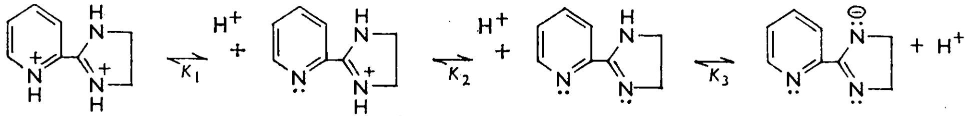
527. *The Effect of Co-ordination on Ionization. Part II.*[1] *The 2-2'-Pyridylimidazoline–Iron*(II) *System.*

By G. I. H. Hanania and D. H. Irvine.

The thermodynamics of the acid ionization of the imidazolinium $\geqslant$NH$^+$ group in 2-2'-pyridylimidazoline and in its tris-ligand–iron(II) complex have been studied in dilute aqueous solution. For the free ligand at 25·0°, $pK_2^0 = 8·92 \pm 0·03$; $\Delta H_2^0 = 13·7 \pm 0·9$ kcal. mole^{-1}, and $\Delta S_2^0 = -4 \pm 3$ e.u. (equation 1). For the complex, $pK_4^0 = 6·09 \pm 0·03$, $\Delta H_4^0 = 6·9 \pm 0·5$ kcal. mole^{-1}, and $\Delta S_4^0 = -5 \pm 2$ e.u. (equation 4). The results are discussed and compared with those for the pyridine-2-aldoxime–iron(II) system.[1]

In our first paper [1] we showed that the effect of co-ordination to iron(II) on the ionization of the oxime (N·OH) group in pyridine-2-aldoxime was large even when no change in charge types was involved, and that it was predominantly an enthalpy effect. We attributed this to enhanced stabilization, through conjugation, of the anionic conjugate base in the complex. In the present work we examine the effect of co-ordination to iron(II) on a group in a ligand where conjugation is not favoured; it is here shown to be smaller despite the fact that the complex carries a higher positive charge than does the free ligand.



$(H_2PimH)^{2+}$ $(HPimH)^+$ $(PimH)^0$ $(Pim)^-$

Ionization of the Imidazolinium $\geqslant$NH$^+$ *Group in 2-2'-Pyridylimidazoline.*—For 2-2'-pyridylimidazoline three acid ionizations are possible, as indicated in the annexed scheme. pK_1 refers to the ionization of the pyridinium $\geqslant$NH$^+$ group and is ~2. The increased acidity of this group (normal value in pyridine 5·2) is probably due to the electrostatic effect of the positive charge on the adjacent imidazolinium group. pK_3 refers to the acid ionization of an aliphatic-type secondary amine and is expected to be very high. For the other ionization, that of imidazolinium $\geqslant$NH$^+$, Harkins and Freiser [2] report p*K* 8·54 at 25° and unspecified ionic strength in 50% dioxan-water.

We have measured the ionization constant, K_2, for dilute solutions over a range of ionic strengths, *I*, and temperatures. At 25·3° and three different ionic strengths the pK_2 values are: $9·06 \pm 0·01$ ($I = 0·11$M); $9·01 \pm 0·02$ ($I = 0·044$M); and $8·99 \pm 0·22$ ($I = 0·022$M). These values approximately fit the theoretical relation

$$pK_2 = pK_2^0 + 0·5I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which is expected for an ionization of the type 1+ to 0. We have confirmed that these are the charges involved in the ionization from studies of electrophoretic mobility over the pH range 6·0—12·0, using iron(II) as indicator. At this temperature, $pK_2^0 = 8·93 \pm 0·02$ at $I = 0$.

This value of 8·93 in aqueous solution is higher than the corresponding value of 8·54 in 50% dioxan–water reported by Harkins and Freiser [2] (these authors also found that for the acid ionization of the $\geqslant$NH$^+$ group of *o*-phenanthroline the value of p*K* was 1·0 unit higher when measured in aqueous solution than in 50% dioxan–water).

We have measured pK_2 at three temperatures and (constant) $I = 0·044$M. The results are: $9·34 \pm 0·01$ (15·3°), $9·00 \pm 0·02$ (25·3°), and $8·68 \pm 0·02$ (35·2°). A plot of pK_2

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[1] Part I, Hanania and Irvine, preceding paper.

