Kinetics and Thermodynamics of Fast Square-planar–Octahedral Interconversion. Part II.† Influence of the Basicity and Steric Hindrance of Heterocyclic Amines in the Reaction with [Biacetyl bis-α-hydroxybenzylidenehydrazone(2−)-$N^1N^{1\prime}OO^\prime$]nickel(II) in Chlorobenzene

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A comparative thermodynamic and kinetic study has been made of reaction (i) [bbh = biacetyl bis-α-hydroxy-

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

benzylidenehydrazone(2−)-$N^1N^{1\prime}OO^\prime$; L = 4-cyano-, 3-chloro-, 2-methyl-, 2,4-dimethyl-, and 3,5-dimethylpyridine, morpholine, or piperidine] in chlorobenzene. Apart from a drastic steric-hindrance effect, variations of the structure and basicity of the amine have little effect on the values of the rate constant k_1, which refers to the release of one molecule of amine from the octahedral complexes as in (ii). The values of k_1 are correlated with the

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

equilibrium constants K for reaction (i). Rate and activation parameters associated with reactions (ii) are discussed. Thermodynamic parameters $\Delta H^\ominus$, $\Delta S^\ominus$, and $\Delta G^\ominus$ obtained for reaction (i) in chlorobenzene are also discussed and compared with the analogous values for reaction in benzene.

In studies of the mechanisms of substitution reactions of transition-metal complexes, the lability of an amine leaving group and its basicity have often been correlated.[1] Although much work has been done on square-planar metal complexes,[2-4] systematic studies concerning octahedral complexes are much less numerous; generally, amines are too firmly bound to the metal atom to be removed unless a strong labilizing group is present in the molecule.

Most information on this subject comes from kinetic studies of nickel(II) complexes.[5-7] Although the range of basicity explored has never been very large, the trend which emerges is that the rate of amine replacement decreases with increasing base strength. In the preceding paper [8] I reported the results of a kinetic investigation of reaction (1) [bbh = biacetyl bis-α-hydroxy-

$$\underset{\text{square planar}}{[\mathrm{Ni(bbh)}]} + 2\,\mathrm{L} \rightleftharpoons \underset{\text{octahedral}}{[\mathrm{Ni(bbh)L_2}]} \qquad (1)$$

benzylidenehydrazone(2−)-$N^1N^{1\prime}OO^\prime$; L = pyridine (py), 3-methylpyridine (3Me-py), or 4-methylpyridine (4Me-py)] where the addition of base leads to a change in geometry of the complex from square planar to octahedral. According to the mechanism proposed, the values of the rate constants k_1 obtained from the observed rates refer to reaction (2). This process is

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

formally identical to substitution reactions of octahedral complexes where the first dissociative step is rate determining. Because of its simplicity, this process appears to be particularly suitable for a systematic study of the dependence of the dissociation of amines on their basicity.

In this paper I report the results of a thorough investigation of reaction (1) in chlorobenzene with a series of cyclic amines differing in size, aromatic properties, and basicity. The purpose is to correlate the values of k_1 for the various leaving amines with the basicity expressed by the pK_a or other parameters related to the amine nucleophilicity. Although the pK_a values refer to water, it has been previously pointed out that the base strength in water can be used as an index of the base strength in organic solvents.[9] Furthermore the use of pyridines with methyl groups in the 2 position is expected to furnish useful indications of the effect of steric hindrance on the system. Equilibrium constants for reaction (1) have been determined, together with thermodynamic and activation parameters.

EXPERIMENTAL

Experimental details are described in the preceding paper.[8]

RESULTS

All the kinetic runs were made under pseudo-first-order conditions with excess of base. Only one relaxation was observed; the relaxation time, which was in the microsecond region, was independent of the concentration of complex. The values of k_1 were calculated from the intercept of the straight lines obtained on plotting the reciprocal of the relaxation time, τ^{-1}, against the square of the concentration of amine, using a least-squares program. The values are reported, with their standard deviations, in Table 1.

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† Part I is ref. 8.

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TABLE 1

Rate and equilibrium constants for reaction of [Ni(bbh)] with heterocyclic amines (L) in chlorobenzene at various temperatures. Concentration of [Ni(bbh)] $\leqslant 1 \times 10^{-4}$ mol dm^{-3}; the gradient and intercept refer to the plot of τ^{-1} against $[L]^2$

