Inorg. Chem. **1989**, *28*, 3667-3671

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Ionization of Pyridine Bases and Their Reactions with Cobalt(II) and Nickel(II) Acetates in Anhydrous Acetic Acid

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Received December 21, 1988

A spectroscopic study was done to find a principle governing the interactions of cobalt(II) and nickel(II) acetates with pyridine bases in acetic acid, with special emphasis given to the ionization of solutes. The ionization constant of pyridine bases in this solvent ($B + HOAc \rightleftharpoons BH^+OAc^-$, K_i) was determined by UV spectroscopy, and log K_i was found to increase monotonically with pK_a in water. Cobalt(II) acetate was found to react with 2,4- and 2,6-lutidines (B) to give the violet complexes $BH^+Co(OAc)_3^-$, quite similar to those observed when either lithium or sodium acetate is added instead of the lutidine. The UV spectra indicate that these changes are caused by a structural conversion of the Co(II) polyhedron from pseudo-O_h to pseudo-T_d. Direct coordination of OAc^- was confirmed in the case of 2,4-lutidine, from the fact that ^{13}C NMR spectra of the lutidine were not modified appreciably on addition of cobalt(II) acetate. Co(II) ion, however, caused a drastic change in the ^{13}C NMR spectra of 3-chloropyridine, which indicates its nitrogen coordination to the metal ion. Only the latter type of complex was detected with nickel(II) acetate, possibly because Ni(II) does not give an appreciable change in electronic spectra even if an acetato complex is formed at all. An analysis of spectral data gave the formation constant for a 1:1 complex K_1, which is smaller for a pyridine base with a greater pK_a in water. This peculiarity can be understood in terms of ionization of the base, since the more basic ligand is ionized to a greater extent to give BH^+OAc^-, which can no longer be coordinated to a metal ion through a nitrogen atom. When this effect is corrected for by defining an "intrinsic" formation constant as $K_1^\circ = (1 + K_i)K_1$, K_1° was found to increase with pK_a. This fact illustrates the importance of the ionization process and the necessity of the correction for it, when anhydrous acetic acid is used as a solvent for chemical reactions.

Acetic acid is a typical acidic solvent[1,2] and exhibits a leveling effect for bases stronger than pyridine.[3-5] Thus, pyridine is a strong base in this solvent, though it is rather a weak one in water.

A pyridine base reacts with a metal ion almost exclusively by forming a metal-nitrogen bond in aqueous solutions. However, this is not always the case in acidic solvents, since the base may react with a solvent molecule to give rise to pyridinium and lyoate (acetate in this case) ions, the latter of which in turn may interact with the metal ion. This type of solvolysis reaction has not yet been studied in enough detail, partly because of some difficulty in distinguishing between the two kinds of metal complexes.

On the other hand, some controversies have been found in the discussions about the transition-metal complexes formed in anhydrous acetic acid,[6-10] possibly because of the complexity of reactions in this solvent and also the lack of a comprehensive understanding of the reactions and information especially about the ionization as well as the dissociation in this solvent. The present paper is aimed at reporting the equilibrium states of a series of pyridine bases and their reactions with cobalt(II) and nickel(II) acetates in glacial acetic acid, on the basis of quantitative analyses of the data from UV-visible, IR, and NMR spectroscopies and electrochemical techniques, with special emphasis given to the distinction between the two types of complexes with nitrogen and oxygen donors as well as to the ionization of species present.

Experimental Section

Materials. Anhydrous Acetic Acid. Reagent grade acetic acid (Wako) was purified according to the method described elsewhere,[9] and the water content ((1-2) × 10^{-3} M[11]) was determined by the Karl Fischer method.

2,4-, 3,4-, and 3,5-Lutidines.[12] To a mixture of 85 g of $ZnCl_2$, 35 cm^3 of concentrated HCl, 69 cm^3 of ethanol, and 69 cm^3 of water was added about 140 cm^3 of a lutidine. The resulting precipitate was filtered and recrystallized from anhydrous ethanol. This product was then added to an NaOH solution (22 g in 22 cm^3 of water), and the resulting liquid portion was separated and dried on NaOH, followed by distillation.

2,6-Lutidine.[12] A commercial product (100 g) was dissolved in a urea solution (40 g in 75 cm^3 of water), which was cooled to 5 °C. The precipitate was filtered and vapor-distilled. The distillate was then dried on NaOH and distilled.

