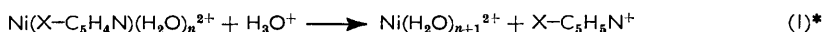


**654.** *Factors Influencing the Rates of Dissociation of Metal Complexes. Part VI.<sup>1</sup> Substituent Effects on the Dissociation Rates of Nickel(II)-Pyridine Complexes.*

By P. MOORE and R. G. WILKINS.

The rates of dissociation, in excess of acid, of nickel(II) mono-complexes with a series of 3- and 4-monosubstituted pyridines have been investigated spectrally by the stopped-flow method, and, where possible, Arrhenius parameters obtained. It has been found that the stronger the pyridine base, the slower its complex dissociates, although a change in the acid dissociation constant ( $K_{HL}$ ) of  $10^6$  only causes the rate constant to vary by a factor of 10. An estimate has been made of the  $K_{HL}$  value of a thermodynamically unstable species  $3\text{-C}_5\text{H}_4\text{N}\cdot\text{NH}_3^+$ . No spectral evidence was found for complex-formation in solution by 2-methyl- or 2-amino-pyridine with nickel(II).

PREVIOUS studies<sup>1-4</sup> have shown that flow techniques<sup>5</sup> are necessary in order to follow the rates of dissociation, in excess of acid, of nickel(II), and some copper(II), complexes with basic ligands. Since the dissociation of the pyridine complex [reaction (1); X = H] is measurable<sup>3</sup>



it was then possible to investigate the effect of substitution in the pyridine ring on the reactivity of the nickel complex. Substituents X were chosen to provide a wide range of  $pK_{HL}$  values (1.4—6.6) for the pyridine base, in addition to providing positive and negative inductive and mesomeric effects. The series of monosubstituted pyridines studied included the 3- and 4-CN, -Me, -Br, and -OMe, as well as the 3-CONH<sub>2</sub> and -NH<sub>3</sub><sup>+</sup> derivatives.

#### EXPERIMENTAL

*Materials.*—Commerical 2-, 3-, and 4-methylpyridine and 3-bromopyridine were distilled over sodium hydroxide, the middle fractions being used; these had b. p.s in agreement with literature values. 3-Bromopyridine, in ice-cold ethanol, was converted into the *nitrate* by

\*  $n$  probably equals 5; co-ordinated water will be omitted subsequently.

<sup>1</sup> Part V, Melson, and Wilkins, *J.*, 1963, 2662.

<sup>2</sup> Ahmed and Wilkins, *J.*, 1960, 2901.

<sup>3</sup> Melson and Wilkins, *J.*, 1962, 4208.

<sup>4</sup> Wilkins, *J.*, 1962, 4475.

<sup>5</sup> "Investigation of Rates and Mechanism of Reaction," Vol. VIII of Part II of "Technique of Organic Chemistry," ed. Friess, Lewis, and Weissberger, Interscience, New York, 1963, ch. 14.

cautious dropwise addition of ice-cold concentrated nitric acid. It had m. p. 140° (Found: C, 27.3; H, 2.6%; Equiv., 221. C<sub>5</sub>H<sub>5</sub>BrN<sub>2</sub>O<sub>3</sub> requires C, 27.2; H, 2.3%; Equiv., 221). 3-Methoxypyridine was prepared<sup>6</sup> by heating 3-bromopyridine with sodium methoxide and methanol in a sealed glass Carius tube for 48 hr. at 160°; the product distilled at 178–180°. It was converted into the *nitrate*, m. p. 88–89° (Found: C, 41.3; H, 4.4; N, 16.3. C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>O<sub>4</sub> requires C, 41.8; H, 4.65; N, 16.3%). 4-Methoxypyridine was prepared from 4-nitropyridine *N*-oxide by the method of Hertog and Combe.<sup>7</sup> It was converted into the *nitrate*, m. p. 149–150° (Found: C, 41.8; H, 4.6; N, 16.5%). The remaining pyridine derivatives were commercial materials, and were recrystallised before use as follows: 3-cyano- (ligroin, plus a few drops of ethanol; m. p. 50–51°); 4-cyano- (benzene; m. p. 76°); 2-amino- (benzene; m. p. 56°); and 3-amino-pyridine (benzene; m. p. 64°); nicotinamide (benzene: ethanol 9:1; m. p. 130–131°); pyridinium nitrate [ethanol; equiv., 141.5 (calc. 142)]; and 4-bromopyridinium chloride [methanol, equiv., 191 (calc. 194)]. The m. p.s are similar to the literature values. Anal. reagents were used throughout, nickel solutions being estimated complexometrically with EDTA.<sup>8</sup>

