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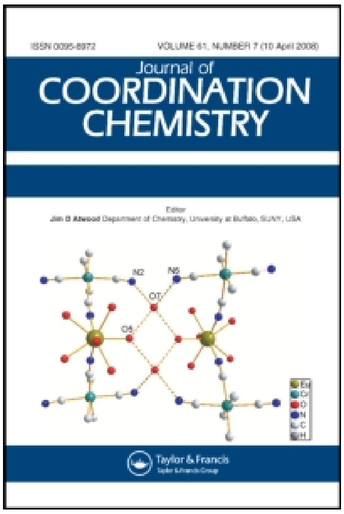

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KINETICS AND EQUILIBRIUM STUDIES OF IRON(II) COMPLEXES WITH PYRAZINECARBOXYLATE AND 1,10 BIPYRIDYL LIGANDS

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KINETICS AND EQUILIBRIUM STUDIES OF IRON(II) COMPLEXES WITH PYRAZINECARBOXYLATE AND 1,10 BIPYRIDYL LIGANDS

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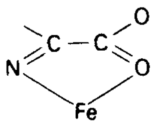
The properties and stability constants of a series of iron(II) complexes with the pyrazinecarboxylate ligand (pz) have been investigated spectrophotometrically, in aqueous solutions, in the presence of 0.10 M lithium perchlorate. The association constant K_1 obtained in this work for the $Fe(pz)^{+}_{aq}$ complex was equal 2.5×10^3 M^{-1}, while β_2 and β_3 for the successive 1 : 2 and 1 : 3 complexes, were 1.3×10^6 M^{-2} and 4.8×10^7 M^{-3}, respectively. The iron(II)-pyrazinecarboxylate complexes react with bipyridyl, producing intermediarily the deep red $Fe(pz)(bipy)^{+}_{2}$ complex, which is converted, after a few seconds, to the stable $Fe(bipy)^{2+}_{3}$ complex. From a detailed investigation of the kinetics of the formation and decomposition reactions, it was possible to solve for the stability constants of the mixed complexes, $Fe(pz)(bipy)^{+}_{aq}$ ($\beta_{11} = 5.6 \times 10^7$ M^{-1}), $Fe(pz)_2(bipy)$ ($\beta_{21} = 2.8 \times 10^{10}$ M^{-3}) and $Fe(pz)(bipy)^{+}_{2}$ ($\beta_{12} = 2.1 \times 10^{12}$ M^{-3}). Based on spectral, kinetics and equilibrium data, a discussion on the chemistry of the iron(II)-iminocarboxylates and the iron(II)-diimines is presented.

INTRODUCTION

It has been known, for a very long time,[1,2] that *N*-heterocyclic ligands having a carboxyl group in the α-position can form intensely colored complexes with aqueous iron(II) ions. Based on analogies from the chemistry of the iron(II)-α-diimines,[3] Krumholz[4] has associated the spectral properties of those complexes to the iron(II)-α-iminocarboxylate chromophore (IA, IB).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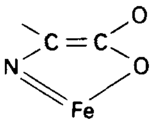
(IB)

In contrast with the chemistry of the iron(II)-α-diimines, the chemistry of the iminocarboxylate derivatives remains little explored. Exception is the case of some iron(II)-pyridinecarboxylates which have been employed in electron transfer[5] and equilibrium[6] studies. Krumholz has also shown that the spectra and the reactivity of the iron(II)-α-iminocarboxylates are consistent with a high spin configuration. The possibility of reaching the crossover point[7] by increasing the backbonding properties of the iminocarboxylate ligand, or by forming mixed complexes with strong field ligands, has attracted our interest to these series of complexes. Studies in this area can produce significant results for the understanding of charge-transfer interactions in high spin and low spin complexes, and of their role in determining the spin equilibrium condition.

The work reported here deals basically with the chemistry of iron(II) complexes with the pyrazinecarboxylate ligand and of mixed complexes formed with bipyridyl in aqueous solution. It shows some interesting aspects of substitution reactions of labile iron(II) complexes, which, to our surprise, have been little studied.[8] This paper also introduces a useful approach to the calculation of equilibrium constants, and illustrates an example of combination of kinetics and equilibrium methods in the investigation of complex equilibria.

EXPERIMENTAL SECTION

Materials

Pyrazine-2-carboxylic acid from Aldrich was recrystallized from saturated aqueous solution as white-colorless needles. The solid was kept under vacuum in the presence of calcium chloride for several weeks. The ligand 2.2′bipyridyl (Aldrich) was purified by an analogous procedure.

Stock solutions of iron(II) perchlorate were prepared by dissolving the pure metal (Merck) in diluted perchloric acid solutions containing 5% excess of free acid, under argon atmosphere. After several days, the pH was adjusted to 5–6 with lithium hydroxide. The concentration of the stock solution was checked periodically with the 1.10 phenanthroline colorimetric reagent.

Lithium perchlorate was prepared from lithium carbonate (Fisher) and perchloric acid (Merck). The solid was recrystallized first from a basic solution (pH 11) to remove ferric impurities, then from an acid solution and finally from a neutral solution. The amount of iron impurities was below the limit of detection with 1.10 phenanthroline.

Physical Measurements

The electronic spectra of the iron(II)-pyrazinecarboxylate complexes were recorded on a Cary 17 spectrophotometer. The spectra of the intermediates containing mixed ligands were obtained with the stopped-flow technique.

Potentiometric measurements were made with a digital Orion 801-A instrument, using combined glass-Ag/AgCl or platinum-Ag/AgCl electrodes. The determination of the equilibrium constants of the iron(II)-pyrazinecarboxylate complexes was carried out spectrophotometrically, using a Cary 14 instrument fitted with thermostatted cell compartments.

A cylindrical reservoir was especially designed to be directly attached to the conventional 10 mm or 50 mm cells in order to allow for successive addition of reagents. Ultraprecision Gilmont syringes (2.000 or 0.2000 ml) were used for the spectrophotometric titrations under argon atmosphere.

