Kinetics and Thermodynamics of Fast Square-planar–Octahedral Interconversion. Part I. The Reaction of [Biacetyl bis-α-hydroxybenzylidenehydrazone(2−)-$N^1N^{1\prime}OO'$]nickel(II) with some Pyridines in Chlorobenzene

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A kinetic study has been made of the equilibrium (i) [bbh = biacetyl bis-α-hydroxybenzylidenehydrazone(2−)-

$$\underset{\text{square planar}}{[\mathrm{Ni(bbh)}]} + 2\mathrm{L} \rightleftharpoons \underset{\text{octahedral}}{[\mathrm{Ni(bbh)L_2}]} \qquad \text{(i)}$$

$N^1N^{1\prime}OO'$; L = pyridine, 3-methylpyridine, and 4-methylpyridine] in chlorobenzene by using a microwave temperature-jump apparatus. The experimental results are consistent with the mechanism in (ii) and (iii) where (ii) is

$$[\mathrm{Ni(bbh)L_2}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Ni(bbh)L}] + \mathrm{L} \qquad \text{(ii)}$$

$$[\mathrm{Ni(bbh)L}] \rightleftharpoons [\mathrm{Ni(bbh)}] + \mathrm{L} \qquad \text{(iii)}$$

the rate-determining step. Activation parameters associated with the rate constant k_1 are in agreement with the dissociative nature of the reaction.

THERE are few kinetic data for reactions involving structural interconversions,[1-4] the high rate of the reactions and the thermodynamic requirements being severe limitations to their study. Most of the investigations have been made in water or other co-ordinating solvents where the double role of the solvent, as a medium of reaction and as a potential ligand, is a serious obstacle to a thorough study. The kinetic study of configurational equilibria between a neutral complex and a base in poorly co-ordinating solvents is however free from these complications, since the reagents are uncharged and anhydrous and the reactions consist simply of the addition of the base to the complex.

Sacconi and his co-workers[5] thoroughly investigated the thermodynamics of the reaction (1) of [biacetyl bis-α-hydroxybenzylidenehydrazone(2—)-$N^1N^{1\prime}OO'$]nickel(II), [Ni(bbh)], with amines (L) in benzene. Here the addition of two molecules of amine to the diamagnetic

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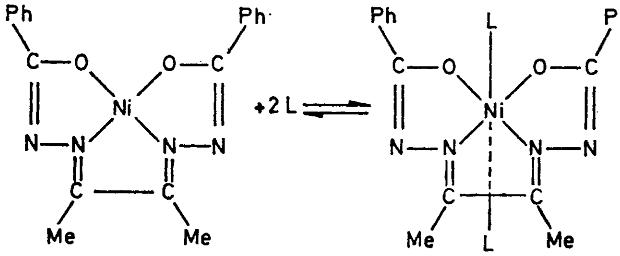
square-planar complex leads to complete conversion into the paramagnetic octahedral adduct. The large enthalpy change and the spectral variations associated with these systems make them suitable for relaxation studies by the temperature-jump method. The present paper reports the results of a kinetic study of the equilibria between [Ni(bbh)] and pyridine (py), 3-methylpyridine (3Me-py), and 4-methylpyridine (4Me-py) in the solvent chlorobenzene at several temperatures.



(1)

EXPERIMENTAL

Materials.—The complex [Ni(bbh)] was prepared according to the literature.[6] Pyridine and substituted pyridines were heated under reflux over potassium hydroxide and distilled. Commercial chlorobenzene was carefully purified by shaking it several times with concentrated sulphuric acid until the acid was colourless, then washing with sodium hydrogencarbonate solution, drying over P_4O_{10}, and distilling over anhydrous sodium sulphate.