Pyridine and 2- and 3-Chloropyridines. Each reagent grade product was dried on NaOH and distilled. The base concentration was determined by weighing the corresponding pyridine base and dissolving it in a given quantity of anhydrous acetic acid.

Cobalt(II) Acetate Solution. Reagent grade cobalt(II) acetate tetrahydrate was dissolved in anhydrous acetic acid, to which acetic anhydride was added slightly in excess over the water content. The precipitate formed was then centrifuged and dried in a vacuum desiccator after washing with acetic acid several times. The cobalt(II) solution was prepared by dissolving the purified cobalt(II) salt in anhydrous acetic acid, and it was titrated with EDTA by use of MTB (methylthymol blue) as an indicator at pH 5-6.[13]

Nickel(II) Acetate Solution. The procedure was quite the same as that for the cobalt(II) solution, and the complexometric titration was carried out by using Cu(II) EDTA and TAR (4-(2-thiazolylazo)resorcinol) as a system indicator at pH 5-6.[14]

Lithium Acetate Solution. Reagent grade lithium acetate was recrystallized from acetic acid and then dissolved in anhydrous acetic acid. Its concentration was determined by titrating with perchloric acid in acetic acid by use of crystal violet as indicator.[15]

Measurement and Apparatus. Electronic spectra were recorded on a Union-Giken SM-401 high-sensitivity spectrophotometer and on a Hitachi 323 spectrophotometer (near-IR region). The absorption at a wavelength was measured with a Carl Zeiss PMQ II spectrophotometer. Infrared spectra were taken with a Jasco IRA-3 infrared spectrophotometer, by use of a CaF_2 cell with a light path of 0.05 mm. The absorbance of solvents (CCl_4 and 10% acetic acid in CCl_4) was subtracted with a Jasco A-3DP data processor. The effect of paramagnetic ions on the NMR spectra of a base was measured with a JEOL FX-100 NMR spectrometer.

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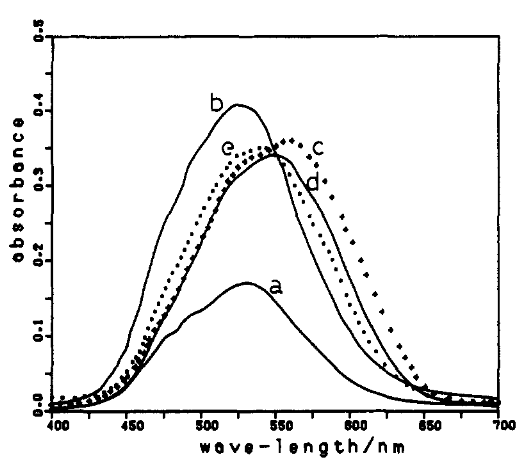

Figure 1. Change in electronic spectra on addition of various pyridine bases (total concentrations of a base and cobalt(II) acetate are shown in parentheses (C_B/C_{Co})): (a) $Co(OAc)_2$ alone (0 M/1.08 × 10^{-2} M); (b) 3-chloropyridine (0.338 M/1.08 × 10^{-2} M); (c) lithium acetate (0.309 M/0.843 × 10^{-2} M); (d) 2,4-lutidine (0.413 M/0.964 × 10^{-2} M); (e) pyridine (0.421 M/1.0, × 10^{-2} M).

The hydrogen ion activity was measured with a Horiba G84-B1 glass electrode and a Horiba calomel electrode, which were specially manufactured by Horiba Ltd. (Kyoto, Japan). Potentiometry was carried out with an Orion 701A digital ionalyzer, connected to the two electrodes.

Formation constants were calculated by processing with a Fortran program on a Facom M 382 computer at the Nagoya University Computation Center.

Results and Discussion

Reactions of Cobalt(II) Acetate with Lutidines. Cobalt(II) acetate in acetic acid solutions shows quite different changes in electronic spectra on addition of different pyridine bases, as shown in Figure 1. Cobalt(II) acetate itself has an absorption maximum at 525 nm; the intensity of this band increases monotonously, with a slight blue shift, as 3-chloropyridine is added. On the other hand, 2,4-lutidine exhibits a remarkable red shift, and the band intensity increases gradually with its addition. The same phenomenon was found with 2,6-lutidine and also with lithium acetate. Proll et al. have reported quite a similar reversible change in visible spectra for the acetic acid solution of cobalt(II) acetate with temperature variation on the addition of sodium acetate.[10]

