_3^{2+}$ . The latter author<sup>3</sup> proposed the existence of the intermediate  $\text{Fe}(\text{bipy})_3\text{H}^{3+}$  to explain the dependence of the process on the acid concentration. The resulting equation for the rate constant fitted very well the experimental results. The influence of the nature and quantity of the salt and acid present in the solution was pointed out. The mixture  $\text{LiCl} + \text{HCl}$  was suggested as the most appropriate to maintain the ionic strength of the medium<sup>3</sup>.

Considering that the protonated intermediate proposed by Krumholz was not detected and to explain the difference between the acid hydrolysis of  $\text{Fe}(\text{phen})_3^{2+}$  and that of  $\text{Fe}(\text{bipy})_3^{2+}$ , Basolo, Hayes and Newmann<sup>4</sup> proposed another mechanism, where the possibility of the existence of

a half bonded unprotonated intermediate is considered. In the case of the 2,2'-bipyridine complex, a rotation around the 2,2' carbon-carbon bond is possible and such an intermediate could be protonated on the leaving nitrogen, leading to dissociation. In the 1,10-phenanthroline complex, acid must be also present to avoid complex reformation, but due to the rigidity of the ligand molecule, this mechanism is not possible and the reaction independence of the acid concentration could be understood.

Murmann and Healy<sup>5</sup>, in the study of the acid hydrolysis of tris(pyridine-2-carboxaldehyde-N-alkylimine)iron(II) complexes, reconsidered Krumholz's hypothesis that supposes the formation of a protonated intermediate. They suggested the existence of mono- and bi-protonated species and proposed a quadratic equation to fit kinetic results.

More detailed studies, however, of the acid dissociation of tris(pyridine-2-carboxaldehyde-N-metilimine)iron(II), tris(pyridine-2-carboxaldehyde-N-propylimine)iron(II)<sup>6</sup> and tris(pyridine-2-acetaldehyde-N-methylimine)iron(II)<sup>7</sup>, at constant ionic strength, showed a very good quantitative

fit with the mechanism proposed by Basolo *et al.*<sup>4</sup>

Gillard<sup>8</sup> in order to explain the small decrease of the acid hydrolysis rate constant of  $\text{Fe}(\text{phen})_3^{2+}$  with increasing acid concentration and other kinetic, thermodynamic and spectroscopic properties in the dissociation of iron(II)- $\alpha$ -diimines complexes, proposed another mechanism where the ligand is considered to be the site of the nucleophilic attack. If water is the nucleophile, a hydrate is initially considered to be formed, followed by a proton dissociation that leads to the formation of a pseudo-base.

The influence of the cations and anions present in solution on the mechanism of the aqueous acid dissociation of such complexes, including  $\text{Fe}(\text{phen})_3^{2+}$ , however, can be visualized through ion-pair formation, water molecules transference from complex to salt ions "atmosphere", etc., without the necessity to assume the nucleophilic attack on the ligand<sup>9-12</sup>.

Notwithstanding the different approaches to these systems, a convergence can be noted, i.e., most authors agree that the presence of water is essential in the dissociative process<sup>10-15</sup>.

After more than four decades of studies in this subject, the mechanism of acid aqueous dissociation of such complexes has not been unequivocally established.

The present work was done with the intention to contribute to the understanding of this kind of mechanism.

## Experimental

**Chemicals:** 2-pyridinecarboxaldehyde (picolinaldehyde) 99% (Aldrich), methylamine (40% solution-Riedel), ethylamine (50% solution-Riedel), n-propylamine (Sigma), n-butylamine (Riedel),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Carlo Erba, PA), LiCl (Fluka, PA), HCl (36%, Merck, PA),  $\text{NaClO}_4$  (Reagen, PH) were used without further purification.

Pure ethanol was prepared from good quality commercial 96% product using the method of Lund and Bjerrum<sup>16</sup>.

Water utilized was obtained from a glass distiller.

