Reaction between Iron(III) and Pyrazoic Acid

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Abstract

In the reaction of $[Fe(H_2O)_6]^{3+}$ with pyrazoic acid, reduction of iron(III) to iron(II) is observed. When an excess of iron is present, the reaction involves a transfer of four electrons per mole of acid. At room temperature the redox reaction, which is dependent on hydrogen ion, iron(III) and pyrazoic acid concentrations, is rather slow and is the rate-determining step. The kinetic study was carried out at 50.0 ± 0.1 °C. The redox reaction is followed by a fast reaction of the iron(II) with an excess of ligand, resulting in the production of well-known complexes, where the acid acts as a chelating ligand through the nitrogen and oxygen atoms.

Introduction

The complexing properties of pyrazinecarboxylate derivatives are well known, and several papers have described the obtained results. Among them, a few papers from this laboratory reported the studies of the reaction of transition metal ions with pyrazinecarboxylic acids [1–4]. However, no data are available in the literature on the redox properties of these heterocyclic ligands.

In the present paper we report in detail the reaction of iron(III) with pyrazine-2-carboxylic acid (pyrazoic acid, HL) and show that the complex-formation reaction occurs after a redox reaction which gives iron(II) and an oxidation product of the organic ligand. The kinetics of the redox reaction, the equilibria of the formed complexes in aqueous solution and the stoichiometry of the precipitated complex were also investigated.

Experimental

Apparatus

Varian Superscan 3 spectrophotometer with 1.000 cm silica cells; Beckman DBG spectrophotometer; Perkin Elmer 125 grating IR spectrophotometer; DuPont 951 thermobalance and 990 differential thermal analyzer; Amel 334 pH-meter equipped with Ingold 303-NS electrode; Lauda R-10 and Gibertini thermostat.

Reagents

All solutions were prepared from distilled-deionized water. Pyrazine-2-carboxylic acid: purchased from Fluka, was purified by crystallization from water and dried at 105 °C. The purity was checked by melting point measurement, thermal analysis and potentiometric titration.

Stock solutions (0.1 M) were prepared by weighing the required amount of acid and dissolving this in water; sodium hydroxide solution was added up to pH = 3 to obtain complete dissolution.

Iron(III) perchlorate stock solutions (0.1 M): prepared by weighing the required amount of the salt Rudi Point, purified by crystallization from perchloric acid, and dissolving this in water; the hydrogen ion concentration was maintained at not less than 0.1 M by adding the proper quantity of perchloric acid. Iron(III) concentration was determined by complexometric titration. Sodium perchlorate stock solution (5 M): prepared by dis-

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solving the salt (BDH) in distilled-deionized water. Potassium dichromate standard solution: prepared by weighing the required amount of salt Merck (purified by two recrystallizations from water and dried at 150–200 °C), and dissolving this in water. All other chemicals used were analytically pure.

Analyses and Physical Measurements

The redox and the complex-formation reactions were investigated at different metal to ligand molar ratios and at different acidities. The ionic strength was adjusted to 1 M (ClO_4^-) by adding sodium perchlorate stock solution. The acidity of the solutions was adjusted by perchloric acid or sodium hydroxide solutions. In order to avoid local high OH^- concentration in the solution containing iron(III) ions it is important to add the sodium perchlorate and the pyrazoic acid solutions, adjusted with NaOH aqueous solution to achieve the required final acidity value, into a 250 ml calibrated flask containing the iron(III) solution, filling to the mark with water and checking the pH of the final solution. The NaOH solution must not be added directly to the iron(III) solution. Following this procedure the analytical results were reproducible. All kinetic experiments were performed at 50.0 ± 0.1 °C. The reaction occurs even at room temperature but its rate is slow; on the other hand, temperatures higher than 50 °C give rise to serious experimental difficulties. The redox reaction was studied by measuring the change in the concentration of iron(III) drawing an amount of the solution at fixed time (one or two hours), immediately cooling and titrating the iron(II) with potassium dichromate [5]. In these conditions the oxidation reaction of pyrazoic acid by the chromium(VI) is too slow to interfere with the iron(II) determination. The equilibria of the complexes in aqueous solution were studied at 25.0 ± 0.1 °C by a spectrophotometric method [6].