In this acidic solvent, these lutidines, B, behave as strong bases (pK_a = 6.7–7.1 in water[16-19]). Hence, they react with a solvent molecule to give rise to pyridinium and acetate ions according to the scheme[20]

$$\mathrm{B + HOAc \rightleftharpoons BH^+OAc^-} \qquad K_i, \text{ ionization} \qquad (1)$$

$$\mathrm{BH^+OAc^- \rightleftharpoons BH^+ + OAc^-} \qquad K_d, \text{ dissociation} \qquad (2)$$

Therefore, the spectral changes may reasonably be interpreted in terms of the reaction of cobalt(II) ion with the acetate ion formed, rather than that with the pyridine base itself

$$\mathrm{Co(OAc)_2} + n\mathrm{B'} \rightleftharpoons \mathrm{(BH^+)}_n(\mathrm{Co(OAc)}_{2+n}{}^{n-}) \qquad K_n \qquad (3)$$

where B′ denotes a pyridine base in all forms including free B and pyridinium acetate, not bound to the central metal ion.

This interpretation was confirmed by ^{13}C NMR spectra, as illustrated in Figure 2. Addition of cobalt(II) acetate provoked a drastic change in the NMR pattern of 3-chloropyridine, whereas it effected little change in the spectra of 2,4-lutidine except for a minor line broadening. The former change can readily be understood in terms of a direct interaction of the base with paramagnetic center, which leads to such line broadening that the peaks are no longer discernible. However, the reaction of acetate ion with cobalt(II) ion is not a direct interaction of the pyridine base itself, so the spectra of the base remain practically unchanged in the latter case.

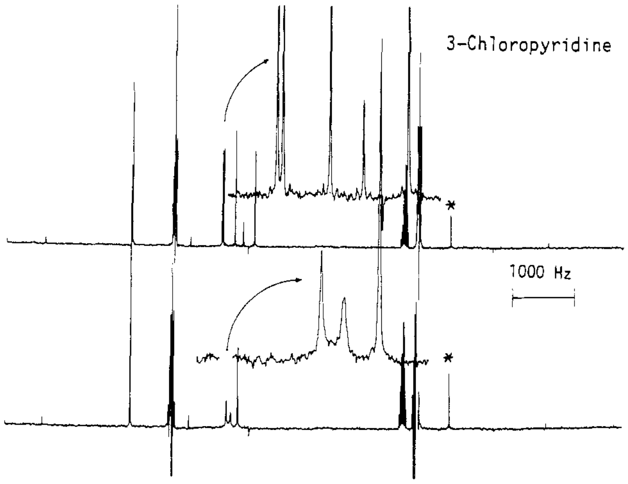

Figure 2. Line broadening in proton-decoupled ^{13}C NMR spectra indicating a direct interaction of Co(II) ion (C_{Co} = 0.84 × 10^{-2} M for the bottom spectrum) with 3-chloropyridine (C_B = 0.25 M). The spectrum of 3-chloropyridine alone is shown at the top with partial enlargement. The peak with an asterisk corresponds to TMS, and the pyridine peaks are between those of acetone-d_6 and solvent carbonyl.

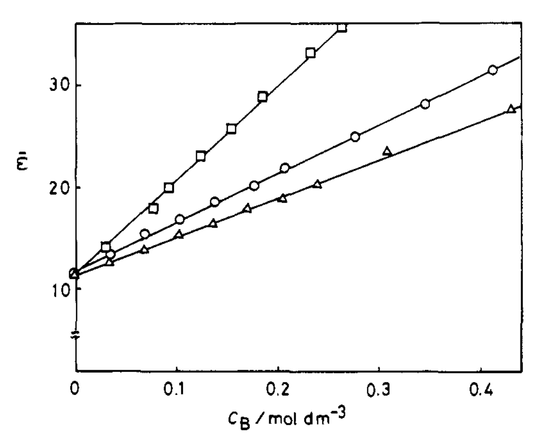

Figure 3. Linear dependence of the apparent molar absorption coefficient $\bar{\epsilon}$ of cobalt(II) acetate at 560 nm on the total base concentration C_B: (□) C_{Co} (10^{-2} M) = 0.843, lithium acetate; (○) C_{Co} = 0.964, 2,4-lutidine; (△) C_{Co} = 1.07, 2,6-lutidine.