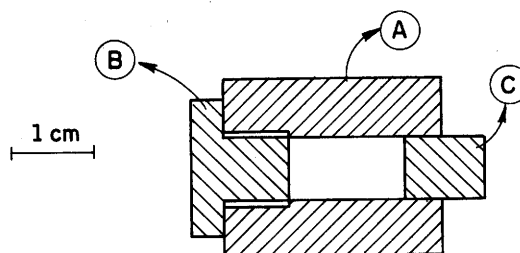
**Synthesis of the complexes<sup>5,19</sup>:** The procedure utilized for the synthesis of the studied complexes was similar in the four cases. In a flask purged with argon about 10 ml of ethanol were added. Argon was bubbled during some minutes and then 20 mmol of 2-pyridinecarboxaldehyde were introduced followed by gentle addition of 20 mmol of the aliphatic amine. The mixture was allowed to react during 1 hour at room temperature (ca. 25°C) under argon atmosphere. Then 10 ml of a carefully deaerated aqueous solution containing about 6.5 mmol of the iron(II) were slowly added under argon current. A dark violet color was immediately formed. The mixture was allowed to react during two hours at room temperature and then was filtered through sinterized glass filter to remove solids such as iron hydroxides, etc. The filtrated was cooled in an ice bath and the complexes were precipitated as perchlorates by careful dropwise adding of  $\text{NaClO}_4$ , 0.5 M, 1.0 M and 4.0 M aqueous solutions, in this sequence. The flask was kept in a refrigerator at 5°C overnight and then the precipitate was filtered and washed with 0.1 M and 0.002 M solutions of sodium perchlorate. The solid was dried in a desiccator over silica gel. *Obs: do not dry in an oven.* The crude product was recrystallized from ethanol-water solution by dropwise adding sodium perchlorate solutions 0.1 M, 1.0 M and 4.0 M. Fractions were always tested kinetically and recrystallization was considered satisfactory when two or more of

them gave the same rate constant within the accepted experimental deviation of  $\pm 1\%$ . These fractions were jointed and used for the experiments.

**Kinetic experiments:** The rate studies were carried out spectrophotometrically at the maximum absorbance wavelength of each complex, i.e., 551 nm for tris(pyridine-2-carboxaldehyde-N-methyl-imine)iron(II), PMI, 556 nm for tris(pyridine-2-carboxaldehyde-N-ethylimine)iron(II), PEI, 560 nm for tris(pyridine-2-carboxaldehyde-N-n-ethylimine)iron(II), PPI and 560 nm for tris(pyridine-2-carboxaldehyde-N-n-butylimine)iron(II), PBI. The temperatures of the solutions were chosen to obtain suitable reaction times, i.e., 43.00°C (PMI), 40.02°C (PEI), 35.00°C (PPI) and 35.02°C (PBI). The activation volumes were assumed, as usual, to be constant in a small temperature range.

The kinetic runs, under atmospheric pressure, were performed in glass tubes immersed in a thermostatic bath. Sampling of the solutions was done in adequate time intervals and absorbance was measured on a Carl Zeiss PM2D spectrophotometer at the maximum absorbance wavelength of each complex. Experiments were done in triplicates. Temperature oscillations were less than  $\pm 0.01^\circ\text{C}$ . Temperature was measured with a 1/10 scale JUMO mercury thermometer standardized to  $\pm 0.02^\circ\text{C}$ . Oscillations of temperature were observed with a thermistor coupled to a Wheatstone bridge and registered on a chart recorder. Rate constants were reproduced to within  $\pm 1\%$ .

Experiments under higher pressures were performed in a high pressure thermostated steel cell containing the reaction cell (Figure 1) with the solutions of the complexes. This steel cell is similar to, but bigger than, that described by Merbach *et al.*<sup>18</sup>. It has an external diameter of 6 cm, an internal of 3 cm and was 10 cm long. The control of temperature was done by vigorously circulating thermostated water through a helical groove carved in the outer surface of the cylinder. The temperature measurements were done in a 4 1/2 digit CIE multimeter. Resistance values were transformed to temperatures through a standard table. The temperature of laboratory was controlled to  $\pm 1^\circ\text{C}$  to avoid significant oscillations in the temperature of the reaction, as there is not an external isolation Jacket<sup>18</sup>. The observed temperature oscillation in the cell was less than  $\pm 0.05^\circ\text{C}$ .