Thermodynamics.—Equilibrium constants for reaction (1) in chlorobenzene were determined spectrophotometrically[5a] by use of a Unicam SP 8000 recording spectrophotometer equipped with a thermostatted cell holder. Solutions of fixed [Ni(bbh)] concentration containing different known amounts of amines were prepared and their absorbances recorded at four or more different temperatures in a 1-cm stoppered silica cell, the temperature being controlled to within ±0.2 °C by means of an electronic thermometer. Plots of $(1 - \alpha)/\alpha$ (where α is the ratio of the difference in absorbance between the equilibrium mixture and the octahedral complex and of the difference between the octahedral and the square-planar forms of the complex) against [free base]^2 ([free base] $= \{C_B - 2(1 - \alpha)C_C\}$ where C_B and C_C are respectively the formal base and complex concentrations) gave straight lines passing through the origin (Figure 1). The equilibrium constants were obtained from the gradients of these plots.

Kinetics.—Kinetic runs were made by using a microwave temperature-jump apparatus.[7,8] The rapid perturbation of the equilibria was produced by microwave irradiation generated by the discharge of a high-voltage pulse across a magnetron. The chemical relaxation to the new position of equilibrium was followed by monitoring the change in light intensity (450—490 nm) incident on a photomultiplier, displayed as an exponential trace (Figure 2) on a Tektronix 549 storage oscilloscope. The traces were photographed and the values of the relaxation time were evaluated by matching the experimental traces with similar ones produced by an exponential generator[9] on the same oscilloscope. Each experimental relaxation time is the average from at least five experiments. The temperature of the reaction mixture, which was kept constant by passing heptane through a jacket surrounding the sample cell, was measured to within ±0.2 °C by use of a thermocouple immersed in the cell. No relaxation was observed in absence of base; this shows that the observed signal was not due to spurious cavitation effects.

RESULTS AND DISCUSSION

Kinetic data were obtained under pseudo-first-order conditions using an excess of base. Only one relaxation was observed; this occurred always in the microsecond region and it was independent of the complex concentration (Table 1).

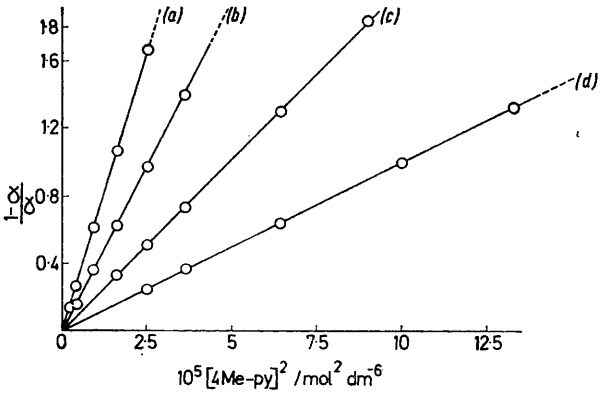


FIGURE 1 Plots of $1 - \alpha/\alpha$ against $[4Me\text{-}py]^2$ for the reaction $[Ni(bbh)] + 2L \rightleftharpoons [Ni(bbh)L_2]$ in chlorobenzene. $[Ni(bbh)] = 1 \times 10^{-4}$ mol dm^{-3} at (*a*) 12.2, (*b*) 17, (*c*) 23, and (*d*) 30 °C

TABLE 1

Rate constants for the reaction of [Ni(bbh)] with 4-methylpyridine at various complex concentrations. [4Me-py] $= 4.49 \times 10^{-3}$ mol dm^{-3}, 17 °C

10^4[Ni(bbh)] / mol dm^{-3}	$10^{-4}\,\tau^{-1}$ / s^{-1}
0.5	1.38
0.75	1.40
1.00	1.39
1.25	1.40
1.50	1.39
2.00	1.40

