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A Temperature-Jump Study of the Formation Reactions of Nickel(II)-Pyridine Complexes in Aqueous Solutions

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A temperature-jump study reveals two relaxation phenomena in aqueous nickel(II)-pyridine solutions. One is observed in a metal-rich and low-concentration system, while the other is found only in a ligand-rich and high-concentration system. The relaxation processes are ascribed to the complex formation reactions:

$$\mathrm{Ni^{2+} + py \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni(py)^{2+}} \quad \text{and} \quad \mathrm{Ni(py)_2{}^{2+} + py \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ni(py)_3{}^{2+}}$$

The rate constants reported are: 3.6×10^3 $\mathrm{M^{-1}\,s^{-1}}$ for k_1 and k_3, 37 $\mathrm{s^{-1}}$ for k_{-1}, and 760 $\mathrm{s^{-1}}$ for k_{-3}, at 25 °C. The effect of the coordinated pyridine molecules on the reactivity of the metal is discussed.

Considerable information now exists on the kinetics of the complex formation reactions of metal ions with organic and inorganic ligands.[1,2] In particular, much effort has been directed toward characterizing the solvent lifetimes within the inner coordination spheres of the metal ions. However, these studies have been concerned almost entirely with the formation reactions of mono-ligand complexes, and considerably less is known about the kinetics of multi-ligand complexes, in particular, of unidentate ligands. This is because a fundamental difficulty exists in these studies. For obtaining kinetic information on these complexes, experiments have to be made on solutions in a ligand-rich concentration range. However, this condition generally produces many kinds of complexes in solution and introduces a complication in reaction analysis.

In the present study, complex formation reactions in the aqueous nickel(II)-pyridine system were investigated to begin with. Although many studies[1,2] have been made on the kinetics of the reactions of $\mathrm{Ni^{2+}}$ with unidentate and multidentate heterocyclic amines, few systematic studies have been made on the nickel(II)-pyridine system, especially from the above point of view. Any information obtained will be helpful in elucidating the detailed reaction mechanism of the formation of multidentate complexes.

Experimental

Pyridine of a reagent grade was dried over KOH and distilled once. The other chemicals used were of a reagent grade and were used without further purification. Distilled water was degassed by boiling it immediately before use. Sample solutions were prepared by mixing appropriate amounts of aqueous stock solutions of $\mathrm{Ni(NO_3)_2}$, pyridine and, when necessary, Bromothymol Blue as a colorimetric pH-indicator. The ionic strength, I, was brought to the desired level by the addition of $\mathrm{KNO_3}$. The pH was adjusted by the addition of NaOH and/or $\mathrm{HNO_3}$.

The temperature-jump apparatus used and the experimental procedure have been described elsewhere.[3] The only change in the apparatus was that the cathode follower previously used was replaced by a 1 : 1 probe (Iwatsu 117B2). This improvement has resulted in an increase in the signal-to-noise ratio by a factor of two. The relaxation measurement was carried out at 25±1 °C.

Results

The experimental conditions and the kinetic data obtained are summarized in Table 1. All the solutions studied showed a single relaxation phenomenon. The reciprocal relaxation times, τ_1^{-1} and τ_2^{-1}, quoted in Table 1 represent an average of at least four experiments. The maximum errors are about ±10 and 15%, respectively. As is shown in Table 1, the kinetic studies were carried out for two different concentration ranges.

TABLE 1. KINETIC DATA FOR THE NICKEL-PYRIDINE SYSTEM AT 25 °C[a)]

ΣNi (M)	Σpy (M)	pH[b)]	τ_1^{-1} (10^2 $\mathrm{s^{-1}}$)	τ_2^{-1} (10^2 $\mathrm{s^{-1}}$)
		I=0.10[c)]		
0.00496	0.00102	7.04	0.573	
0.00496	0.00508	6.78	0.661	
0.00992	0.00254	7.23	0.711	
0.00992	0.0102	6.89	0.837	
0.0101	0.00102	7.13	0.727	
0.0149	0.0102	7.13	0.921	
0.0198	0.00102	7.12	1.11	
0.0198	0.00508	7.29	1.05	
0.0198	0.0203	6.75	1.09	
0.0198	0.0254	7.02	1.15	
0.0236	0.0242	7.16	1.18	
0.0248	0.0101	7.28	1.28	
		I=0.30		
0.100	0.154	6.90		9.0
0.100	0.206	6.87		11.2
0.100	0.257	6.89		13.4
0.100	0.257	6.51		11.7
0.100	0.257	5.96		11.0
0.100	0.309	6.89		14.0
0.100	0.360	6.89		14.7

a) The equilibrium constants used:[5)] $\mathrm{p}K_\mathrm{H}=5.44$, $\log K_1=1.91$, $\log K_2=1.28$, and $\log K_3=0.52$, at 25 °C and I=0.6. b) Converted to [$\mathrm{H^+}$] by the use of $\gamma_\mathrm{H}=0.825$ and 0.806 at I=0.10 and 0.30, respectively. c) Solutions contain 2×10^{-5} M Bromothymol Blue indicator ($\mathrm{p}K_\mathrm{In}=7.10$, I=0.1).[6)]

One has relatively low concentrations, mostly in the metal-rich region (I=0.10), and the other, high concentrations in the ligand-rich region (I=0.30).