The kinetics of the formation and dissociation reactions in the iron(II)-pyrazinecarboxylate-bipyridyl system were investigated with a Durrum D-110 stopped-flow instrument. The data were recorded on a Hewlett Packard oscilloscope equipped with a polaroid camera.

All the calculations were carried out on a Hewlett Packard 97 calculator with the aid of several programs, including iterative and least square analysis.

RESULTS AND DISCUSSION

Basicity Constants and Spectra

The pyrazinecarboxylic acid is relatively strong in aqueous solution. Before starting the complexation studies, we have determined its pKa in 0.100 M solutions of lithium perchlorate, from direct acid-base titrations. Eq. (1) was used for the equilibrium.

$$\mathrm{pzCO_2H} \xrightleftharpoons{K_a} \mathrm{pzCO_2^-} + \mathrm{H^+}$$

$$\mathrm{pKa} = -\log[\mathrm{H^+}] + \log\left\{\frac{[\mathrm{Pz}]_T - ([\mathrm{Li^+}] + [\mathrm{H^+}] - [\mathrm{OH^-}])}{[\mathrm{Li^+}] + [\mathrm{H^+}] - [\mathrm{OH^-}]}\right\} \tag{1}$$

where the subscript T refers to the total concentration of the pyrazine species and the lithium ion concentration corresponds to the lithium hydroxide added during the titration. The hydrogen ion concentration was obtained from pH measurements, using activity coefficients estimated from Davies equation.[9] The pKa was equal 2.82 ± 0.01.

Application of Speakman's method[10] for dibasic acids gave little information on the protonation constant of the pyrazine group. However, we have obtained a reasonable estimate of pKa equal 0.45 ± 0.1 (at 25°C, 3.0 M lithium perchlorate/perchloric acid solution) based on systematic spectral changes at 310 nm with the pH. This wavelength corresponds to a n-π^* transition of the aromatic ligand, which is expected to be sensitive to protonation effects.

In the case of the pyridinecarboxylic acid, the pKa of the carboxylic and aromatic nitrogen groups have been reported[6] to be 5.32 and 1.01 respectively. The comparison shows that the presence of a second nitrogen in the aromatic ring reduces considerably the basicity of the ligand. The stronger π-acceptor ability of the pyrazinecarboxylate ligand, as compared with the pyridine analog, is evident in the electronic spectra of the complexes formed with iron(II) ions. In these complexes, the intense absorption band in the visible arises from a metal-to-ligand charge transfer transition. Using the simplified equation[11]

$$E_{CT} = I - A - C \tag{2}$$

where I is the ionization potential of the donor, A the electron affinity of the acceptor and C is a coulombic term, we can see that the energies of the charge transfer transition for two closely related complexes should vary directly with the electron affinities of the acceptor ligands.

The electronic spectrum of the tris(pyrazinecarboxylate) ferrate(II) complex is illustrated in Figure 1. For the pyridinecarboxylate analog, the charge transfer transition is observed at 445 nm (22.5×10^3 cm^{-1}), having an intensity smaller, by a factor of two, than the pyrazine complex. The bathochromic shift from 445 nm to 490 nm (20.4×10^3 cm^{-1}) in the last

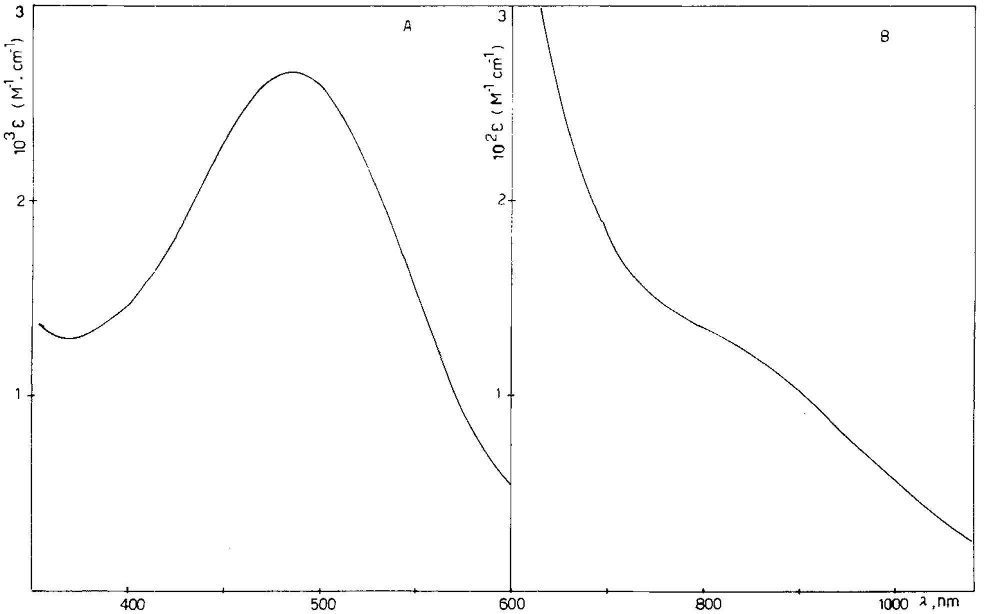

FIGURE 1 Electronic spectrum of an aqueous solution of the tris-(pyrazinecarboxylate)ferrate(II) complex (8×10^{-4} M), containing 0.10 M of free ligand, at 25°C, argon atmosphere, pH 6.

one is consistent with an enhancement of the charge transfer interaction, which is also corroborated by an increase in the intensity of the absorption band.

An attempt of measuring the ligand field spectra of the tris(pyrazinecarboxylate)ferrate(II) complex can be seen in Figure 1b. For high spin iron(II) complexes the $^5T_{2g} \rightarrow {}^5E_g$ transition is observed around 7000–12000 cm^{-1}, usually as two bands, due to the Jahn-Teller distortion. For the low spin complexes, $Fe(phen)_3^{2+}$ and $Fe(phen)_2(CN)_2$, the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition is observed[13] at 12260 and 12500 cm^{-1}, respectively. The transition appearing as a shoulder around 12000 cm^{-1} in the pyrazinecarboxylate complex lies within the crossover region[12] and is close to the ligand field transition of the related low spin complexes. In order to have a better understanding of the nature of the iron(II)-pyrazinecarboxylates, we have started a careful investigation on the kinetics and equilibrium involved in the system.