The experimental data have been interpreted in terms of a stepwise mechanism in which reaction (2)

$$\underset{\text{octahedral}}{[Ni(bbh)L_2]} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ni(bbh)L] + L, \quad K_1 \qquad (2)$$

$$[Ni(bbh)L] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{square planar}}{[Ni(bbh)]} + L, \quad K_2 \qquad (3)$$

equilibrates slowly compared to (3). The observed relaxation is therefore attributable to reaction (2) coupled with (3). The relaxation expression for this system[1] is (4), and plots of τ^{-1} against $[L]^2$ gave straight

$$\tau^{-1} = k_1 + (k_{-1}/K_2)[L]^2 \qquad (4)$$

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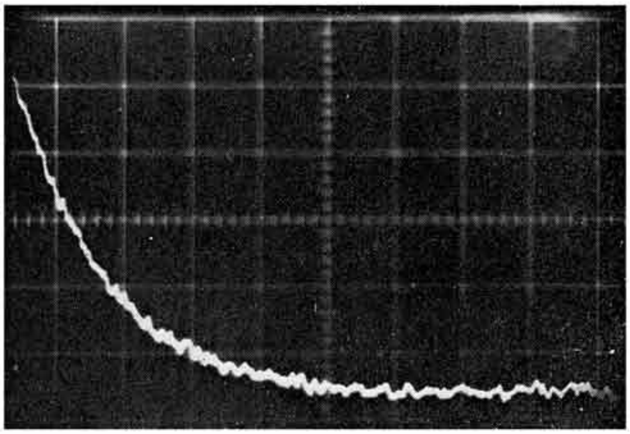

FIGURE 2 Typical oscilloscope trace for the reaction of [Ni(bbh)] (1×10^{-4} mol dm^{-3}) with pyridine (1.75×10^{-2} mol dm^{-3}) in chlorobenzene at 25 °C. The time base is 10 μs per division

lines with gradients k_{-1}/K_2 and intercepts k_{-1} (Figures 3 and 4). The values of k_1 and k_{-1}/K_2 obtained by a least-squares program are reported in Table 2.

Whereas the values of k_1 increased with increasing temperature, the corresponding values of k_{-1}/K_2, depending on the amine, increased or decreased. Since k_{-1} must increase with temperature, the decrease of k_{-1}/K_2 with temperature for 4-methylpyridine implies that $\Delta H_2^{\ominus} > \Delta H_{-1}^{\ddagger}$, while the increase for pyridine implies that $\Delta H_2^{\ominus} < \Delta H_{-1}^{\ddagger}$. Activation parameters associated with k_1, which were calculated (by means of a least-squares program) from plots of log k against $1/T$, are quoted, together with their standard deviations, in Table 3.

TABLE 2

Rate constants for the reaction of [Ni(bbh)] with various amines (L). Complex concentration $\leqslant 1 \times 10^{-4}$ mol dm^{-3}; the gradient and intercept refer to the plot of $k_{obs.}$ against $[L]^2$

Amine	$\frac{\theta_c}{^{\circ}C}$	$\frac{10^3[L]}{\text{mol dm}^{-3}}$	No. of experi-ments	$\frac{10^{-4}\ \tau^{-1}}{s^{-1}}$	$\frac{10^{-8}\ \text{Gradient}}{\text{dm}^6\ \text{mol}^{-2}\ s^{-1}}$	$\frac{10^{-4}\text{Intercept}}{s^{-1}}$	$\frac{10^{-4}\ (\text{Gradient/Intercept})}{\text{dm}^6\ \text{mol}^{-2}}$	$\frac{10^{-4}K(\text{spect.})}{\text{mol}^{-2}\ \text{dm}^6}$
Pyridine	10	5.00—17.50	11	1.08—4.40	1.17 ± 0.15	0.81 ± 0.02	1.44	1.55 ± 0.05
	15	5.00—9.70	9	1.60—4.85	1.17 ± 0.18	1.30 ± 0.03	0.90	1.05 ± 0.04
	17	5.00—17.50	9	1.85—6.85	1.26 ± 0.08	1.56 ± 0.10	0.81	0.87 ± 0.03
	25	7.50—27.50	8	4.20—16.40	1.72 ± 0.03	3.49 ± 0.05	0.49	0.45 ± 0.00
	33	15.00—42.43	9	18.00—39.00	1.76 ± 0.3	6.98 ± 0.3	0.25	0.24 ± 0.01
3-Methyl-pyridine	14.5	4.00—12.50	9	1.48—3.85	1.73 ± 0.05	1.20 ± 0.04	1.45	1.18 ± 0.07
	22	7.50—17.30	8	3.02—6.80	1.52 ± 0.03	2.20 ± 0.05	0.69	0.59 ± 0.05
	28.2	10.00—30.00	8	6.69—19.00	1.56 ± 0.03	4.92 ± 0.13	0.32	0.33 ± 0.02
	33	10.00—30.00	7	9.04—22.46	1.67 ± 0.05	7.41 ± 0.23	0.22	0.22 ± 0.01
4-Methyl-pyridine	12.2	2.00—5.50	8	0.67—1.52	3.36 ± 0.16	0.54 ± 0.03	6.21	6.69 ± 0.33
	17	2.50—7.00	10	0.99—2.37	3.24 ± 0.13	0.75 ± 0.03	4.30	3.89 ± 0.18
	23	3.00—9.00	8	1.84—3.79	2.81 ± 0.26	1.61 ± 0.08	1.74	2.04 ± 0.04
	30	5.00—15.00	9	3.33—8.20	2.38 ± 0.18	3.03 ± 0.24	0.78	1.00 ± 0.09