Amine, L	θ_c/°C	$10^3[L]$/mol dm^{-3}	No. of experiments	$10^{-4}\,\tau^{-1}$/s^{-1}	$10^{-3}\,k_1$/s^{-1}	10^{-2} (Gradient/intercept)/dm^6 mol^{-3}	$10^{-2}\,K$(spect.)/dm^6 mol^{-3}
4-Cyanopyridine	10.2	16.00—44.00	8	1.67—3.19	14.2 ± 0.1	6.41	68.9 ± 0.32
	16	24.00—64.00	9	3.15—6.70	26.9 ± 1.9	3.34	3.91 ± 0.12
	22.3	32.00—72.00	9	5.50—9.22	46.8 ± 0.8	1.87	2.17 ± 0.13
	28	64.00—120.00	7	10.20—18.55	69.3 ± 0.4	1.17	1.29 ± 0.05
3-Chloropyridine	11.4	20.25—66.58	8	2.70—7.10	21.8 ± 0.9	4.95	6.03 ± 0.42
	17	40.43—95.12	9	5.91—14.28	40.9 ± 1.1	2.76	3.58 ± 0.14
	22.8	53.51—111.80	8	9.70—22.80	60.9 ± 2.8	2.19	2.12 ± 0.08
	28	59.46—111.80	6	14.93—29.35	93.2 ± 1.9	1.72	1.34 ± 0.04
3,5-Dimethylpyridine	10.5	4.20—11.40	9	1.45—3.85	10.5 ± 0.3	205.0	199.0 ± 7.91
	16	6.00—15.00	9	2.65—6.35	18.9 ± 0.7	103.0	127.1 ± 3.81
	22	7.80—15.90	7	4.35—7.93	32.2 ± 1.3	58.7	70.9 ± 4.25
	28	9.60—15.90	6	7.50—10.10	55.2 ± 1.4	37.3	43.5 ± 1.22
2-Methylpyridine	9	60.00—200.00	8	13.78—27.00	128.4 ± 6.5	0.28	0.30 ± 0.01
	12	80.00—180.00	11	19.49—29.13	169.4 ± 6.3	0.23	0.22 ± 0.01
	17	130.00—200.00	8	28.74—37.60	231.6 ± 11.6	0.16	0.14 ± 0.00
	21	170.00—220.00	6	40.70—46.32	287.5 ± 7.2	0.14	0.10 ± 0.01
2,4-Dimethylpyridine	12	72.00—104.02	9	20.03—26.12	160.3 ± 2.3	0.74	0.70 ± 0.03
	16	72.00—120.00	8	26.02—34.68	201.8 ± 5.6	0.44	0.48 ± 0.01
	20	88.00—160.00	8	32.80—47.00	263.0 ± 8.3	0.30	0.38 ± 0.02
Morpholine	13	1.73—4.32	10	0.25—0.64	1.8 ± 0.0	1 350.0	1 890.0 ± 85.84
	19	2.30—5.40	9	0.42—1.01	2.9 ± 0.1	834.0	977.0 ± 39.10
	26	2.88—6.48	9	0.78—1.59	6.0 ± 0.2	390.0	475.0 ± 28.48
	30.6	3.46—7.20	8	1.25—2.15	9.3 ± 0.6	259.0	289.0 ± 11.57
Piperidine	16.4	0.81—1.67	10	0.25—0.55	1.7 ± 0.1	7 540.0	8 870.0 ± 621.0
	22	1.05—2.19	10	0.41—0.87	2.7 ± 0.1	4 760.0	4 700.0 ± 235.1
	28	1.13—2.19	8	0.69—1.18	5.1 ± 0.1	2 790.0	2 470.0 ± 148.1
	33	1.68—3.02	7	1.10—1.78	8.1 ± 0.2	1 310.0	1 450.0 ± 73.2

TABLE 2

Rate and equilibrium constants and activation parameters for reactions of [Ni(bbh)] with heterocyclic amines in chlorobenzene at 25 °C

Amine	pK_a [a]	$\log k_1$	$\log K$	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
4CN-py	1.90	4.76	2.24	14.5 ± 0.9	12 ± 3
3Cl-py	2.84	4.87	2.24	14.0 ± 0.8	11 ± 3
py [b]	5.17	4.51	3.66	15.7 ± 0.2	15 ± 4
3Me-py [b]	5.68	4.54	3.65	17.1 ± 1.2	20 ± 4
4Me-py [b]	6.02	4.27	4.22	16.1 ± 1.1	17 ± 4
3,5Me_2-py	6.34	4.28	3.74	15.4 ± 0.3	14 ± 1
2Me-py	6.10	5.58	0.83	10.3 ± 0.8	2 ± 3
2,4Me_2-py	6.99	5.53	1.31	9.7 ± 0.6	−1 ± 4
Morpholine	8.40	3.74	4.71	15.7 ± 0.6	11 ± 3
Piperidine	11.12	3.59	5.53	16.0 ± 0.7	12 ± 2

[a] pK_a of the conjugate acid in water. [b] From ref. 8.