*Spectra.*—The spectra of aqueous solutions of each pyridine derivative (0.10M) and nickel nitrate (0.30M), using nickel nitrate solution (0.20M) as blank, were obtained on a Perkin-Elmer 137 (u.v.) or a Unicam S.P. 600 spectrophotometer at room temperature. Using the stability constants of nickel-pyridine complexes<sup>9</sup> as a guide, it was estimated that *ca.* 85% of the ligand was present as the mono-complex species under these conditions. The spectra were all similar, with peaks at 387 m $\mu$  ( $\epsilon_M = 5-8$ ) and 650 m $\mu$  ( $\epsilon_M = 3-3.5$ ) and a shoulder at *ca.* 725 m $\mu$  ( $\epsilon_M \sim 2.5$ ). The greatest change in optical density for reaction (1) was at *ca.* 625 m $\mu$ , which was chosen as the monitoring wavelength. For 2-amino- and 2-methyl-pyridine there was no evidence for complex-formation, the spectra being almost identical with that of nickel nitrate solution (0.10M).

*Kinetic Experiments.*—The stopped-flow apparatus previously described<sup>3</sup> was used. The small optical-density changes at 625 m $\mu$  in reaction (1) were detected by means of a photomultiplier, and the signal was displayed on two oscilloscopes. One of the traces was photographed and enlarged. Solutions were freshly prepared before each set of runs, and the ionic

TABLE I.

Dissociation of [Ni(X-C<sub>5</sub>H<sub>4</sub>N)]<sup>2+</sup> to nickel ions (temp. in °; *k* in sec.<sup>-1</sup>).

X	3-CN			4-CN				3-Br									
Temp. ...	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	6.0	6.0	9.8	9.8	
<i>k</i> .....	24	22	24	18	17	17	16	9.4	8.5	8.4	9.7	15	17	25	24		
X	3-Me			4-Br				3-Me									
Temp. ...	0.8	0.8	0.8	0.8	7.0	7.0	7.0	12.0	12.0	0.8	0.8	0.8	0.8	10.0	10.0	10.0	
<i>k</i> .....	4.7	4.1	4.1	5.0	5.3	8.7	10.5	7.8	16	13	2.4	2.5	2.4	2.5	7.8	8.1	7.6
X	3-Me (contd.)			4-Me				3-CONH <sub>2</sub>									
Temp. ...	10.0	20.0	20.0	0.8	0.8	0.8	10.1	10.1	20.0	20.0	0.8	0.8	0.8	7.9	7.9	12.0	
<i>k</i> .....	7.6	20	20	2.0	1.9	1.9	5.4	5.4	17	16	7.3	7.6	7.8	14	14	28	
X	3-NH <sub>3</sub> <sup>+</sup>			3-OMe													
Temp. ...	1.0	10.0		0.8	0.8	0.8	6.0	6.0	6.0	6.0	11.0	11.0	11.0	11.0	11.0	11.0	
<i>k</i> .....	17	37		5.0	4.9	4.6	8.2	7.1	8.1	6.8	7.8	11	10	11	11	12	
X	4-OMe			H													
Temp. ...	0.8	0.8	0.8	10.0	10.0	10.0	18.0	0.8	0.8	0.8	0.8	8.0	8.0	8.0	15.0	15.0	15.0
<i>k</i> .....	1.7	1.8	1.8	5.8	5.4	5.2	12	3.4*	3.0	3.9	3.5	6.5	6.5	6.9	15	15	13

\* In 0.20M HNO<sub>3</sub>.

strength was increased to 1.0M with sodium nitrate. The temperature was controlled to  $\pm 0.2^\circ$ . Details of the kinetic results are given in Table I. In all runs the conditions were: syringe (1) [Ni<sup>2+</sup>](total) = 0.30M, [pyridine derivative](total) = 0.150M, *I* = 1.0M; and

<sup>6</sup> Weidel and Blau, *Monatsh.*, 1885, **6**, 651.<sup>7</sup> Hertog and Combe, *Rec. Trav. chim.*, 1951, **70**, 589.<sup>8</sup> Schwarzenbach, "Complexometric Titrations," transl. by Irving, Methuen, London, 1957.<sup>9</sup> Stability Constants, Part I, Chem. Soc. Special Publ., 1957, No. 6.

syringe (2)  $[\text{HNO}_3] = 1.0\text{M}$ . First-order dissociation was always observed. The Arrhenius parameters were obtained in the usual way from the slope and intercept of the plots of  $\log_{10}k$  against  $T^{-1}$  [in  $(^\circ\text{K})^{-1}$ ]. The data are collected in Table 2, together with  $pK_{\text{HL}}$  and  $\sigma$  values as

TABLE 2.