Equilibrium Studies

The use of spectrophotometric methods in the present work was favored by the fact that the reactants are practically colorless while the products are highly colored. To avoid the large number of successive non-linear extrapolations involved in the majority of the methods of determination of equilibrium constants[14–16] we have divided the study in two parts. Initially we have investigated the simplest equilibrium below,

$$Fe^{2+}\ (aq) + pz^- \overset{K_1}{\rightleftharpoons} Fe(pz)^+_{aq}$$

by working with some excess of Fe(II) ions over the pyrazinecarboxylate (pz) ligand (e.g. [pz] = 3×10^{-4} M, [Fe(II)] = $7–14 \times 10^{-4}$ M), and keeping the concentration of the complex as lowest as possible in order to prevent successive equilibria or dimerization processes.

The equilibrium constant K_1 can be expressed in the following way:

$$K_1 = \frac{[ML]}{[M][L]} = \frac{A/\varepsilon_1}{([M]_T - A/\varepsilon_1)([L]_T - A/\varepsilon_1)} \tag{3}$$

or

$$K_1 = \frac{\varepsilon_1 \cdot A}{(\varepsilon_1[M]_T - A)(\varepsilon_1[L]_T - A)}$$

where ε_1 is the extinction coefficient of the ML = $Fe(pz)^+$ complex, A is the absorbance measured for each pair of concentration of M = Fe(II) and L = pz, and the subscript T refers to the total concentration.

In the present system, the approximation $[M]_T$ = $[M]$ usually employed in the calculation of K_1 and ε_1 is a little crude and iterative[17,18] procedures should be preferred. By using eq. (3), we can start with an initial value of ε_1 (e.g. 400 M^{-1} cm^{-1}) and make a series of calculations of K_1 for each experimental measurement.

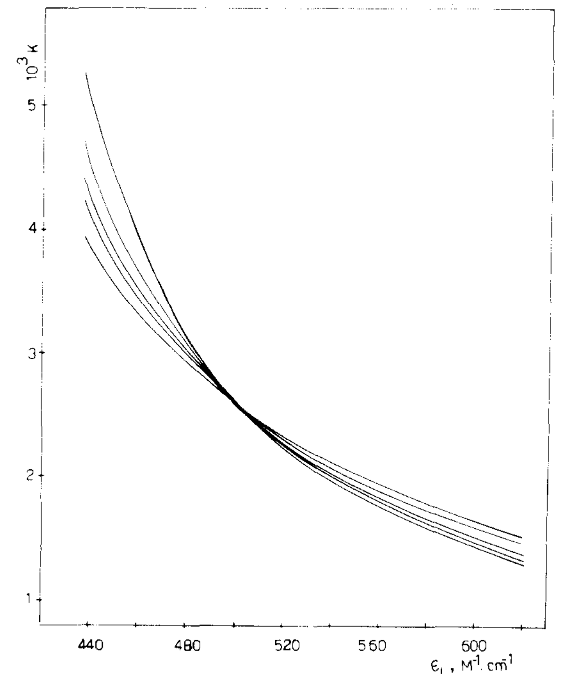

FIGURE 2 Plots of K_1 against the assumed extinction coefficients for the iron(II)-pyrazinecarboxylate complex in aqueous solution, with $[pz]_T = 2.9 \times 10^{-4}$ M and $[Fe(II)]_T$ varying from 7.4×10^{-4} to 1.3×10^{-4} M, at 25°C, in the presence of 0.10 M lithium perchlorate, argon atmosphere, $\lambda = 455$ nm.

Then, for each ε_1, the several K_1 values can be analysed statistically. Minimization of the standard deviation over K_1 implies in a good approximation for ε_1. For the $Fe(pz)^+$ complex, the best value of ε_1 was 505 $M^{-1} cm^{-1}$ (at 455 nm) yielding K_1 equal 2.5×10^3 M^{-1}, with a standard deviation (minimum) of 0.03×10^3. The method can be illustrated graphically as shown in Figure 2. In the plots of the calculated K_1 values against the assumed extinction coefficients, the occurrence of an intersection point yields the best pair of K_1 and ε_1 which can satisfy to all the measurements. The agreement with the numerical method was excellent.

After this step, we have investigated the formation of the successive complexes by working with an excess of ligand (varying from 4×10^{-4} M to 3×10^{-2} M) over the metal (10^{-4} M). The addition of the ligand intensifies the absorption band in the visible, shifting the maximum from 455 nm to 490 nm. Assuming the following equilibria,

$$Fe^{2+}(aq) + pz^- \rightleftharpoons Fe(pz)(aq)^+ \qquad K_1, \varepsilon_1$$
$$Fe^{2+}(aq) + 2pz^- \rightleftharpoons Fe(pz)_2(aq) \qquad \beta_2, \varepsilon_2$$
$$Fe^{2+}(aq) + 3pz^- \rightleftharpoons Fe(pz)_3^- \qquad \beta_3, \varepsilon_3$$

the total absorbance, per 1 cm of optical pathlength, is given by

$$A = \varepsilon_i[ML] + \varepsilon_2[ML_2] + \varepsilon_3[ML_3] \tag{4}$$

Now, we can define ε_i as

$$\varepsilon_i = \frac{A}{[M]_T} = \frac{\varepsilon_1 \cdot K_1[L] + \varepsilon_2 \cdot \beta_2[L]^2 + \varepsilon_3 \cdot \beta_3[L]^3}{1 + K_1[L] + \beta_2[L]^2 + \beta_3[L]^3}$$