**Figure 1.** Reaction optical cell. (A) PTFE body. (B) Acrylic screw window. (C) Acrylic sliding window. Pressure is transmitted from the external water bath to the internal solution by the sliding movement of C. The cell is filled with the solution and closed by B.

The reaction was monitored by a Micronal B-382 UV-VIS spectrophotometer in which the high pressure cell was mounted. The high pressure was generated with a screw-piston system compressing a mineral oil. A liquid-liquid separator allows compression of the reaction cell with water, thus avoiding reading problems in the spectrophotometer due to the presence of oil in the optical path. Transmission of the high pressure from the generation system to the steel cell was done through a flexible capillary steel tube. Pressure readings were performed with a standardized 4 1/2 digit piezoelectric system.

The initial concentration of the complexes was about  $1.10^{-4}$  M. In the beginning of the reaction the absorbance was always very high to permit a delay (minimum 15 minutes) for good thermostaticization. Solutions always contained 0.100 M hydrochloric acid and 1.900 M lithium chloride ( $\mu = 2.000$  M, HCl + LiCl). Reactions were followed for at least 3 half lives. The data were treated as usually done for first order reactions to obtain rate constants. Infinite absorbances were considered when no further variation of the reading was observed. Rate constants under high pressure were reproduced to within  $\pm 1.5\%$ . Most of the reported constants are a mean of at least two experiments.

The activation volumes  $\Delta V^*$  were calculated using the equation:

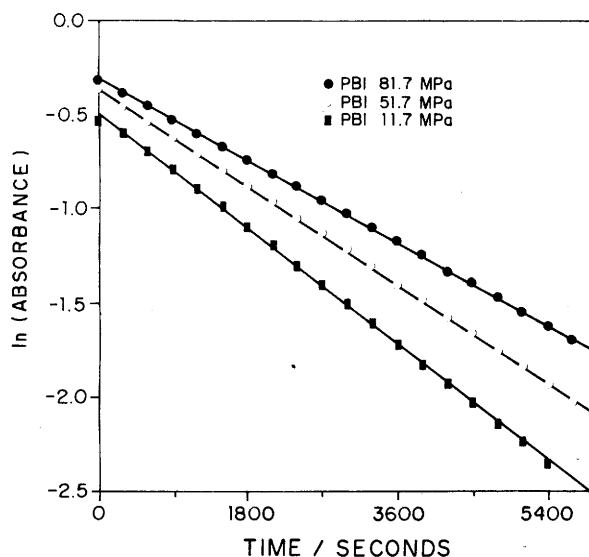
$$\ln k = \ln k_0 - \Delta V_0^* P/RT + \Delta\beta^* P^2/2RT$$

In the quadratic fits, the compressibility coefficients of activation  $\Delta\beta^*$  were equal to zero within experimental errors. Therefore, the second order term was neglected and linear fits were used.

Calculations were performed with a personal computer using a least squares program.

**Table 1.** Experimental pseudo first order rate constants of PMI, PEI, PPI and PBI complexes at various pressures and activation volumes for the aqueous acid dissociation. Temperatures of the reactions: PMI = 43.00°C; PEI = 40.02°C; PPI = 35.00°C; PBI = 35.02°C.

Pressure / (MPa)	k/(10 <sup>-4</sup> s <sup>-1</sup> )			
	PMI	PEI	PPI	PBI
0.1	1.42	5.26	4.37	3.60
11.7	1.38	5.11	4.10	3.43
21.7	1.32	4.74	3.94	3.25
31.7	1.29	4.42	3.76	3.10
41.7	1.14	4.18	3.57	2.95
51.7	1.08	3.86	3.36	2.81
61.7	1.10	3.68	3.16	2.74
71.7	0.98	3.53	3.05	2.54
81.7	0.96	3.39	2.83	2.29
91.7	0.93	3.17	2.71	2.24
101.7	0.91	2.98	2.57	2.15
$\Delta V^*$ (cm <sup>3</sup> /mol)	11.5 ± 0.03	14.02 ± 0.03	13.0 ± 0.03	13.1 ± 0.03