Pyridine derivative	$pK_{\text{HL}}^a$	$\sigma^{n,o,p}$	$k$ (0.8°) (sec. <sup>-1</sup> )	$E$ (kcal. mole <sup>-1</sup> )	$\log A$ (log sec. <sup>-1</sup> )
3-Cyano .....	1.45 <sup>b,c</sup>	0.68 <sup>n</sup> 0.56 <sup>o</sup>	24	—	—
3-Bromo .....	2.84 <sup>d</sup>	0.39	8.5	17.1	14.6
3-Amido .....	3.35 <sup>e</sup> 3.40 <sup>b</sup>	0.28	7.5	16.5	14.0
4-Bromo .....	3.66 <sup>f</sup>	0.23	4.6 <sup>m</sup>	15.9	13.4
3-Methoxy .....	4.83 <sup>g</sup> 4.91 <sup>h</sup>	0.12	5.3	ca. 12.4	10.6
Pyridine .....	5.20 <sup>i</sup>	0.00	3.5	15.6 <sup>r</sup>	13.0 <sup>r</sup>
3-Methyl .....	5.52 <sup>h</sup> 5.63 <sup>j</sup> 5.68 <sup>i</sup> 5.82 <sup>b,c</sup>	-0.07	2.5	17.7	14.6
4-Methyl .....	5.98 <sup>j</sup> 6.02 <sup>k</sup> 6.08 <sup>n</sup> 6.11 <sup>b</sup>	-0.17	1.9	17.8	14.5
4-Methoxy .....	6.47 <sup>h</sup> 6.62 <sup>p</sup>	-0.27	1.8	18.1	14.7
4-Cyano .....	(1.7) <sup>l</sup>	0.63 <sup>n</sup> 0.66 <sup>o</sup>	17	—	—
3-Ammonium .....	(1.7) <sup>l</sup>	0.63 <sup>n</sup>	17	ca. 13 <sup>q</sup>	ca. 12 <sup>q</sup>

<sup>a</sup> At 25°. <sup>b</sup> At 24°. <sup>c</sup> Jaffé and Doak, *J. Amer. Chem. Soc.*, 1955, **77**, 4441. <sup>d</sup> Brown and McDaniel, *J. Amer. Chem. Soc.*, 1955, **77**, 3752. <sup>e</sup> Hughes, Jellinieck, and Ambrose, *J. Phys. Colloid Chem.*, 1949, **53**, 410. <sup>f</sup> Determined spectrophotometrically by method outlined in Albert and Sergeant, "Ionisation Constants of Acids and Bases," Methuen, London, 1962. Analytical wavelength 242  $\mu$ . Error  $\pm 0.07$ .  $I = 0.010\text{M}$ . <sup>g</sup> Albert and Phillips, *J.*, 1956, 1294. <sup>h</sup> Murmann and Basolo, *J. Amer. Chem. Soc.*, 1955, **77**, 3484. <sup>i</sup> Average of 7 values, Bryson, *J. Amer. Chem. Soc.*, 1960, **82**, 4871. <sup>j</sup> Andon, Cox, and Herington, *Trans. Faraday Soc.*, 1954, **50**, 918. <sup>k</sup> Brown and Mihm, *J. Amer. Chem. Soc.*, 1955, **77**, 1723. <sup>l</sup> Values estimated from Fig. 1. <sup>m</sup> Chloride medium. <sup>n</sup> Jaffé, *Chem. Rev.*, 1953, **53**, 171. <sup>o</sup> McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420. <sup>p</sup> Wells, *Chem. Rev.*, 1963, **63**, 171. <sup>q</sup> Estimated from two temperatures only. Melson and Wilkins (ref. 3) report  $E = 16.3$ ,  $\log A = 13.6$ .

appropriate. The errors in  $k$  are about  $\pm 12\%$  for  $k \sim 20$ ,  $\pm 5\%$  for  $k \sim 10$ , and  $\pm 3\%$  for  $k \sim 2$  sec.<sup>-1</sup>. The errors in the energies of activation are estimated to be  $\pm 2$  kcal. mole<sup>-1</sup> for the higher rates (when a small temperature range of only 10° could be used), and  $\pm 1$  kcal. mole<sup>-1</sup> for the lower rates.

## RESULTS AND DISCUSSION

Only a small amount of work has been reported on the effects of substituents in the ligand molecule on the rates of metal-ligand bond cleavage.<sup>10,11</sup> Ellis, Hogg, and Wilkins<sup>10</sup> studied the effect of substitution on the dissociation rates of nickel(II)-phenanthroline and -bipyridyl complexes. Certain correlations were drawn, but because the ligands were complicated, the conclusions were not completely unequivocal. In the present study, simpler ligands have been used, and the effects of substituents on the rates of dissociation of monopyridinenickel(II) complexes examined.