Rearranging equation 5 more conveniently in terms of K_1, β_2 and β_3, we obtain

$$\frac{\varepsilon_i - (\varepsilon_1 - \varepsilon_i)K_1[L]}{(\varepsilon_3 - \varepsilon_i)[L]^2} = \beta_3[L] + \frac{\varepsilon_2 - \varepsilon_i}{\varepsilon_3 - \varepsilon_i}\beta_2 \tag{6}$$

or

$$H_i = \beta_3[L] + \frac{\varepsilon_2 - \varepsilon_i}{\varepsilon_3 - \varepsilon_i}\beta_2$$

Eq. (6) can be readily applied to the calculation of β_2 and β_3, provided that ε_3 is known. In the present system, since it is highly improbable the coordination of more

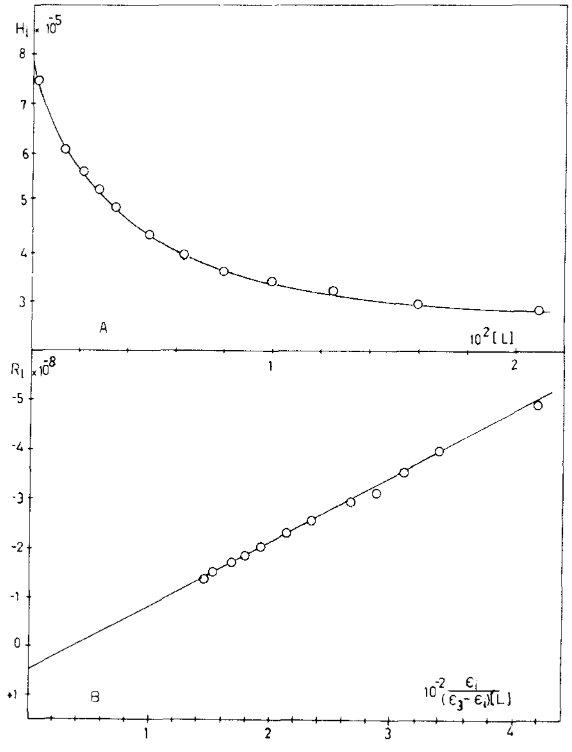

FIGURE 3 Plots of a) H_i versus $[L]$, and b) R_i versus $\varepsilon_i/(\varepsilon_3 - \varepsilon_i)[L]$ (see text) used in the determination of β_2 and β_3, with $[Fe(II)]_T$ varying from 1.30×10^{-4} M to 1.03×10^{-4} M, $[pz]_T$ varying from 2.83×10^{-4} M to 2.127×10^{-2} M, $T = 25$°C, $\mu = 0.10$ (mainly $LiClO_4$), $\lambda = 482$ nm, 5.00 cm pathlength cell, argon atmosphere.

than three ligands, ε_3 can be obtained from the extrapolation of the experimental ε_i values to infinite ligand concentration, or better, to $1/[L]$ going to zero. The extrapolated value for ε_3 was equal 2,650 ± 100 $\text{M}^{-1}\,\text{cm}^{-1}$ at 480 nm.

Considering that the ligand concentration is in large excess, we can make the initial assumption that $[L]_T = [L]$ and calculate the H_i values for a series of measurements. A typical plot of H_i against $[L]$ is illustrated in Figure 3*a*. From the extrapolation of H_i to $[L] \rightarrow 0$, we have

$$\lim_{[L]\rightarrow 0} H_i = \frac{\varepsilon_2 \cdot \beta_2}{\varepsilon_3} = 7.9 \times 10^5\ \text{M}^{-2} \qquad (7)$$

and therefore

$$\varepsilon_2 \cdot \beta_2 = 2.09 \times 10^9\ \text{M}^{-3}\,\text{cm}^{-1}$$

To evaluate β_2 and β_3, eq. (6) can be rearranged in the following way:

$$\frac{H_i}{[L]} - \frac{\varepsilon_2 \cdot \beta_2}{(\varepsilon_3 - \varepsilon_i)[L]} = \beta_3 - \beta_2 \frac{\varepsilon_i}{(\varepsilon_3 - \varepsilon_i)[L]} \qquad (8)$$

or,

$$R_i = \beta_3 - \beta_2 \frac{\varepsilon_i}{(\varepsilon_3 - \varepsilon_i)[L]}$$

Introducing the calculated value of $\varepsilon_2 \cdot \beta_2$ into eq. (8), we can plot R_i against $\varepsilon_i/(\varepsilon_3 - \varepsilon_i)[L]$, as shown in Figure 3b. The constants β_3 and β_2 result immediately from the intercept and slope of the linear plot. With the calculated values of β_2 and β_3, it is possible to analyse for the distribution coefficients

$$\alpha_0 = \frac{[M]}{[M]_T} = \left\{1 + \sum_{i=1}^{3} \beta_i |L|^i\right\}^{-1} \qquad (9)$$

$$\alpha_1 = K_1[L]\,\alpha_0 \qquad (10)$$

$$\alpha_2 = \beta_2[L]^2\alpha_0 \qquad (11)$$

$$\alpha_3 = \beta_3[L]^3\alpha_0 \qquad (12)$$

and in this way, to estimate the actual free ligand concentrations. Finally, performing a series of refinement cycles using the corrected values of $[L]$ instead of $[L]_T$, we have obtained

$\varepsilon_2 = 1.61 \times 10^3\ \text{M}^{-1}\,\text{cm}^{-1}$ (at 480 nm)

$\beta_2 = 1.30 \pm 0.01 \times 10^6\ \text{M}^{-2}$

$\beta_3 = 4.8 \pm 0.4 \times 10^7\ \text{M}^{-3}$

The corresponding distribution plots are shown in Figure 4, in comparison with the $\bar{n}$ function plot.