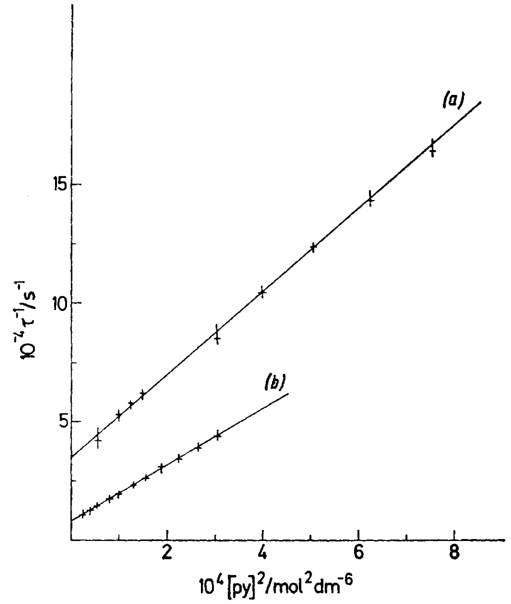

FIGURE 3 Plots of reciprocal relaxation time against $[py]^2$ for reaction of [Ni(bbh)] with pyridine in chlorobenzene at (*a*) 25, (*b*) 10 °C

The mechanism that fits the data [equations (2) and (3)] implies the slow release of one molecule of base from the octahedral complex with formation of an intermediate (presumably with a reduced co-ordination number), which is rapidly converted into the square-planar form by loss of the second molecule of base. The intermediate product may be a five-co-ordinate species, probably with a square-pyramidal structure. A large number of five-co-ordinate complexes of Ni^{II} have

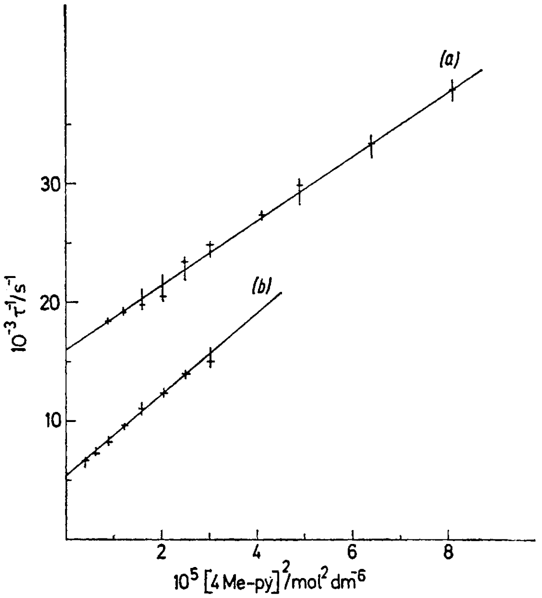

FIGURE 4 Plots of reciprocal relaxation time against $[4Me\text{-}py]^2$ for the reaction of [Ni(bbh)] and 4Me-py in chlorobenzene at (*a*) 23, (*b*) 12.2 °C