The low concentration system contained Bromothymol Blue indicator, and the temperature-jump relaxation phenomenon was observed by following the absorbance at the wavelength of 617 nm. A representative relaxation effect is shown in Fig. 1. Blank solutions of the nickel-indicator and pyridine-indicator systems showed no relaxation effect in the same time range.

On the other hand, the indicator method is not effective in the ligand-rich region, because the amplitude of the relaxation signal decreases with an increase in the concentration of pyridine. Therefore, the experiments in this region were carried out at high concentrations and without a pH-indicator. The wavelength of the observation was 605 nm, where the nickel–pyridine solution exhibits an absorbance maximum. Figure 2 shows a representative relaxation effect. A solution containing only 0.1 M $Ni(NO_3)_2$ at pH=6.8 showed no relaxation effect in the same time range.

The above results indicate that the relaxation times in Table 1 are really associated with nickel–pyridine interactions.

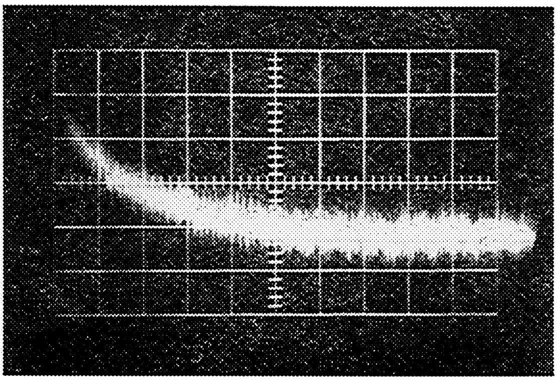

Fig. 1. Relaxation effect in nickel-pyridine system: $\Sigma Ni = 9.92\times10^{-3}$ M, $\Sigma\, py = 2.54\times10^{-3}$ M, pH=7.23, I=0.10 with 2×10^{-5} M Bromothymol Blue as an indicator. The abscissa scale is 10 ms per division, and the vertical scale is in arbitrary unit of absorbency. The relaxation effect corresponds to an increase in absorbance with time.

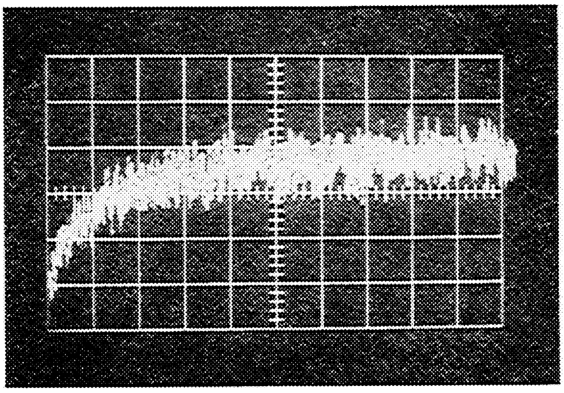

Fig. 2. Relaxation effect in nickel-pyridine system: $\Sigma\, Ni = 0.100$ M, $\Sigma\, py = 0.257$ M, pH=6.89, I=0.30. The abscissa scale is 0.5 ms per division, and the vertical scale is in arbitrary unit of absorbency. The relaxation effect corresponds to a decrease in absorbance with time.

Treatment of Data

Under the experimental conditions studied, the formation of nickel(II)–pyridine complexes may proceed most generally by the following reaction mechanism:

$$Hpy^+ \overset{\text{fast}}{\rightleftharpoons} H^+ + py \qquad K_H,$$

$$Ni^{2+} + py \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni(py)^{2+} \qquad K_1, \qquad (1)$$

$$Ni(py)^{2+} + py \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ni(py)_2{}^{2+} \qquad K_2, \qquad (2)$$

$$Ni(py)_2{}^{2+} + py \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ni(py)_3{}^{2+} \qquad K_3, \qquad (3)$$

where py denotes the pyridine molecule and where K_H, K_1, K_2, and K_3 are the equilibrium constants for the corresponding reactions. If the relaxation process is ascribed to one of the reactions, (1—3), the corresponding relaxation time is given by:

$$\frac{1}{\tau} = k_n\{[Ni(py)^{2+}_{n-1}] + [py]\} + k_{-n}, \quad n=1,\ 2,\ \text{or}\ 3, \qquad (4)$$

where the brackets indicate the molar concentration at equilibrium. The protolytic reactions of pyridine and the pH-indicator (when it is added in solution) reach equilibrium much faster than the metal complex reactions (1—3), and they can be assumed to be in equilibrium at all times. However, the contributions of these equilibria to the relaxation times can be ruled out under the experimental conditions studied,[4] and so this effect has been ignored in Eq. 4.