Methyl substitution at the 2-position seems to be most effective in producing the red shift, which is comparable to the effect caused by the addition of lithium acetate.[10] Since the steric hindrance of the methyl group is quite probable,[21] this fact reinforces the above explanation. Thus, the reaction of 2,4- and 2,6-lutidines may reasonably be formulated as in eq 3.

The following equation should then be valid for the optical measurement at 560 nm

$$C_{Co}\bar{\epsilon} = \epsilon_0[\mathrm{Co(OAc)_2}] + \sum\epsilon_n[(\mathrm{BH})_n(\mathrm{Co(OAc)}_{2+n})] \qquad (4)$$

where C_{Co} is the total cobalt(II) concentration, ϵ_0 and ϵ_n are the molar absorption coefficients of cobalt(II) acetate and $(BH)_n$-$(Co(OAc)_{2+n})$, respectively, and $\bar{\epsilon}$ is the apparent ϵ with respect to cobalt(II). Thus

$$\bar{\epsilon} = (\epsilon_0 + \sum\epsilon_n K_n[\mathrm{B'}]^n)/(1 + \sum K_n[\mathrm{B'}]^n) \qquad (5)$$

The apparent absorption coefficient is plotted as a function of total

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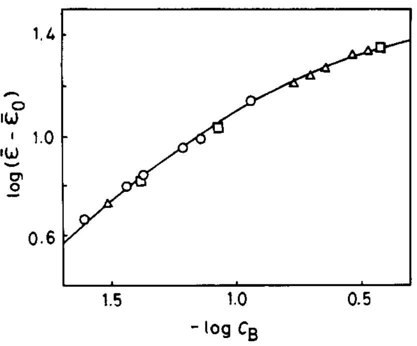

Figure 4. Logarithmic plot of $\tilde{\epsilon} - \epsilon_0$ versus the 3-chloropyridine concentration in the presence of cobalt(II) acetate. The solid line is a normalized curve, calculated by using the constants determined in this work. C_{Co} (10^{-2} M) = 1.08 (□), 0.782 (○), and 1.04 (△).

base concentration, C_B, as illustrated in Figure 3. As the concentration of B′ can be approximated well to C_B, this linear relationship shows that K_1 is rather small and that further terms may be negligible. Data processing on the computer resulted in the following formation constants: $K_1 = 0.026$ for 2,6-lutidine (pK_a in water 6.71), 0.033 for 2,4-lutidine (pK_a 6.74), and 0.063 for lithium acetate (pK_a = 4.74) ($\epsilon_1 = 1.70 \times 10^3$ M^{-1} cm^{-1} at 560 nm).

This situation is essentially the same as that in the system investigated by Proll et al.,[10] but they have interpreted the linearity in terms of the predominance of the species $Co(OAc)_4^{2-}$ rather than $Co(OAc)_3^-$. This interpretation may be a natural consequence from their assumption of the presence of charged complexes such as $Co(OAc)_4^{2-}$ instead of the corresponding ion pair such as $(Na^+)_2Co(OAc)_4^{2-}$. Since acetic acid has a low dielectric constant, such a dissociated divalent ion should be present in only a trace quantity. Hence, the data of Proll et al. should be reinterpreted in terms of predominant undissociated species as mentioned above.

Cobalt(II) acetate gave rise to a new absorption maximum at about 1450 nm in the near-IR region, when lithium acetate was added (C_B = 0.5 M vs C_{Co} = 0.013 M). This spectrum was quite similar in shape to that of tetrakis(trifluoroacetato)cobalt(II) species, for which the coordination environment was found to be nearly tetrahedral from X-ray crystallography.[22] This structural conclusion is consistent with the spectral change characteristic of the formation of a tetrahedral environment around cobalt(II) ion (from pale to deep violet, larger molar absorption coefficient ϵ_1 = 1700 M^{-1} cm^{-1} compared to ϵ_0 = 11.5 M^{-1} cm^{-1} for $Co(OAc)_2$), which has been interpreted on the basis of ligand field theory.[23]

Reactions of Cobalt(II) Acetate with Chloropyridines. Cobalt(II) acetate reacts with 2- and 3-chloropyridines in a way very different from that for the aforementioned lutidines. The wavelength of the maximum absorption does not shift appreciably, with its absorbance increased gradually on addition of a chloropyridine. As can be seen from Figure 4, the change in absorbance is no longer linear with the ligand concentration.