TABLE 3

Activation parameters for the reaction of [Ni(bbh)] with various amines in chlorobenzene (1 cal = 4.184 J)

Amine	log k_1 (25 °C)	$\frac{\Delta H^{\ddagger}}{\text{kcal mol}^{-1}}$	$\frac{\Delta S^{\ddagger}}{\text{cal K}^{-1}\ \text{mol}^{-1}}$
py (pK_a 5.17)	4.53	15.7 ± 0.2	14.9 ± 1.3
3Me-py (pK_a 5.68)	4.54	17.1 ± 1.2	19.7 ± 3.9
4Me-py (pK_a 6.02)	4.27	16.6 ± 1.1	16.7 ± 3.6

been isolated;[10,11] furthermore, substitution reactions of some octahedral[12] and square-planar[13] complexes are believed on kinetic grounds to proceed *via* formation of a five-co-ordinate intermediate, and in one case a stable five-co-ordinate intermediate has been isolated during the course of the reaction.[14]

The self consistency of the proposed mechanism is confirmed by the good agreement between the values of the equilibrium constants for reaction (1) obtained spectrophotometrically and those calculated using the kinetic values (k_{-1}/k_1K_2, *i.e.* gradient/intercept from the plots of τ^{-1} against $[L]^2$).

The large positive values of the activation entropy, which are characteristic of dissociative reactions, give further support to the scheme proposed. An alternative mechanism similar to that proposed by Farina and Swinehart[1,15] does not account for the results. These workers suggested that for the system (5) (X = Cl or Br)

$$[CoX_2(py)_4] \rightleftharpoons [CoX_2(py)_2] + 2\ py \qquad (5)$$

in nitromethane there is a fast pre-equilibtium (octahedral $\rightleftharpoons$ five-co-ordinate species) followed by a slow conversion into the tetrahedral adduct. This mechanism leads to equation (6). Plots of $\tau^{-1}[py]^{-1}$ against

$$\tau^{-1}[py]^{-1} = k_{-2} + (k_2K_1/[py]^2) \qquad (6)$$

$[py]^{-2}$, however, are invariably curved (Figure 5). The entropies of the present reactions are also incompatible with an associative mechanism.

Finally, the values of k_1 are related to the ease of breaking the nickel–amine bonds in the octahedral complex. These values, therefore, may be used to evaluate the nucleophilic effectiveness of the amines toward their five-co-ordinate acceptor [Ni(bbh)L] and to compare it with their basicity. Although the range of pK_a of the amines used in this work is fairly narrow (5.17—6.02), it seems that the rate of dissociation of the octahedral complex (k_1) is little affected by the pK_a. Investigations are being made which extend the range of pK_a and use bulky amines in order to determine the role of the basicity and the steric hindrance of these nucleophiles in the rates of reaction.

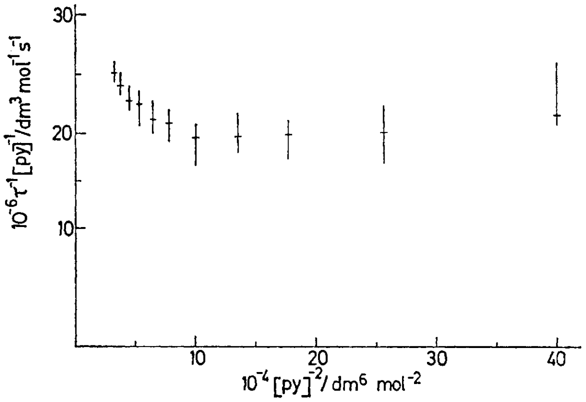

FIGURE 5 Plot of $\tau^{-1}[py]^{-1}$ against $[py]^{-2}$ for reaction of [Ni(bbh)] and py in chlorobenzene at 10 °C

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