The equilibrium constants used are listed in the footnote of Table 1. The values of the constants at I=0.6 were used without further corrections to the present systems at I=0.10 and 0.30. This approximation may not cause serious errors in the results because of the charge types of the reactions concerned. The equilibrium concentrations of various species in solution were calculated from the $\Sigma\, Ni$, $\Sigma\, py$, and pH values in Table 1 by using these equilibrium constants.

Table 1 shows the two concentration-dependent relaxation times (τ_1 and τ_2), which were observed in very different concentration ranges. Since these relaxation times could be ascribed to different processes, they will be discussed separately.

Low-concentration Time (τ_1). An examination of the equilibrium concentrations shows that the predominant species in the solution are Ni^{2+}, py, and $Ni(py)^{2+}$. Then, the relaxation process can be attributed primarily to the complexation reaction (1). As is shown in Fig. 3, a graph of τ_1^{-1} *vs.* $[Ni^{2+}]+[py]$ plot gives a straight line. The slope and intercept of this line correspond to the rate constants k_1 and k_{-1}, respectively. The ratio of these values, 97±13, conforms with the equilibrium constant for this process. The rate constants obtained are shown in Table 2.

High-concentration Time (τ_2). The relaxation time was observed only in the solutions at high nickel concentrations with a pyridine-rich region. When the concentration of pyridine decreases further than those

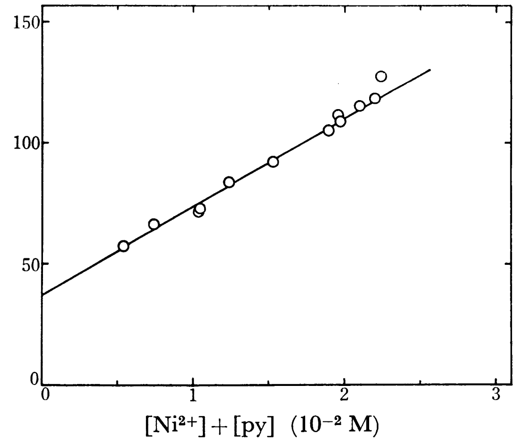

Fig. 3. $1/\tau_1$ *vs.* $[Ni^{2+}]+[py]$ plot of nickel-pyridine system at 25 °C, $I=0.10$.

Table 2. Kinetic results for the formation of nickel-pyridine complexes at 25 °C

n	k_n ($M^{-1}\,s^{-1}$)	k_{-n} (s^{-1})
1	$(3.6\pm0.3)\times10^3$	37 ± 4
3	$(3.6\pm1.5)\times10^3$	760 ± 280

studied here, the amplitude of the relaxation effect decreases rapidly. This fact indicates that the relaxation process could not be ascribed to Reaction 1. In fact, the τ_1^{-1} value expected in this concentration range was estimated to be lower by a factor of 0.25—0.41 than the τ_2^{-1} value in Table 1. Therefore, the investigation was carried out by associating the relaxation process with one of the reactions, (2 or 3). By using Eq. 4, it was found that only the case of $n=3$ is consistent with the present data.7) As is shown in Fig. 4, a graph of τ_2^{-1} *vs.* $[Ni(py)_2^{2+}]+[py]$ plot gives a straight line. From the slope and intercept of this line, the rate constants k_3 and k_{-3} were obtained; they are also shown in Table 2. The ratio of these values gives $K_3=4.7\pm2.7$, which is close to the corresponding value used.

In the system of interest here, an additional complication is introduced by the fact that the contribution of Reaction 2 to the relaxation process must be taken into account. By a relaxation treatment coupling the two reactions, (2 and 3), we obtain:8)

$$\frac{1}{\tau}=\frac{a_{11}+a_{22}}{2}+\left[\left(\frac{a_{11}-a_{22}}{2}\right)^2+a_{12}a_{21}\right]^{1/2}, \quad (5)$$

where $a_{11}=k_2\{[Ni(py)^{2+}]+[py]\}+k_{-2}$, $a_{12}=k_2[Ni(py)^{2+}]-k_{-2}$, $a_{21}=k_3\{[Ni(py)_2^{2+}]-[py]\}$, and $a_{22}=k_3\{[Ni(py)_2^{2+}]+[py]\}+k_{-3}$. The relaxation time was calculated by means of Eq. 5, with the k_3 and k_{-3} values in Table 2, together with appropriately assumed k_2 values and by use of the relation $k_{-2}=k_2/K_2$. Thus, the k_2 value in the range, $(2—5)\times10^3\ M^{-1}\,s^{-1}$, is proven to affect the relaxation time only 8% at most. Therefore, the relaxation process can be ascribed solely to Reaction 3.