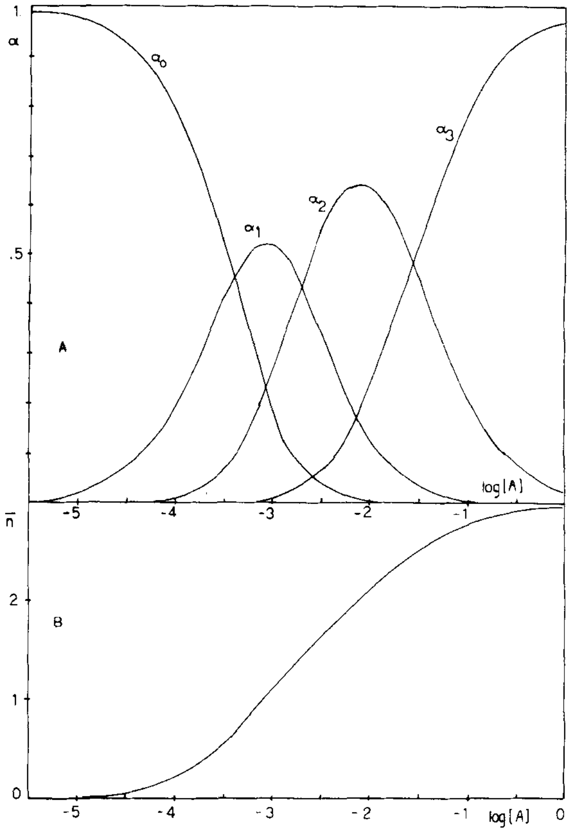

FIGURE 4 Plots of a) distribution function and b) $\bar{n}$ function versus $[L]$, for the iron(II)-pyrazinecarboxylate system, at 25°C, 0.10 M lithium perchlorate.

Substitution Kinetics in the Fe(II)-Pyrazinecarboxylate-Bipyridyl System

The typical reaction pattern observed when the iron(II)-pyrazinecarboxylate complexes react with bipyridyl, consists of the rapid formation of a red-wine intermediate which decomposes nearly a hundred times slower, to yield the thermodynamically stable and inert Fe(bipy)_3^{2+} complex. We have investigated in some detail the kinetics of this system because of the good chances of detecting a number of new, mixed complexes with the two series of ligands.

The spectra of the reactants, intermediates and products, recorded with the stopped-flow technique, can be seen in Figure 5a. It should be noted in that figure, the high extinction coefficient of the intermediate, which is comparable to that of the low spin, tris(bipyridyl)iron(II) complex. The lifetime of the intermediate seems to long for a high spin iron(II) complex in the presence of bipyridyl. It seems logical that, in order to stabilize the intermediate, both

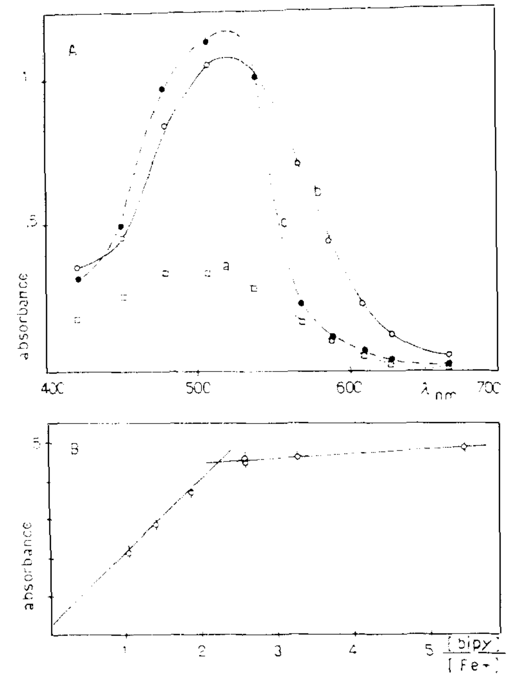

FIGURE 5 A) Spectra of the Fe(II)-pyrazinecarboxylate-bipyridyl system, obtained with the stopped-flow technique: $[Fe(II)]_T = 5 \times 10^{-5}$ M, $[pz] = 6.0 \times 10^{-3}$ M, $[bipy] = 3.7 \times 10^{-4}$ M, 2 cm optical pathlength, at a) 3 ms, b) 25 ms, c) 1 s, approximately. B) Kinetic molar-ratio plot, at 570 nm.

kinetically and thermodynamically, the combination of the two series of ligands should provide the highest ligand field strength as possible. Based on this simple argument, the intermediate should be formulated as the tris-substituted $Fe(pz)(bipy)_2^{+}$ complex. To confirm this assignment, we have done a kinetic molar-ratio study at 570 nm, as shown in Figure 5b.

Under the conditions employed in this work (see Table I) the kinetics showed a first order behavior for at least three half lives. We have observed that the results obtained by reacting the iron(II)-pyrazinecarboxylate complex with bipyridyl are identical to those obtained by mixing a solution of the two ligands with aqueous iron(II) ions. The formation of the iron(II)-pyrazinecarboxylate complex was found to be too fast for our stopped-flow instrument (dead time ~ 2 ms) even at the lowest concentrations of the pyrazine ligand, as possible. The lower limit estimated for the second order rate constant in this case was 1×10^6 M^{-1} s^{-1}.

According to these observations a rapid equilibrium may be initially established, involving a number of species, including some labile mixed complexes. Because the equilibrium constants are not all known, one can not make a prior selection of the species. For this reason we have included the $Fe(pz)^+$, $Fe(pz)_2$ and $Fe(pz)_3^-$ ions, as well as the $Fe(bipy)^{2+}$, $Fe(bipy)_2^{2+}$ and the mixed $Fe(bipy)(pz)^+$, $Fe(bipy)(pz)_2$ complexes into the reaction mechanism. These species are expected to be labile, in comparison with the $Fe(pz)(bipy)_2^{3+}$ and the $Fe(bipy)_3^{3+}$ complexes.

TABLE I
Observed rate constants of substitution reactions in the iron(II)-pyrazinecarboxylate system with bipyridyl.