As a chloropyridine has an electron-withdrawing group, its basicity is greatly reduced from that of pyridine; i.e., the pK_a in water is 0.49 (2-chloropyridine) and 2.84 (3-chloropyridine). This will result in weaker protonation, and hence the following scheme of reaction can be assumed

$$Co(OAc)_2 + B' \rightleftharpoons Co(OAc)_2B \quad K_1 \tag{6}$$

which leads to

$$\log(\tilde{\epsilon} - \epsilon_0) = \log(\epsilon_1 - \epsilon_0) + \log\{K_1[B']/(1 + K_1[B'])\} \tag{7}$$

The curve-fitting method gave approximate values of the formation constant K_1 as well as the molar extinction coefficient ϵ_1, which were subsequently refined by processing on the computer.

Table I. Apparent and Intrinsic Formation Constants (K_1, $K_1°$) and Molar Absorption Coefficients ϵ_1 at 560 nm of Cobalt(II) and Nickel(II) Complexes with Pyridine Bases

	Co^b			Ni			
base	K_1	$K_1°$	$\epsilon_1{}^a$	K_1	$K_1°$	ϵ_1	p$K_a{}^c$
2-chloropyridine	0.2	0.2	45				0.49
3-chloropyridine	6.3	7.4	49	13	16	27	2.84
pyridine				8.6	19	29	5.19
3,4-lutidine				2.8	24	25	6.47

[a] ϵ_{Co} = 11.5 M^{-1} cm^{-1} at 560 nm; all ϵ_1 values in M^{-1} cm^{-1}. [b] For the tetrahedral cobalt(II) complexes; see text. [c] pK_a of the conjugate acid in water.

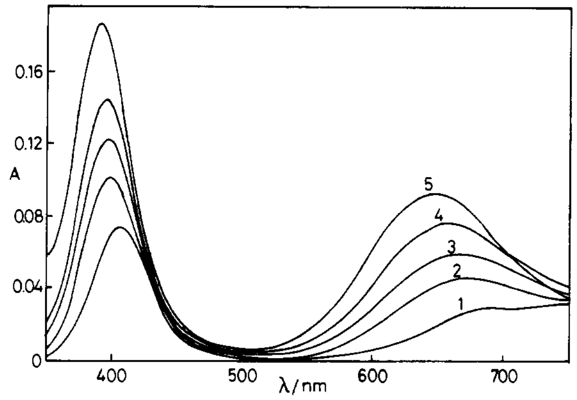

Figure 5. Change in electronic spectra of nickel(II) acetate on addition of 3-chloropyridine: C_{Ni} (10^{-2} M) = 0.709; C_B (M) = (1) 0, (2) 0.0422, (3) 0.0918, (4) 0.230, (5) 2.0.

As can be seen from Table I, the formation constant of the Co(II)–2-chloropyridine complex is smaller than that for the 3-chloropyridine complex, possibly because of the steric hindrance of the substituent group. Since the electronic spectra of the species formed are essentially the same as that of the initial cobalt(II) acetate, the coordination polyhedron in these complexes is considered to be nearly octahedral.

Reactions of Nickel(II) Acetate with Pyridine Bases. Nickel(II) acetate shows a considerable spectral change on addition of 3-chloropyridine, as illustrated in Figure 5. However, it reacts little with 2-chloropyridine and 2,4-lutidine, judging from the indiscernible change, possibly because of the steric hindrance of these bases.

These facts suggest that nickel(II) ion is coordinated directly to a pyridine base, and hence the corresponding equilibrium may be expressed as

$$Ni(OAc)_2 + B' \rightleftharpoons Ni(OAc)_2B \quad K_1 \tag{8}$$

This leads to quite the same expression as eq 7 for the optical change, and the formation of higher complexes is negligible in the curve-fitting procedure. As summarized in Table I, the formation constant K_1 is larger for a less basic ligand, which seems rather curious in view of the general tendency in aqueous solution chemistry. This paradox will be discussed later in light of the ionization of pyridine bases in this solvent.

As mentioned above, the 2-substituted pyridine effects only a small change in visible spectra, which makes it difficult to determine the corresponding formation constant. Nevertheless, 2-chloropyridine tends to shift the peak at 405 nm of nickel(II) acetate toward the UV region, and this is indicative of a behavior similar to that of 3-chloropyridine. In contrast, 2,4-lutidine has no such tendency, while the intensity increases only to a slight extent. This may be interpreted in terms of the formation of $BH^+Ni(OAc)_3^-$.