A solid complex was prepared by adding 50 ml of about 0.3 M aqueous solution of pyrazoic acid at pH 5 (adjusted by NaOH) to 2.2 g of $Fe(ClO_4)_3 \cdot 6H_2O$ dissolved in a few ml of water. The mixture was refluxed for 30 min and then cooled at room temperature. The dark red-violet precipitate was collected on a sintered glass, washed with water and dried *in vacuo* over silica gel for at least 48 h.

Results and Discussion

Redox Reaction

The experimental results showed that iron(III) reacts with pyrazoic acid in a 4:1 molar ratio to give iron(II) and an unidentified oxidation product of the heterocyclic ligand. In fact, the iron(III) was reduced quantitatively both in ligand and metal excess but, in the last case, only if molar ratio $C_M/C_L \leqslant 4$. The overall analysis of the kinetic curves indicated a first order dependence on both iron(III) (Fig. 1) and pyrazoic acid (Fig. 2) concentrations.

The pH-rate profile, reported in Fig. 3, showed a maximum rate at about pH 1.7. These profiles may be justified by the occurrence of secondary reactions which increase or slow the rate of the redox reaction (*e.g.* acido-base equilibria of pyrazoic acid) [1], hydrolysis reactions of iron(III) [7] and complexation equilibria of the iron(II) with excess of pyrazoic acid [2].

Complex Formation

When the reaction is carried out with a large excess of metal ion the final solution is colourless, showing that the oxidised form of the ligand does not react to form stable complexes. When the redox rection was performed with an excess of the heterocyclic ligand, the final solution was red in colour and its intensity, under the same conditions (pH,

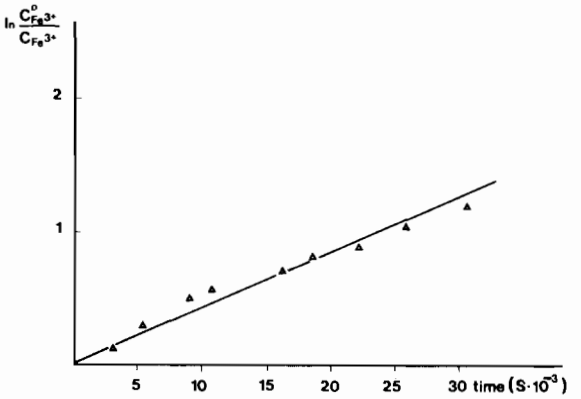


Fig. 1. Plot of an experimental run according to equation $\ln(C^o_{Fe^{3+}}/C^o_{Fe^{3+}}) = K't$ at pH = 1.50; $C^o_{Fe^{3+}} = 5.0 \times 10^{-4}$ M; $C_L = 2.0 \times 10^{-2}$ M. The solid line is calculated by linear regression method.

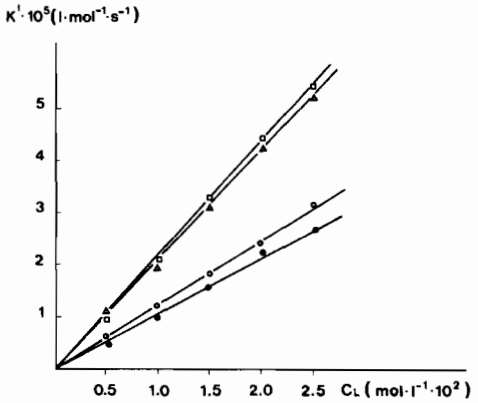


Fig. 2. Pyrazine-2-carboxylic acid dependence of K' at pH = 1.03 (○); pH = 1.52 (△); pH = 2.05 (□); pH = 2.48 (●). $C^o_{Fe^{3+}} = 5.0 \times 10^{-4}$ M.