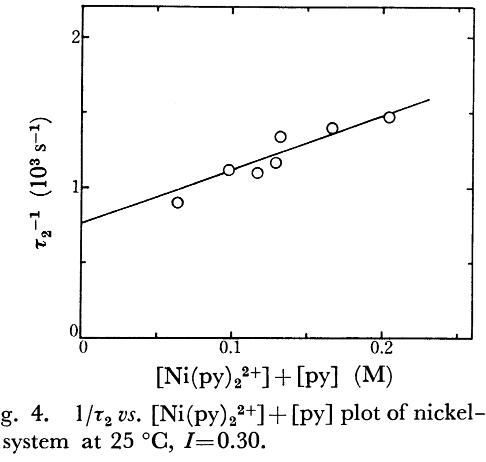

Fig. 4. $1/\tau_2$ *vs.* $[Ni(py)_2^{2+}]+[py]$ plot of nickel-pyridine system at 25 °C, $I=0.30$.

Discussion

The k_1 value in Table 2 is close to the corresponding rate constants reported for the reactions of Ni^{2+} with neutral unidentate ligands1,2) and is also consistent with the first-order rate constant of the water exchange of the nickel ion measured by NMR.9,10) This result indicates that the formation reaction of $Ni(py)^{2+}$ proceeds *via* the Eigen mechanism,11) which involves the loss of a water molecule in the rate-determining step. Table 2 shows also that the value of k_3 is the same as that of k_1. This result leads one to conclude that the formation reaction of the $Ni(py)_3^{2+}$ complex proceeds by a mechanism similar to that cited above and that the rate of water release from $Ni(py)_2^{2+}$ is close to that of Ni^{2+}. This conclusion is similar to that already reached by Hammes and Steinfeld8) for the consecutive formations of nickel(II)-imidazole complexes, although they obtained a slightly decreasing tendency of $k_1>k_2>k_3$.

On the other hand, the dissociation rate constants, k_{-1} and k_{-3}, are very different from each other; these values determine the corresponding stability constants of the complexes. It is interesting to note that the k_{-3} value is much higher than the k_{-1} value, even taking into account the fact that the chance of the liberation of a pyridine molecule from $Ni(py)_3^{2+}$ is three times larger than that from $Ni(py)^{2+}$. The conclusion remark is that the pyridine molecules coordinated to the nickel ion enormously enhance their own lability, but little affect the lability of the coordinated water molecules. This fact suggests that the crowding of the bulky ligand molecules in the inner coordination sphere loosens solely the Ni–N bonds and facilitates their rupture. The dissociation rate constants of the mono-, bis-, and tris-imidazole-nickel(II) complexes8) and those of the mono- and tris-(2,2′-bipyridine)-nickel(II) complexes12) also support this idea, although in the latter complexes the absolute values of the rate constants are extremely low as a result of the stabilization effect of chelation.

References

1) M. Eigen and R. G. Wilkins, *Adv. Chem. Ser.*, **49**, 55 (1964).

2) D. J. Hewkin and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1970).

3) K. Tamura, *Bull. Chem. Soc. Jpn.*, **46**, 1581, 3626 (1973).

4) By including the rapid protolytic reactions, the relaxation time is expressed by (Ref. 8): $1/\tau=k_n\{[Ni(py)^{2+}_{n-1}]/(1+\alpha)+[py]\}+k_{-n}$. However, the quantity α is less than 0.01

under the experimental conditions in Table 1 and can be ignored with respect to unity in the above expression.

5) M. S. Sun and D. G. Brewer, *Can. J. Chem.*, **45**, 2729 (1967).

6) I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930).

7) From a graph of τ_2^{-1} *vs.* $[\mathrm{Ni(py)^{2+}}]+[\mathrm{py}]$ plot, the k_2 and k_{-2} values were estimated to be $4.9\times10^3\ \mathrm{M^{-1}\,s^{-1}}$ and $670\ \mathrm{s^{-1}}$, respectively. However, the ratio of these values, 7.4, is very different from the equilibrium constant for Reaction 2.

8) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

9) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

10) R. E. Connick and D. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966); T. J. Swift and G. P. Weinberger, *J. Am. Chem. Soc.*, **90**, 2023 (1968).

11) M. Eigen and L. De Maeyer, "Technique of Organic Chemistry," Vol. VIII, Part II, 2nd ed, ed by S. L. Friess, E. S. Lewis, and A. Weissberger, Interscience Publishers, Div., John Wiley & Sons, New York (1963), p. 1031.

12) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).