In summary, a pyridine base can be coordinated to both cobalt(II) and nickel(II) ions directly through the nitrogen atom in acetic acid, unless the steric hindrance operates significantly. Both cations can also complex with the acetate ions resulting from solvolysis, but this type of complex can be detected only in the case of the tetrahedral cobalt(II) species, which is deeply colored.

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Table II. Overall Dissociation Constants K_d' As Determined Potentiometrically

base	$-\log K_d'$	pK_a[b]
3-chloropyridine	8.26 ± 0.03	2.84
pyridine	6.10[a]	5.19
3,4-lutidine	5.73 ± 0.05	6.47
2,4-lutidine	5.72 ± 0.07	6.74
lithium acetate	6.60 ± 0.05 6.79[a]	4.74

[a] Assuming $pK_d' = 6.10$ and $pK_s = 14.45$ (Bruckenstein, S.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1956**, *78*, 2974–2979). [b] pK_a of the conjugate acid in water.

Potentiometric Measurement of the Dissociation Constants of Bases. Quantitative interpretation of the complex formation requires knowledge about the ionization and dissociation constants of bases in acetic acid, but these are not necessarily available. Hence, potentiometric titrations were carried out, without adding a supporting electrolyte, so as to avoid any side reactions due to its presence.

The so-called dissociation constant K_d' is given in the expression[20]

$$K_d' = [BH^+][OAc^-]/([B] + [BH^+OAc^-]) \qquad (9)$$

which will be referred to as the overall dissociation constant.

Substitution of eq 1 and 2 gives

$$K_d' = K_d/(1 + K_i^{-1}) \qquad (10)$$

Since dissociation into ions is generally unimportant in acetic acid, the total concentration of a pyridine base C_B may be approximated as

$$\begin{aligned} C_B &= [B] + [BH^+OAc^-] + [BH^+] \\ &= [B] + [BH^+OAc^-] \qquad (11) \end{aligned}$$

The electroneutrality principle leads to

$$[BH^+] = [OAc^-] \qquad (12)$$

because H_2OAc^+ is negligible in this solvent containing a base. Hence, the overall dissociation constant is given as

$$K_d' = [OAc^-]^2/C_B \qquad (13)$$

On the other hand, a glass electrode should respond to the hydrogen ion activity. As the overall dissociation constant is on the order of magnitude of 10^{-5} even for a strong electrolyte in acetic acid, the ionic strength in the solvent amounts to 10^{-5}–10^{-4} M at most, and then the variation in activity coefficient in the solvent may be negligible compared to experimental errors. Hence, the measured potential E is related to the H^+ concentration as

$$E = E° + (RT/F) \ln [H^+] \qquad (14)$$

which results in

$$E = E° + (RT/F) \ln K_s - (RT/2F) \ln K_d' - (RT/2F) \ln C_B \qquad (15)$$

where K_s is the autoprotolysis constant of acetic acid. A linear variation was found experimentally between E and $\log C_B$. A non-Nernstian small change in E was only observed on addition of 2-chloropyridine, which made accurate determination of the corresponding constant impossible. The smallest quantity of water should affect the potential because of the very low basicity of this compound, and $\log K_d'$ should be apparently much smaller than that of the 3-chloro analogue. The standard potential $E°$ varied up to several millivolts from day to day in all cases, and after correction for this change the dissociation constants were calculated and are summarized in Table II.

According to the classical model of electrolytes, K_d should be primarily determined by the size of the cation BH^+. Since the pyridine bases studied here are not very different in size, the values of K_d should be similar to each other. Thus, K_d' should be related to K_i according to eq 10. Since K_i increases with pK_a, the overall dissociation constant increases in turn with the basicity. As log K_d' values of chloropyridines are smaller than that of lithium acetate by ca. 1.5, 2–3% at most of the pyridines must be present in an ionic form.