[2] Harkins and Freiser, *J. Amer. Chem. Soc.*, 1956, **78**, 1143.

against $1/T$ is linear and yields $\Delta H_2 = 13{\cdot}7 \pm 0{\cdot}9$ kcal. mole^{-1}, which may be assumed to be the value of ΔH_2^0. From the temperature variation, pK_2 at 25·0° and $I = 0{\cdot}044$M is found to be $9{\cdot}01 \pm 0{\cdot}02$, which on the basis of equation (1) gives pK_2^0 (25·0°) $= 8{\cdot}92 \pm 0{\cdot}02$. Consequently ΔS_2^0 (25·0°) is -5 ± 3 e.u. The thermodynamic results for this ionization are very similar to corresponding results for secondary aliphatic ammonium ions, which is not unexpected in view of the lack of aromatic character in the imidazoline ring.

Ionization of the Imidazolinium $\geqslant$NH$^+$ *Group in the 2-2′-Pyridylimidazoline–Iron*(II) *Complex*.—Walter and Freiser[3] first observed that 2-2′-pyridylimidazoline forms an unstable violet complex with ferrous ion in aqueous solution, and that the complex is stable in the presence of hydroxylamine. Further, they demonstrated that the optical density of this complex increases with pH, reaching a maximum value at pH 9·0. There was a corresponding shift to longer wavelength in the peak (560 mμ) of the visible absorption spectrum. No further change in optical density or in band position was observed in the pH range 9·0—11·0.

We have shown, using the method of continuous variation, that at pH 7·0 the complex contains 1 g.-atom of iron per 3 moles of ligand. The complex was unstable when the ligand was not in large excess, even in the presence of hydroxylamine, the optical density decreasing rapidly with time. It was therefore necessary to measure the optical density after various times for each mixture and to use the extrapolated values in calculating the composition of the complex. It was not possible to determine the composition of the complex either at pH 5·0 or at pH 9·0 because of its very marked instability under these conditions.

The mobility of the complex on paper electrophoresis shows it to be positively charged throughout the pH range 6·0—9·5. If it is assumed, by analogy with the pyridine-2-aldoxime–iron(II) system,[1] that the colour change observed by Walter and Freiser[3] is the result of an ionization, then it follows that this ionization involves the charge types 2+ to 1+, the charge of 2+ being derived from the iron(II) atom. Accordingly the formation and ionization of the complex may be represented by the equations:

$$\mathrm{Fe^{2+} + 3PimH = [Fe(PimH)_3]^{2+}} \quad (K) \qquad (2)$$

$$\mathrm{[Fe(PimH)_3]^{2+} + H_2O = [Fe(PimH)_2Pim]^+ + H_3O^+} \quad (K_4) \qquad (3)$$

where K is the pH-independent formation constant, and K_4 the first acid ionization constant of the complex. It is reasonable to assume that the proton is lost from one of the three free $>$NH groups.

The ionization constant K_4 was measured spectrophotometrically. However, the optical density of a solution containing 100% of conjugate acid could not be read directly on account of rapid dissociation of the complex in solutions more acidic than pH 6·0. The method used in the measurement of pK_2 for the tri(pyridine-2-aldoxime)–iron(II) complex[1] was therefore adopted in this case. At $I = 0{\cdot}107$M the following results were obtained: p$K_4 = 6{\cdot}57 \pm 0{\cdot}03$ (18·0°); $6{\cdot}46 \pm 0{\cdot}02$ (25·0°); $6{\cdot}28 \pm 0{\cdot}03$ (35·0°). The plot of pK_4 against $1/T$ is linear and leads to: $\Delta H_4 = 6{\cdot}9 \pm 0{\cdot}5$ kcal. mole^{-1} which is assumed to be the value of ΔH_4^0. Since the ionization in equation (3) involves the charge types 2+ to 1+ it may be assumed that K_4 varies with ionic strength according to the relation

$$\mathrm{p}K_4 = \mathrm{p}K_4^0 + 1{\cdot}5I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}),$$

whence $$\mathrm{p}K_4^0\ (25{\cdot}0^\circ) = 6{\cdot}09 \pm 0{\cdot}03, \text{ and } \Delta S_4^0\ (25{\cdot}0^\circ) = -5 \pm 2 \text{ e.u.} \qquad (4)$$

The results for this ionization could refer to proton removal from an imino-group ($>$NH $\longrightarrow$ $>$N:$^-$) or from an imidazolinium group ($\geqslant$NH$^+$ $\longrightarrow$ $\geqslant$N:). In the former case the ionization is to be compared with that of the acid ionization of an aliphatic secondary amine. Thermodynamic data are not available for an ionization of this type, but pK is