$10^3 \times [pz]$ (M)	$10^4 \times [bipy]$ (M)	k_f (s^{-1})	k_d(s^{-1})
2.00	5.37	207	1.17
4.00	5.46	160	0.71
5.00	5.74	148	0.60
6.00	5.68	130	0.51
8.00	5.83	108	0.43
8.00	4.00	67	0.30
8.00	7.00	127	0.52
8.00	8.00	150	0.62
8.00	9.00	150	0.63
8.00	10.0	184	0.71

$T = 25.0$°C, 0.100 M lithium perchlorate, argon atmosphere, pH = 5.9–6.4, $[Fe^{2+}] = 1.00 \times 10^{-4}$ M, $\lambda = 580$ nm.

$$Fe^{2+} + pz^- \xrightleftharpoons{K_{10}} Fe(pz)^+$$
$$Fe^{2+} + 2\,pz^- \xrightleftharpoons{\beta_{20}} Fe(pz)_2$$
$$Fe^{2+} + 3\,pz^- \xrightleftharpoons{\beta_{30}} Fe(pz)_3^-$$
$$Fe^{2+} + bipy \xrightleftharpoons{\beta_{01}} Fe(bipy)^{2+}$$
$$Fe^{2+} + 2\,bipy \xrightleftharpoons{\beta_{02}} Fe(bipy)_2^{2+}$$
$$Fe^{2+} + pz^- + bipy \xrightleftharpoons{\beta_{11}} Fe(pz)(bipy)^+$$
$$Fe^{2+} + 2pz^- + bipy \xrightleftharpoons{\beta_{21}} Fe(pz)_2(bipy)$$

Neglecting termolecular processes, the most probable ways of producing $Fe(pz)(bipy)_2^+$ are from the $Fe(pz)(bipy)^+$ and $Fe(bipy)_2^+$ species.

$$Fe(pz)(bipy)^+ + bipy \xrightarrow{k_1} Fe(pz)(bipy)_2^+$$
$$Fe(bipy)_2^{2+} + pz^- \xrightarrow{k_2} Fe(pz)(bipy)_2^{2+}$$

The parallel formation of $Fe(bipy)_3^{2+}$ intermediate is also possible.

$$Fe(bipy)_2^{2+} + bipy \xrightarrow{k_3} Fe(bipy)_3^{2+}$$

Considering these three pathways leading to the products P, and the several equilibria involved in the system, one can derive the following rate law

$$\frac{d[P]}{[P]_\infty - [P]} = k_{obsd} \cdot dt \qquad (13)$$

$$\text{where } k_{obsd} = \frac{(k_1\beta_{11} + k_2\beta_{02})[L]^2[\text{pz}] + k_3\beta_{02}[L]^3}{1 + \beta_{01}[L] + \beta_{02}[L]^2 + \beta_{10}[\text{pz}] + \beta_{20}[\text{pz}]^2 + \beta_{30}[\text{pz}]^3 + \beta_{11}[\text{pz}][L] + \beta_{21}[\text{pz}]^2[L]}$$

(L = bipy)

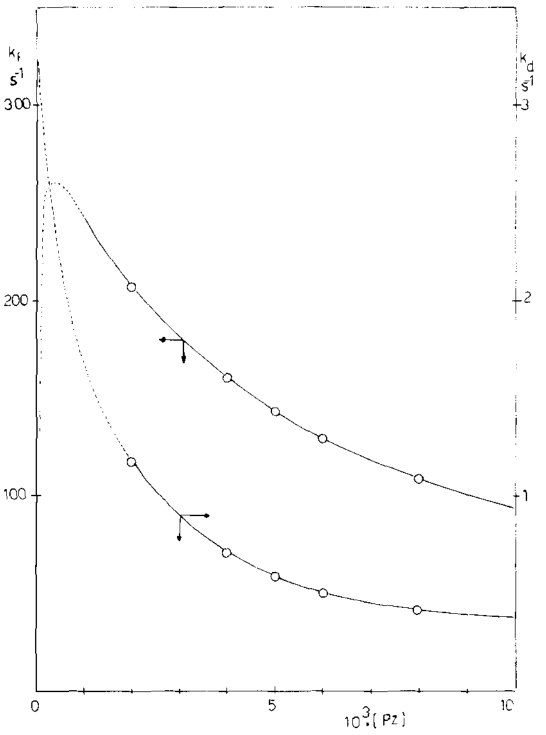

FIGURE 6 Dependence of the observed rate constant for the formation and dissociation of the Fe(pz)(bipy)$_2^+$ intermediate, on the concentration of the pyrazinecarboxylate lingand, at 25.0°C, [bipy] = 5.6×10^{-4} M, 0.100 M lithium perchlorate, pH 5.9–6.4, argon atmosphere, $[\text{Fe(II)}]_T = 1.0 \times 10^{-4}$, λ = 580 nm. The solid lines refer to the theoretical values calculated from the best set of constants (see text).

The reverse steps, k_{-1}, k_{-2} and k_{-3} have been neglected in the rate law since the dissociation reaction is much slower than the formation reaction. Eq. 13 can be expressed in terms of three parameters X_1, X_2 and X_3, and five variables, A, B, C, D and E.

$$k_{obsd} = \frac{A + B \cdot X_1}{C + D \cdot X_2 + E \cdot X_3} \qquad (14)$$

where

$A = k_3\beta_{02}[\text{bipy}]^3$

$B = [\text{pz}][\text{bipy}]^2$

$C = 1 + \beta_{01}[\text{bipy}] + \beta_{02}[\text{bipy}]^2 + \beta_{10}[\text{pz}] + \beta_{20}[\text{pz}]^2 + \beta_{30}[\text{pz}]^3$

$D = [\text{bipy}][\text{pz}]$

$E = [\text{bipy}][\text{pz}]^2$

$X_1 = k_1\beta_{11} + k_2\beta_{02}$

$X_2 = \beta_{11}$

$X_3 = \beta_{21}$

The rates of formation of the Fe(bipy)$_3^{2+}$ complex from aqueous ferrous ions and bipyridyl have been previously investigated by Baxendale and George[19] and by Holyer *et al.*[20] From these references we have obtained $k_3 = 1.4 \times 10^5$ M^{-1} s^{-1}. The equilibrium constants for the iron(II)-bipyridyl system have been determined by a number ot workers.[21-23] In this paper we have used those recommended by Irving and Mellor[21], $\beta_{01} = 2.0 \times 10^4$ M^{-1} and $\beta_{02} = 1.0 \times 10^8$ M^{-2}.