**2-Substitution.**—No spectral evidence was found for complex-formation in solution by 2-substituted pyridines, in which the substituent is a non-complexing group. This is a little surprising, since *solid* nickel complexes of 2-methylpyridine have been isolated.<sup>12,13</sup>

<sup>10</sup> Ellis, Hogg, and Wilkins, *J.*, 1959, 3308.

<sup>11</sup> Aprile, Caglioti, and Illuminati, *J. Inorg. Nuclear Chem.*, 1961, **21**, 325.

<sup>12</sup> Logan and Carle, *J. Amer. Chem. Soc.*, 1952, **74**, 5224.

<sup>13</sup> Graddon, Schulz, Watton, and Weedon, *Nature*, 1963, **198**, 1299.

Furthermore, the stability of silver(I) complexes of  $\alpha$ - and  $\gamma$ -picolines is similar.<sup>14</sup> However, 2- and 2,9-substituted phenanthrolines complex much less strongly with the first-row transition elements than does the parent compound,<sup>15</sup> and 2-substitution produces steric effects which are very unpredictable from one series of compounds to another.<sup>13</sup>

**3- and 4-Substitution.**—The rates of *acid* dissociation were measured, but (apart from the 3-amino-compound) the results pertain almost certainly to neutral solution also. A dependence of rate upon acidity was not found, and was not expected, since there is no possibility of intermediates of the type found for nickel chelates being formed.<sup>1-4</sup> It has become increasingly apparent<sup>16,17</sup> that the dissociation rate constant ( $k$ ) controls the stability constant ( $K_{ML}$ ) of complexes of the bivalent first-row transition elements:  $M + L \rightleftharpoons ML$ ;  $K_{ML} = k_2/k$ . This means that the smaller the value of  $K_{ML}$  for a series of ligands, the larger the value of  $k$ . This idea could be further tested with the present results, but thermodynamic data are available only for nickel(II) complexes with pyridine,<sup>9</sup>

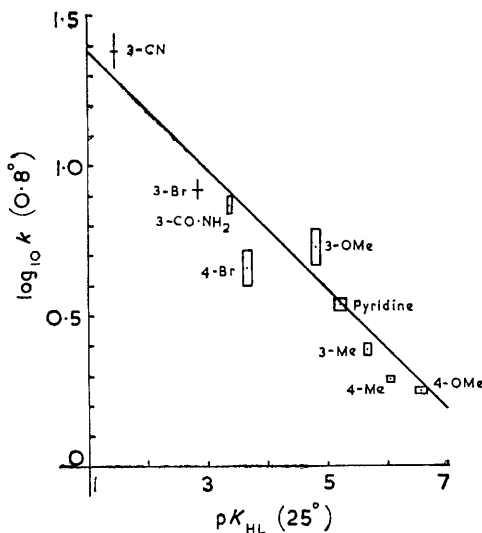


FIG. 1.

Correlation of the rates of dissociation of mono-complexes of Ni(II) and mono-substituted pyridines with  $pK_{HL}$  (Fig. 1) and with  $\sigma$  (Fig. 2).

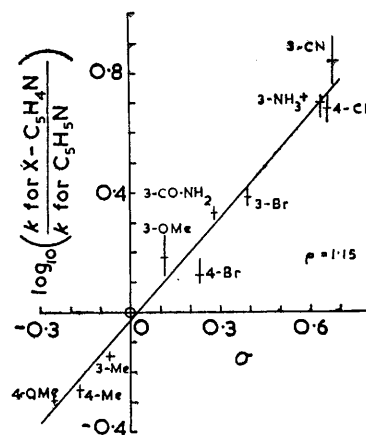


FIG. 2.

picolinic acid,<sup>9</sup> and 2-pyridylmethylamine.<sup>18</sup> However, it has been shown<sup>19</sup> that for a series of related ligands,  $K_{ML}$  values often parallel acid dissociation constants of the (protonated) ligand,  $pK_{HL}$ , unless extraneous effects are present, such as  $\pi$ -bonding.<sup>18</sup> It was therefore expected that the rates of dissociation of the complexes that we have studied would be proportional to  $K_{HL}$ , and the relation  $\log_{10} k = 1.58 - 0.21 pK_{HL}$  was indeed observed (Fig. 1).<sup>\*</sup> Because of the nature of the Hammett equation, a linear relation of  $\log_{10} k$  with  $\sigma$  might also be expected (Fig. 2). The positive  $\rho$  value (1.15) for the latter indicated that the reaction was facilitated by low electron density at the reaction site, as expected. The wide range of  $\sigma$ -values for the substituents produced only a very small

\* Since the rates with some pyridine derivatives could not be measured accurately or extrapolated to 25°, the acid dissociation constants at 25° had to be correlated with rate constants measured at 0.8°.