Table III. Comparison of the Molar Absorption Coefficients for Pyridine in Various Media

medium	$\epsilon_{255}/10^3$ M^{-1} cm^{-1}	$\epsilon_{256}/10^3$ M^{-1} cm^{-1}	ref
HOAc	4.46	4.40	*a*
H_2O	2.80	3.07	*a*
H_2O		3.05 (257 nm)	*b*
$H_2O/HClO_4$	5.70	5.75	*a*
$H_2O/NaOH$	2.55	2.85	*a*
ethanol	2.21	2.49	*a*
methanol		2.46	*b*
hexane		1.90	*b*
HOAc (BH^+)[c]	5.80		*a*

[a] This work. [b] *Sadtler Handbook of Ultraviolet Spectra*; Sadtler: Philadelphia, 1979. [c] Pyridinium perchlorate dissolved in acetic acid.

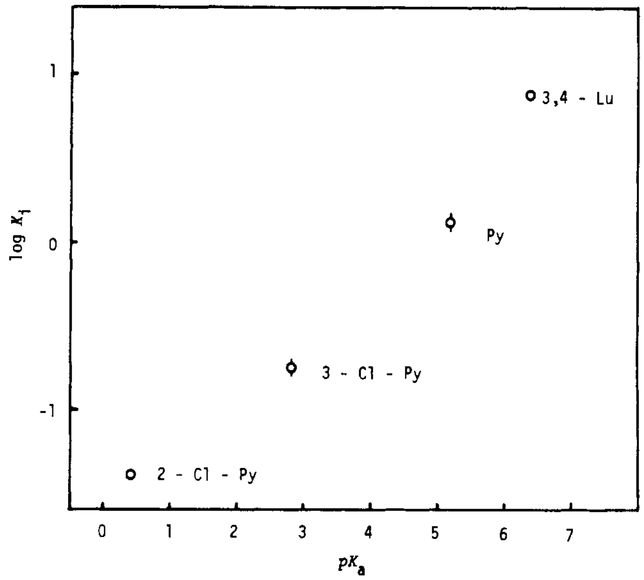

Figure 6. Ionization constants of pyridine bases as a function of protonation constant in water. $\log K_i = -1.41 \pm 0.03$ (2-chloropyridine), -0.75 ± 0.07 (3-chloropyridine), 0.13 ± 0.05 (pyridine), and 0.86 ± 0.05 (3,4-lutidine).

Ionization Constants of Pyridine Bases. As has been discussed earlier, the electrochemical method alone cannot afford the ionization constants K_i, and the lack of this constant has prevented the quantitative interpretation of complexation reactions in this solvent.

Fortunately, a pyridine base absorbs in the ultraviolet region, and this property was utilized for determining the ionization constant. When the average molar absorption coefficient of the base is denoted as $\bar{\epsilon}$ and its total concentration as C_B, the following equations hold:

$$C_B = [B] + [BH^+OAc^-] \qquad (16)$$

$$C_B\bar{\epsilon} = \epsilon_0[B] + \epsilon_i[BH^+OAc^-] \qquad (17)$$

where the completely dissociated species BH^+ is disregarded because of its negligibly small concentration. ϵ_0 and ϵ_i represent the molar extinction coefficients of B and the ionized species, respectively. Substitution of K_i (eq 1) results in the expression

$$K_i = (\epsilon_0 - \bar{\epsilon})/(\bar{\epsilon} - \epsilon_i) \qquad (18)$$

The molar absorption coefficient ϵ_i of the ionized pyridine base may be identified with that of either pyridinium perchlorate in acetic acid or pyridine dissolved in aqueous perchloric acid, as can be seen from Table III. Differences in absorbance between the two alcohols and water in this table should reflect different extents to which pyridine is hydrogen-bonded to solvent molecules. Since the acceptor number of acetic acid (AN = 52.9) is closer to that of water (AN = 54.8) than to those of ethanol (AN = 37.1) and methanol (AN = 41.3),[24] the molar absorption coefficients for aqueous solutions (slightly alkaline and acid) were substituted for those of B and $\mathrm{BH^+OAc^-}$ of pyridine bases in the calculation of K_i, assuming that the degree of hydrogen bonding in acetic acid is similar to that in water.

As is seen from Figure 6, the ionization constant thus determined increases smoothly with the protonation constant of a base in aqueous solution. Bruckenstein et al. have estimated $K_i = 5.37$ for pyridine on the assumption that $\epsilon_0 = 0$,[25] but the nonionized species B absorbs evidently to a certain degree.