Now, using the equilibrium constants determined in this work for the pyrazinecarboxylate complexes, it is possible to calculate the variables A–E. Finally, from the experimental data (Table I) for the dependence of k_{obsd} on the pyrazinecarboxylate ion concentration (only 3 sets of values are required) and the corresponding values for A–E, we have solved for X_1, X_2 and X_3 in eq. (14):

$$k_1\beta_{11} + k_2\beta_{02} = 5.8 \times 10^{13} \text{ M}^{-3} \text{ s}^{-1} \qquad (15)$$

$$\beta_{11} = 5.6 \times 10^7 \text{ M}^{-2}$$

$$\beta_{21} = 2.8 \times 10^{10} \text{ M}^{-3}$$

The internal consistency of the calculations could be verified with the additional points in Table I, as well as, by a curve fitting procedure as shown in Figure 6. The agreement was very good.

Eq. (13) can also explain the dependence of k_{obsd} on the concentration of the bipyridyl ligand, expressed by

$$k_{obsd} = 1.97 \pm 0.05 \times 10^5[\text{bipy}] \qquad (16)$$

as shown in Table I. When the pyrazinecarboxylate ion is in large excess over bipyridyl, the $\beta_{11}[\text{pz}][\text{bipy}]$ and $\beta_{21}[\text{pz}]^2[\text{bipy}]$ terms predominate in the denominator of the equation. Under these conditions, eq. (13) becomes

$$k_{obsd} = \frac{(k_1\beta_{11} + k_2\beta_{02})[\text{bipy}]}{\beta_{21}[\text{pz}] + \beta_{11}} \qquad (17)$$

Introducing the calculated values for the several parameters into eq. (17), we have obtained, in close agreement with eq. (16),

$$k_{obsd} = 2.06 \times 10^5[\mathrm{bipy}]$$

According to the calculations, the $\mathrm{Fe(pz)(bipy)^-}$ and $\mathrm{Fe(pz)_2(bipy)}$ complexes are the major species in the reactants. Instead of postulating a pre-equilibrium condition between these two complexes, it is also possible to explain the results in terms of a mechanism like

$$\mathrm{Fe(bipy)(pz)_2} \underset{k_0}{\overset{k_{-0}}{\rightleftharpoons}} \mathrm{Fe(bipy)(pz)^-} + \mathrm{pz^-}$$

$$\mathrm{Fe(bipy)(pz)^-} + \mathrm{bipy} \xrightarrow{k_1} \mathrm{Fe(bipy)_2(pz)^+}$$

Here, assuming a steady state approximation for the $\mathrm{Fe(pz)(bipy)^-}$ intermediate, the rate law becomes very similar to eq. (17),

$$k_{obsd} = \frac{k_{-0}k_1[\mathrm{bipy}]}{k_0[\mathrm{pz}] + k_1[\mathrm{bipy}]} \tag{18}$$

However, the analysis of the experimental data (Table I) according to eq. (18), indicates that the k_{-0} step should be very fast ($400\ \mathrm{s^{-1}}$). This means that the pre-equilibrium condition can be established in a consistent way as we have proposed before.

The decay of the intermediate (Table I) follows a nearly first order behavior with respect to the concentration of the bipyridyl ligand, with an inverse dependence on the pyrazine carboxylate ion concentration, as shown in Figure 6. The behavior is consistent with the dissociative mechanism

$$\mathrm{Fe(pz)(bipy)_2^+} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \mathrm{Fe(bipy)_2^{2+}} + \mathrm{pz^-}$$

$$\mathrm{Fe(bipy)_2^{2+}} + \mathrm{bipy} \xrightarrow{k_3} \mathrm{Fe(bipy)_3^{2+}}$$

where the dissociation of the coordinated pyrazinecarboxylate ligand is the rate determining step.

Assuming a steady state approximation for the $\mathrm{Fe(bipy)_2^{2+}}$ complex, we can derive the following rate law

$$-\frac{d[\mathrm{Fe(pz)(bipy)_2^+}]}{dt} = k_{obsd}[\mathrm{Fe(pz)(bipy)_2^+}]$$

where

$$k_{obsd} = \frac{k_3 \cdot k_{-2}[\mathrm{bipy}]}{k_3[\mathrm{bipy}] + k_2[\mathrm{pz}]} \tag{19}$$

Eq. (19) predicts an inverse dependence of k_{obsd} on the pyrazinecarboxylate ion concentration, as we have observed experimentally. We can also explain the linear behavior observed with respect to the concentration of the bipyridyl ligand, considering that under the conditions of this work (Table I), $k_2[\mathrm{pz}]$ predominates over $k_3[\mathrm{bipy}]$ in the denominator of eq. (19). In its inverse form, eq. (19) can be used for the evaluation of k_{-2} from the linear plots of k_{obsd}^{-1} against $[\mathrm{pz}]/[\mathrm{bipy}]$.

$$\frac{1}{k_{obsd}} = \frac{1}{k_{-2}} + \frac{k_2}{k_3 \cdot k_{-2}}\,\frac{[\mathrm{pz}]}{[\mathrm{bipy}]} \tag{20}$$

In this way, we have obtained

$$k_{-2} = 3.3\ \mathrm{s^{-1}}\ \text{and}\ \frac{k_2}{k_3} = 0.50$$

With the k_3 value reported by Baxendale and George[19] and Holyer *et al.*,[20] we can calculate

$$k_2 = 7.0 \times 10^4\ \mathrm{M^{-1}\,s^{-1}}$$

$$K_{12} = \frac{k_2}{k_{-2}} = 2.1 \times 10^4\ \mathrm{M^{-1}}$$

and

$$\beta_{12} = \beta_{02} \cdot K_{12} = 2.1 \times 10^{12}\ \mathrm{M^{-3}}$$

By substituting the several constants into eq. (15), k_1 can be calculated as

$$k_1 = \frac{5.8 \times 10^{13} - k_2\beta_{02}}{\beta_{11}} = 9.0 \times 10^5\ \mathrm{M^{-1}\,s^{-1}}$$

This value, which is more than ten times k_2, indicates that the $\mathrm{Fe(pz)(bipy)_2^+}$ intermediate is generated mainly from the $\mathrm{Fe(pz)(bipy)^+}$ complex rather than from the $\mathrm{Fe(bipy)_2^{2+}}$ species.