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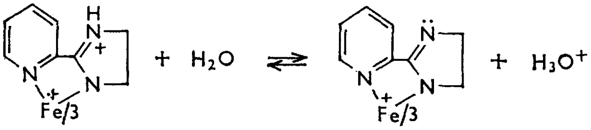
[3] Walter and Freiser, *Analyt. Chem.*, 1954, **26**, 217.

expected to be very high and ΔH to be highly endothermic (for the corresponding ionization in imidazole[4] $pK^0 = 14{\cdot}4$, $\Delta H^0 = 17{\cdot}8$ kcal. mole^{-1}). In the latter case, the ionization is to be compared with that of the acid ionization of the imidazolinium group, for which it is shown in the present study that $pK_2^0 = 8{\cdot}92$, and $\Delta H_2^0 = 13{\cdot}7$ kcal. mole^{-1}. In either case the effect of co-ordination is large, since in the complex $pK_4^0 = 6{\cdot}09$, and $\Delta H_4^0 = 6{\cdot}9$ kcal. mole^{-1}. However, the magnitude of the effect depends on which of the above alternatives is thought to represent better the actual charge distribution in the complex. In an imino-type ionization the conjugate base would have a configuration in which there is a positive charge on iron and a negative charge on nitrogen. Such a configuration should be less stable than that of the corresponding conjugate base in an imidazolinium-type ionization where no such charge separation is involved. It seems reasonable, therefore, to regard the ionization in tri-(2-2′-pyridylimidazoline)iron(II) essentially as an imidazolinium type which may be represented by the equation



On this basis we may conclude that the effect of co-ordinating iron(II) to 2-2′-pyridylimidazoline is to decrease pK of the imidazolinium $\geqslant NH^+$ group by 2·8 units and the endothermicity by 6·8 kcal. mole^{-1}. The entropy of ionization remains unchanged. A similar marked decrease in pK and endothermicity, but not in entropy, was found in the case of the third oxime ionization in tri(pyridine-2-aldoxime)iron(II).[1] In the latter case the effect was attributed mainly to enhanced stabilization through conjugation of the conjugate base in the complex, since the ionizations in the complex and in the ligand involve the same charge type 0 to 1—. In the present case, however, the complex ion carries two extra positive charges relative to the free ligand, but there is little stabilization of the conjugate base through conjugation. Consideration of the two cases thus leads to the conclusion that both electrostatic and resonance factors can contribute to the net effect of co-ordination on ionization

EXPERIMENTAL

Reagents and Materials.—2-2′-Pyridylimidazoline was prepared and recrystallized by Walter and Freiser's procedure[3] and had m. p. 96—97°. Conductivity water and analytical-grade reagents were used. Ionic strengths were adjusted with sodium chloride.

Determination of Ionization Constants.—The ionization in the free ligand and in the complex was studied spectrophotometrically. Optical densities of solutions of the ligand (about $1{\cdot}2 \times 10^{-4}$M) were measured over the pH range 7·0—11·0 at 267 mμ, one of the two ultraviolet absorption peaks for the ligand. The ionization constant at a given ionic strength was calculated by means of the equation $K = a_{H^+}[\text{Base}]/[\text{Acid}]$, where [Base]/[Acid] is the concentration ratio obtained spectrophotometrically, and a_{H^+} is the activity of hydronium ions obtained from pH measurements based on the standards recommended by Bates[5] and Mattock.[6]

A similar procedure was followed in the measurement of the ionization constant of the iron(II) complex, optical densities being taken at 560 mμ. In order to stabilize the complex for these measurements about 1000-fold excess of ligand was used. It was also necessary to add a small amount of hydroxylamine hydrochloride (" AnalaR ") to the buffered solutions, as recommended by Walter and Freiser.[3] Even under these conditions the optical density of a solution containing 100% of conjugate acid could not be measured directly because of rapid dissociation of the complex in solutions more acidic than pH 6·0. Accordingly pK was obtained by the procedure[1] used in the measurement of pK_2.

Optical-density measurements were made on a Unicam S.P. 500 quartz spectrophotometer; pH measurements were made either on a Doran or on a Radiometer model 4 pH-meter, readings

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[4] Hanania and Irvine, unpublished results.
[5] Bates, " Electrometric pH Determinations," Chapman and Hall, London, 1954.
[6] Mattock, " pH Measurement and Titration," Heywood, London, 1961.

being precise to ±0·01. In all experiments temperature was controlled to ±0·02° by circulating water from a thermostat bath, and actual temperatures of solutions were measured with a thermistor calibrated against a standard N.P.L. thermometer.

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