Pyridine in carbon tetrachloride absorbs very strongly at 1585 $\mathrm{cm^{-1}}$ (IR spectrum A), but this peak becomes rather weak, and new ones appear at about 1600 and 1630 $\mathrm{cm^{-1}}$, on addition of acetic acid (10%, IR spectrum B). The former peak has been assigned to $\nu_{\mathrm{C=N}}$ and said to shift to 1630–1640 $\mathrm{cm^{-1}}$ on protonation ($\nu_{\mathrm{C=N^+}}$).[26,27] In spectrum B, a rather strong peak newly appeared at 1760 $\mathrm{cm^{-1}}$ (monomeric carboxyl group), which indicates the formation of monomeric acetic acid resulting from partial cleavage of the dimeric structure of the solvent.[28] Thus, comparison of IR spectra supports the ion-pair formation, i.e. the charge separation.

Now that ionization constants are available, the formation constant K_1° in a proper sense can be calculated

$$\mathrm{M(OAc)_2 + B \rightleftharpoons M(OAc)_2B} \quad K_1^\circ \qquad (19)$$

where B stands for only the nonionized base. Then

$$\begin{aligned} K_1 &= [\mathrm{M(OAc)_2B}]/[\mathrm{M(OAc)_2}][\mathrm{B}] \\ &= (1 + K_i)K_1 \end{aligned} \qquad (20)$$

As is evident from Table I, the values of K_1° increase monotonically with increasing $\mathrm{p}K_\mathrm{a}$, as is ordinarily the case in aqueous solution chemistry. Thus, the aforementioned paradox is now clearly resolved. Acetic acid is not an exceptional solvent with respect to coordination chemistry; only some correction should be made for the ionization of solutes for quantitative interpretation of chemical reactions in this solvent.

Acknowledgment. We wish to thank H. Ohkawa, Horiba Ltd., for having provided us with the glass and calomel electrodes specially manufactured for this study. This research was financially supported in part by Grant-in-Aid for Scientific Research No. 63540449 from the Ministry of Education, Science and Culture of Japan, which is gratefully acknowledged.

Registry No. Co, 7440-48-4; Ni, 7440-02-0; LiOAc, 546-89-4; 2,4-lutidine, 108-47-4; 3,4-lutidine, 583-58-4; 3-chloropyridine, 626-60-8; pyridine, 110-86-1; 2-chloropyridine, 109-09-1.

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Quenching of the ^{2}E Excited State of Tris(polypyridine)chromium(III) Ions with Titanium(III)

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Received March 21, 1989

The kinetics of the quenching of the ^{2}E excited state of chromium polypyridine complexes by Ti(III) were investigated at 25 °C in 1.0 M LiCl/HCl. The dependence of the rate on hydrogen ion concentration indicates that both $\mathrm{Ti(H_2O)_6^{3+}}$ and $\mathrm{(H_2O)_5Ti(OH)^{2+}}$ quench. The quenching rate constants for $\mathrm{Ti^{3+}}$ are in the range $(0.26\text{–}3.7) \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$ and those for $\mathrm{TiOH^{2+}}$ are in the range $(0.81\text{–}9.7) \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ when a value $K_\mathrm{a} = 4.6 \times 10^{-3}$ M is used. The formation of a stable Cr(II) product was observed spectrophotometrically, indicating back electron transfer occurs too slowly to measure. This is explained by the instability of $\mathrm{TiO^+}$, the immediate product of back electron transfer. Plots of log k_q vs ΔE° are linear for the quenching by both $\mathrm{Ti^{3+}}$ and $\mathrm{TiOH^{2+}}$.

Introduction

Electron-transfer reactions of Ti(III) have been widely studied in recent years. Many studies have been carried out with complexes of Ru(III)[1] and of Co(III)[2] as oxidants. Other oxidants include iodine,[3] 1-hydroxy-1-methylethyl radicals,[4] V(IV),[5] V(V),[6] and complexes of Ni(III)[7] and Os(III).[8] Often a rate law term with an inverse dependence on $[\mathrm{H^+}]$ is found, indicating $\mathrm{TiOH^{2+}}$ is an active reductant.[8-11] Since the Ti(IV) product is $\mathrm{TiO^{2+}}$, it might be expected that a species with a shorter Ti–O bond, as in $\mathrm{TiOH^{2+}}$, would be more reactive.

Inner-sphere mechanisms have been found to operate in cases where there is an efficient bridging ligand such as oxalate,[10,12] thiocyanate,[13] salicylate,[14] or acetate.[15] In these reactions, substitution on Ti(III) is sometimes the rate-limiting step.[16] The

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