As a final calculation, we can also evaluate k_{-1} in the equilibrium

$$\mathrm{Fe(pz)(bipy)^+} + \mathrm{bipy} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe(pz)(bipy)_2^+}$$

considering that

$$\beta_{12} = \beta_{11} \cdot \frac{k_1}{k_{-1}}.$$

Therefore,

$$k_{-1} = 24\ \mathrm{s^{-1}}$$

In this way it was possible to solve for all the kinetics and equilibrium constants involved in the reaction of the iron(II)-pyrazinecarboxylate complexes with bipyridyl. One can note that the rates of substitution in the bis-coordinated iron(II) complexes are comparable, in magnitude, with the rates of substitution of aqueous ferrous ions.[8] A similar behavior has been observed in substitution reactions of niquel(II) ions with aromatic diimines.[8,24] In such cases, a stacking interaction involving a coordination and an external aromatic ligand has been postulated.[24] It seems probable that the hydrophobic stacking interaction between bipyridyl molecules should be favored with respect to the analogous interaction between pyrazinecarboxylate anions. This possibility may be related with the fact that the rates of substitution here presented with bipyridyl (k_1 and k_3) are faster than in the pyrazinecarboxylate case (k_2).

CONCLUSION

In Table II the stability constants of the iron(II)-pyrazinecarboxylates and of the mixed complexes containing bipyridyl can be compared with those previously reported for iron(II) complexes of saturated and unsaturated ligands like ethylenediamine and phenanthroline, respectively. The first conclusion is that, in spite of the strong acceptor properties expected for the pyrazinecarboxylate ligand, the corresponding iron(II) complex is relatively weak. An analogous behavior is observed for the complex with the ethylenediamine ligand, which is the strongest donor of the series. In these two cases, as well as in the iron(II)-pyridinecarboxylate complex, the equilibrium constants show a normal behavior characterized by $K_1 > K_2 > K_3$. For the bipyridyl and phenanthroline complexes, the behavior can be considered anomalous in the sense that $K_1 > K_2 < K_3$. The deviation from the behavior arises from changes of configuration, from high spin to low spin, imposed by the strong ligand field stabilization in the tris-substituted complexes.

The pattern observed for the pyrazinecarboxylate complexes is consistent with a high spin configuration. The same is true for the ethylenediamine complex. Therefore, in order to stabilize the low spin configuration of iron(II) complexes, it seems that the ligands should have, simultaneously, strong σ-donor and π-acceptor properties. The cooperative effects involving donor and acceptor interactions are evident when one compares the stability constants of the pyrazine and pyridinecarboxylate complexes. The pyridine ligand, which is more basic than the pyrazine analog, but much less than the ethylenediamine ligand, forms the most stable complexes of the series. Presumably, the donor interactions from the ligands have the effect of increasing the backbonding ability of the metal ion, in a cooperative way which depends on the acceptor properties of the donating species. The effect is probably enhanced in the aromatic diimines, which are simultaneously strong σ-donors and good π-acceptors.

The trends in Table II also support a high spin configuration for the $Fe(pz)(bipy)^+$ and $Fe(pz)_2(bipy)$ complexes. However, one can note that the stability constant for the $Fe(pz)(bipy)_2^+$ complex is borderline between high spin and low spin complexes. The intensity of the charge transfer transition in this complex is rather high, suggesting a strong metal-ligand interaction as in the analogous low spin, tris(bipyridyl)-iron(II) complexes.[25] This conclusion is corroborated in some extent by the kinetics behavior, which is too unusual for high spin iron(II) complexes. The problem of the spin configuration requires further studies; the possibility of spin equilibrium is under investigation at this laboratory, in parallel with the chemistry of a number of mixed complexes containing aromatic diimines and substituted pyridines.

TABLE II
Equilibrium constants of iron(II) complexes in aqueous solution.

Complexes	pKa(L)		K_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	Ref.
	N	O				
$Fe(pz)_3^-$	0.45	2.82	2.5×10^3	1.3×10^6	4.8×10^7	*a*
$Fe(en)_3^{2+}$	9.98		2.2×10^4	4.4×10^7	5.0×10^9	*b*
$Fe(pyc)_3^-$	1.01	5.32	7.9×10^4	1.0×10^9	1.5×10^{11}	*c*
$Fe(pz)(bipy)^+$				5.6×10^7		*a*
$Fe(pz)_2(bipy)$					2.8×10^{10}	*a*
$Fe(pz)(bipy)_2^+$					2.1×10^{12}	*a*
$Fe(bipy)_3^{2+}$	4.34		2.0×10^4	1.0×10^8	3.5×10^{17}	*d*
$Fe(phen)_3^{2+}$	4.98		7.2×10^5	1.3×10^{11}	1.4×10^{21}	*d*

[a]this work, 25°C, 0.10 M $LiClO_4$; [b]ref. 26, 25°C, 1.4 M KCl; [c]ref. 6, 20°C, 0.10 M $NaNO_3$; [d]ref. 21, 25°C, 0.10 M KCl.

Nomenclature: pz = pyrazinecarboxylate, en = ethylenediamine, pyc = pyridinecarboxylate, bipy = 1,10 bipyridyl, phen = phenanthroline, N and O refer to the donor atoms in the ligands.

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