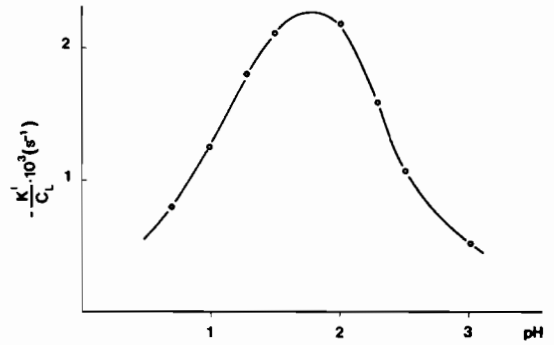


Fig. 3. pH dependence of K'/C_L; $C^o_{Fe^{3+}} = 5.0 \times 10^{-4}$ M.

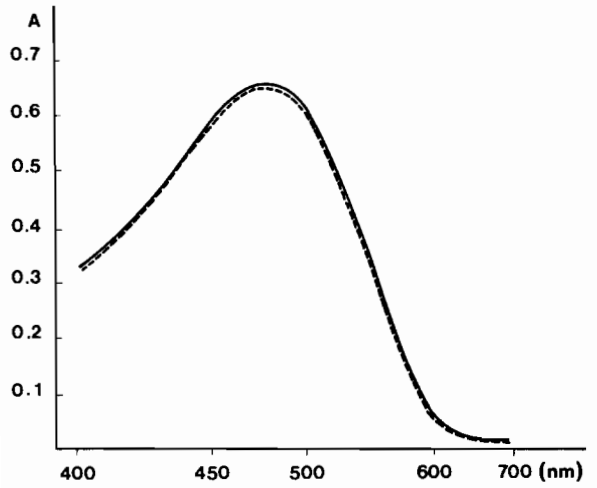


Fig. 4. Absorption spectra (at pH = 2.1; C_L/C_M = 50; $C_M = 5.0 \times 10^{-4}$ M; b = 1.000 cm) of iron(II)–pyrazine-2-carboxylic acid system (dotted line) and iron(III)–pyrazine-2-carboxylic acid (solid line) after that the redox reaction is complete.

C_L/C_M molar ratio), increases as the redox reaction proceeds.

The absorption spectra, recorded in the visible region (Fig. 4), were very similar to those of the iron(II)–pyrazine-2-carboxylic system [2] and the graphical analysis of the absorbance *vs.* acidity or ligand concentrations plots at selected wave-lengths (carried out using the usual equations [6]) proved that the complexation reactions occur between iron(II) and the excess of the ligand forming (FeL_2) and $(FeL_3)^-$ chelates.

The spectrophotometric characteristic of those complexes and the equilibrium constants (collected in Table I) were in agreement with those found for the iron(II)–pyrazoic acid system. It was not possible to examine the $(FeL)^+$ complex in the present study because it predominates only in experimental conditions too different (excess of metal ion or very high acidity). Concerning the solid compound, prepared as described above, on the basis of elemental, thermogravimetric and IR analysis, the $Fe(II)L_2 \cdot 2H_2O$ simplest formula can be assigned proving the above proposed reaction mechanism.

The reported results proved that pyrazoic acid is able to reduce iron(III) to iron(II) giving four electrons per mole at most (metal ion excess). Although it was not possible to separate and/or identify the pyrazoic acid in the oxidised form, we proved that a modification of the molecule occurs so that it loses the capability to form stable complexes with iron(III) or iron(II). Since formation of complexes between iron(III) and carboxylic acid derivatives of pyridine are known to occur without reduction of the metal ion giving stable chelates (*e.g.* aquachlorobis(α-picolinato)iron(III) [8]), the reducing

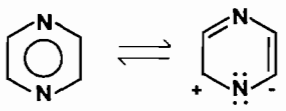
TABLE I. Molar Absorptivities and Equilibrium Constants for the Complexes of Iron(III)–Pyrazoic Acid (after redox reaction) and Iron(II)–Pyrazoic Acid Systems in Experimental Conditions Described in the text (charges and bound water molecules are omitted).