<sup>14</sup> Bruhlmann and Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401.

<sup>15</sup> Irving and Mellor, *J.*, 1962, 5237.

<sup>16</sup> Eigen, in "Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, pp. 371 et seq.

<sup>17</sup> Wilkins, *Quart. Rev.*, 1962, 316.

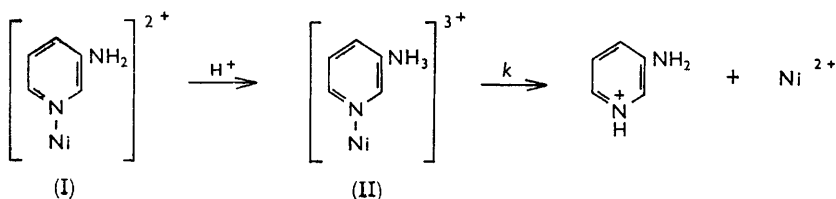
<sup>18</sup> Goldberg and Fernelius, *J. Phys. Chem.*, 1959, **63**, 1246.

<sup>19</sup> Rossotti, in "Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience, New York, 1960, ch. 1.

## 3458 Factors Influencing Rates of Dissociation of Metal Complexes. Part VI.

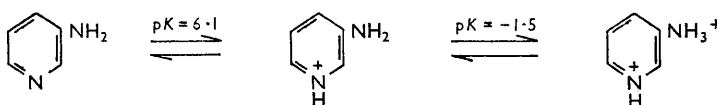
overall change in the rate constants, an insensitivity also observed in the alkaline hydrolysis of substituted benzoatocobalt(III) complexes.<sup>11</sup>

The ligand which most deviates from the linearity depicted in Fig. 1, and presents the most interesting behaviour, is 3-aminopyridine [see (I)]. The rate is much faster than expected from the  $pK_{HL}$  value of 6.1.<sup>20</sup> It was shown, by means of a pH-indicator method,<sup>3</sup> that *ca.* one mole of acid for every mole of ligand present had been consumed by the time the observable reaction commenced (*i.e.*, within about 3 msec.). The subsequent dissociation rate measured therefore refers to (II), and the enhanced rate and low energy of activation are understood as arising from the inductive effect of the positive charge weakening the nickel–nitrogen bond:

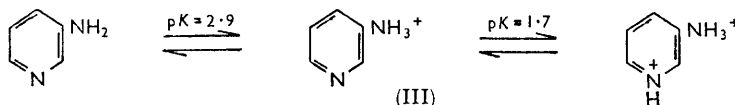


The need to use the  $\sigma$ -value for  $\text{NH}_3^+$ , and not for  $\text{NH}_2$  ( $-0.16$ ), in Fig. 2 supports this mechanism.

The addition of the first proton to 3-aminopyridine occurs at the ring\* ( $pK_{HL} = 6.1$ ), and the second protonation occurs only at high acid concentrations ( $pK_{H,L} = -1.5$ ):<sup>20</sup>



We can use Fig. 1, with some justification, to estimate the  $pK_{HL}$  value for a thermodynamically unstable species (III) as 1.7:



and therefore the  $pK$  value for addition of the *first* proton to the exocyclic nitrogen is  $(6.1 - 1.5) - (1.7) = 2.9$ . This latter value then is consistent with the idea of exclusive first protonation at the hetero-nitrogen atom. This type of approach could be useful in establishing thermodynamic data for other such compounds.

Some other deviations are less marked and less easy to understand. The deviation shown by 4-bromopyridine in Fig. 1 may stem from the non-applicability of the  $pK_{ML}/pK_{HL}$  correlation, since  $\pi$ -bonding between the pyridine nitrogen and nickel(II), but not the proton, is possible. If this is the explanation, however, it is not clear why 4-methoxypyridine, where such  $\pi$ -bonding is equally possible, follows the correlation well. It is possible that the higher rate for the 3-methoxy-compound and the low energy of activation result from a pre-equilibrium involving protonation at the methoxy-group (similar to the case of the 3-amino-compound).

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\* Spinner (*J.*, 1962, 3119) discusses the structure of aminopyridines and proton adducts, and cites previous literature.

<sup>20</sup> Albert, *J.*, 1960, 1020.