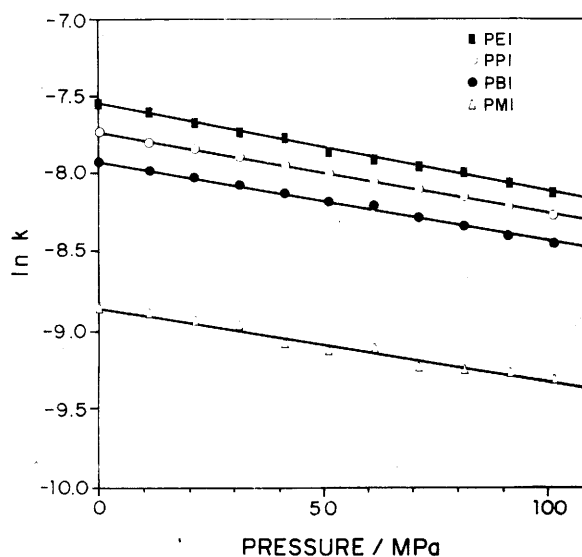


**Figure 2.** Decrease of the logarithm of the absorbance of the complex PBI at various pressures. As other complexes studied, the reaction is always first order, independent of the applied pressure.

## Results and Discussion

As expected, the acid hydrolysis reactions of the four studied complexes are first order in complex, in the range of pressure studied, i.e., from 0.1 up to 101.7 MPa. Figure 2 shows typical curves of the decreasing of the natural logarithm of the absorbance versus time at various pressures.

Figure 3 shows the relations between the natural loga-



**Figure 3.** Pressure dependence of the logarithm of the pseudo first order rate constant.

riethm of the first order rate constants and the pressure for the studied complexes. Table 1 shows the observed rate constants at various pressures and the calculated values of the activation volumes.

The activation volumes obtained for PMI, PEI, PPI and PBI,  $11.5 \text{ cm}^3 \text{ mol}^{-1}$ ,  $14.2 \text{ cm}^3 \text{ mol}^{-1}$ ,  $13.0 \text{ cm}^3 \text{ mol}^{-1}$  and  $13.1 \text{ cm}^3 \text{ mol}^{-1}$ , respectively, indicate a dissociative interchange mechanism, Id. As the hydrolysis of such complexes is acid and ionic strength dependent, the condition  $[\text{HCl}] = 0.100 \text{ M}$  and  $[\text{LiCl}] = 1.900 \text{ M}$  was fixed<sup>3,5-7</sup>. Similar results for activation volumes were obtained for the acid dissociation of tris(2,2'-bipyridine)iron(II) ( $12$  to  $15 \text{ cm}^3 \text{ mol}^{-1}$ , depending on the acid concentration of the solution) and tris(1,10-phenanthroline)iron(II) ( $15.4 \text{ cm}^3 \text{ mol}^{-1}$ ) complexes<sup>15</sup>. The acid dissociation of the latter complex is acid independent but depends on the ionic strength of the solution<sup>11</sup>.

It is very significant that iron(II) complexes with either symmetric or unsymmetric  $\alpha$ -diimines have analogous activation volumes for the acid hydrolysis. This fact probably indicates that a similar mechanism is operating in all cases.

Several authors<sup>19-21</sup> suggested that the low spin - high spin equilibrium could be the rate determining step of this reaction. The volumes expansion calculated for the spin transition in  $\text{Fe}(\text{phen})_3^{2+}$  ( $15.4 \text{ cm}^3 \text{ mol}^{-1}$ )<sup>24</sup> and for tris(picolin-2-amine)iron(II) ( $11 \text{ cm}^3 \text{ mol}^{-1}$ )<sup>15</sup> are very suggestive as they are very close to the experimental values for the acid hydrolysis of iron(II)- $\alpha$ -diimine complexes, including those in this work, with unsymmetrical ligands.