Complex	ϵ (l mol^{-1} cm^{-1}) at 470 nm		Equilibrium	log constant	
	Iron(III)	Iron(II)		Iron(III)	Iron(II)[a]
			$Fe + HL \rightleftharpoons FeL + H$		1.40 ± 0.05
FeL		440 ± 10			
			$Fe + L \rightleftharpoons FeL$		4.10 ± 0.1
			$FeL + HL \rightleftharpoons FeL_2 + H$		0.81 ± 0.05
FeL_2	850 ± 10	865 ± 10			
			$Fe + 2L \rightleftharpoons FeL_2$	7.5 ± 0.2	7.71 ± 0.1
			$FeL_2 + HL \rightleftharpoons FeL_3 + H$	0.2 ± 0.1	0.10 ± 0.05
FeL_3	1680 ± 20	1700 ± 20			
			$Fe + 3L \rightleftharpoons FeL_3$	10.4 ± 0.2	10.51 ± 0.1

[a]Ref. [2].

properties of pyrazine carboxylic acid may be attributed to the effect of the pyrazine ring.

This is less stable than pyridine to the action of oxidizing agent [9] owing to a resonance hybrid:



which allows an intramolecular electron-transfer from pyrazine to the ferric ion. In this case we must suppose a reaction mechanism involving a transient intermediate as proposed by Laurence and Ellis [10] in the oxidation of ascorbic acid by iron(III). The redox reaction is rather slow at room temperature while the formed iron(II) reacts immediately with the excess ligand, forming stable chelates with N–Fe–O sequence of bonds.

An analytical application of this reaction is possible for the selective detection of iron(II) and iron(III) ions, and further investigations are required.

Analogous redox and complex-formation reactions occur between iron(III) and pyrazine-2,3-dicarboxylic acid. Details will be described in a later paper.

Acknowledgement

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References

1 A. L. Magrì, F. Balestrieri, E. Chiacchierini, A. D. Magrì and A. Panzanelli, *Ann. Chimica, 68,* 585 (1978).
2 A. L. Magrì, A. D. Magrì, F. Balestrieri, E. Chiacchierini and G. Rossello, *Ann. Chimica, 69,* 489 (1979).
3 A. L. Magrì, A. D. Magrì, F. Balestrieri, E. Cardarelli, G. D'Ascenzo and L Chiacchierini, *Thermochim. Acta, 38,* 225 (1980).
4 A. L. Magrì, A. D. Magrì, F. Balestrieri, E. Cardarelli, G. D'Ascenzo and A. Panzanelli, *Thermochim. Acta, 48,* 253 (1981).
5 I. M. Kolthoff, E. B. Sandell, E. J. Meehan and S. Bruckenstein, 'Analisi Chimica Quantitativa', P. Piccin, Padua, Italy, 1973.
6 L. Sommer, I. Kucerova, H. Prochazova and M. Hnilickova, *Publ. Fac. Sci. Univ. Brno, 464,* 249 (1965); *C.A, 64,* 13455 (1966).
7 E. Chiacchierini, V. Petrone and A. L. Magrì, *Gazz. Chim. Ital., 105,* 205 (1975).
8 R. V. Thundathil, E. M. Holt, S. L. Holt and K. Watson, *J. Chem. Soc., Dalton Trans.,* 1438 (1976).
9 Y. T. Pratt, in R. C. Elderfield (Ed.) 'Heterocyclic Compounds, Vol. 6', Wiley, New York, p. 401.
10 G. S. Laurence and K. J. Ellis, *J. Chem. Soc., Dalton Trans.,* 1667 (1972).