The transition from the low to the high spin state can be considered as the result of the withdrawal of the entire ligand and, in the case of non rigid ligands, by the almost complete leaving of one nitrogen by the formation of the half bonded intermediate. As water is essential in the dissociative process<sup>10-15</sup>, it will probably collaborate in this transition.

If the attack of water molecules occurs on the central ion, similar values of volumes of activation could be expected for iron (II) complexes with similar ligands, since it is reasonable to suppose that the influence of the ligand would be somewhat minimized in this kind of mechanism. If the attack of the nucleophile occurs on the ligand, as it has been proposed<sup>8</sup>, the influence of the ligand would be certainly enhanced and in such a situation, activation volume would be strongly affected by the nature of the ligand. Since it is known that pyridine-2-carboxaldehyde-N-alkylimines hydrolyze easily, it is possible that this could occur. However, evidence that the acid dissociation of these iron(II) complexes is preceded by ligand hydrolysis was not found<sup>5</sup>.

As the results obtained in this work show similar values of activation volumes of reaction to those obtained for both<sup>15</sup>  $\text{Fe}(\text{bipy})_3^{2+}$  and<sup>21</sup>  $\text{Fe}(\text{phen})_3^{2+}$ , we are forced to admit that in this kind of reaction a similar fundamental dissociative mechanism is occurring. This hypothesis can only be supported if the attack occurs on the iron and not on the ligand molecule where, it is supposed, water molecules could attack forming "hidrato complexes"<sup>8,22</sup> that by dissociation of a proton, can form a "pseudo base"<sup>8,22</sup>. The hypothesis that the ligand is the site of the nucleophilic attack has also been discredited by the observation<sup>23</sup> that the complex bis(2,2'-bipyridine)copper(I) does not dissociate in ethanol-water solution at room temperature (ca.  $25^\circ\text{C}$ ) with

an acid concentration of  $0.08 \text{ M}$  (HCl) over a period of 45 days. If this mechanism was operating, dissociation should occur.

Copper(I) presents a complete  $d^{10}$  configuration while iron(II) and nickel(II) have  $d^6$  and  $d^8$  configurations, respectively. Iron(II)- $\alpha$ -diimine complexes present activation volumes, for the acid hydrolysis, of about  $11$  to  $15 \text{ cm}^3 \text{ mol}^{-1}$  and the analogous complexes of Ni(II) have values<sup>24,25</sup> from  $0$  to  $-1 \text{ cm}^3 \text{ mol}^{-1}$ . These observations are very suggestive and reinforce the supposition that the nucleophilic attack occurs on the central ion, and therefore, the rate depends on the electronic configuration of the metal. It seems that empty d orbitals are necessary in this reaction.

In our point of view, Basolo's mechanism, for the acid hydrolysis of iron(II)- $\alpha$ -diimine complexes, is reinforced by the results discussed above. Other authors have reached the same conclusion by studying similar systems<sup>15,26,27</sup>. Basolo's mechanism is also reinforced by recent NMR studies<sup>28</sup> on the 2,2'-bipyridine proton-deuterium exchange in the tris complexes of ruthenium, osmium and rhodium, which showed that the reaction proceeds by an acid-base mechanism rather than a nucleophilic attack upon the coordinated ligand. Certainly, Gillard's<sup>8</sup> proposition cannot be discharged, at least, as an alternative mechanism which may be valid for other ligands and/or with other transition metals, and in basic aqueous solutions.

In the Basolo's mechanism for Fe(II)- $\alpha$ -diimines acid hydrolysis<sup>4</sup>, the activation volume provide an important criterion for the associative-dissociative character. The high-pressure studies on the hydrolysis<sup>15</sup> of  $\text{Fe}(\text{bipy})_3^{2+}$  and<sup>21</sup>  $\text{Fe}(\text{phen})_3^{2+}$  are important: activation volumes for these complexes are similar to the values of PMI, PEI, PPI and PBI complexes. These results, taken together with the Basolo's mechanism<sup>4</sup> established for  $\text{Fe}(\text{phen})_3^{2+}$ , indicated clearly the importance of bond dissociation in the reaction (interchange dissociative mechanism).

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