TABLE 3

Thermodynamic parameters for the formation of the octahedral complexes $[Ni(bbh)L_2]$ in benzene and chlorobenzene

	Benzene *			Chlorobenzene		
Amine	$\Delta H^\ominus$/kcal mol^{-1}	$\Delta S^\ominus$/cal K^{-1} mol^{-1}	$\Delta G^\ominus$/kcal mol^{-1}	$\Delta H^\ominus$/kcal mol^{-1}	$\Delta S^\ominus$/cal K^{-1} mol^{-1}	$\Delta G^\ominus$/kcal mol^{-1}
4CN-py				−15.9 ± 1.0	−43 ± 3	−3.0
3Cl-py				−15.5 ± 0.5	−42 ± 2	−3.0
py	−14.9	−33	−5.1	−14.1 ± 0.3	−31 ± 1	−5.0
3Me-py	−15.2	−33	−5.3	−15.9 ± 0.3	−37 ± 1	−5.0
4Me-py	−15.6	−32	−6.0	−18.3 ± 0.2	−42 ± 1	−5.8
3,5Me_2-py				−14.8 ± 0.6	−33 ± 2	−5.1
2Me-py	−12.8	−41	−0.7	−15.6 ± 0.7	−49 ± 2	−1.1
2,4Me_2-py	−13.6	−41	−1.4	−16.1 ± 0.2	−48 ± 1	−1.8
Morpholine				−18.5 ± 0.9	−40 ± 3	−6.4
Piperidine	−13.9	−21	−7.7	−19.1 ± 0.3	−39 ± 1	−7.5

* From ref. 10.

The values of the equilibrium constants, K, calculated from the gradients divided by the intercepts obtained from the plots are also listed in Table 1, together with the corresponding values of K determined independently by spectrophotometry. The satisfactory agreement between the two sets of values is evidence for the validity of the mechanism proposed. Activation parameters calculated from plots of $\log k_1$ against $1/T$, by means of a least-squares program, are listed with their standard deviations in Table 2. The thermodynamic parameters $\Delta H^{\ominus}$, $\Delta S^{\ominus}$, and $\Delta G^{\ominus}$ for reaction (1) in chlorobenzene, together with the corresponding values obtained in benzene,[10] are reported in Table 3.

DISCUSSION

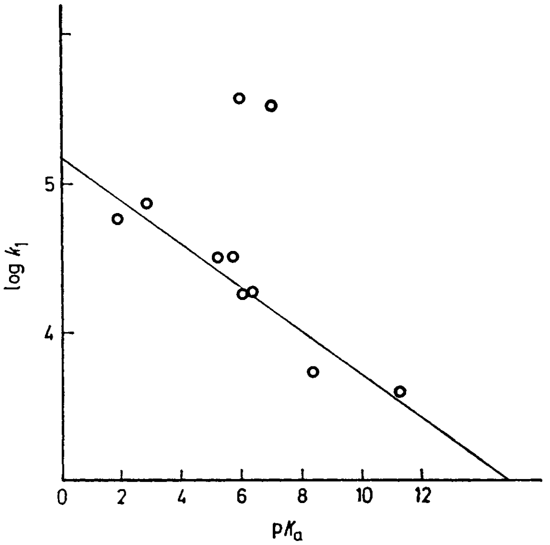

FIGURE 1 Plot of $\log k_1$ for the reaction $[Ni(bbh)L_2] \longrightarrow [Ni(bbh)L] + L$ against pK_a of HL^+

According to reaction (2) the values of k_1 are expected to give indications of the lability of the amine bound to the central nickel(II) atom. The trend of the values found agrees with this expectation since k_1 decreases with increasing pK_a, although the effect is small. Setting aside 2-methyl- and 2,4-dimethyl-pyridine for the moment, the range of values of k_1 is about one order of magnitude when the pK_a varies by more than nine units. A plot of $\log k_1$ against the pK_a of the amine (Figure 1) is reasonably linear for all the amines except 2Me-py and 2,4Me$_2$-py, which appear to be much more labile than the other amines. Although a linear relation is observed, attention must be drawn to the fact that the variations of k_1 cannot be attributed solely to the change of basicity; they must be influenced to different extents by the second amine molecule bound to the nickel atom, depending on its *trans* effect. The *trans* effect will act in a direction opposite to that of the basicity, the former favouring the release of the amine and the latter stabilizing the nickel–amine bond. This sort of compensation could account for the small dependence of the rate constants on the basicity. The gradient of the plot in Figure 1 is -0.15 ± 0.02 and to some extent it indicates the sensitivity of the substrate to changes in the σ-donor ability of the amine. It is interesting to note that this value is close to that (-0.20) which can be calculated from the same type of plot reported by Moore and Wilkins [7] for the rates of dissociation in excess of acid of nickel(II) complexes with a series of substituted pyridines in water.

The large deviations of 2Me-py and 2,4Me$_2$-py from linearity are evidence for the dissociative nature of the process; the steric strain caused by the methyl group in the *ortho*-position to the nitrogen co-ordinated to the metal favours the breaking of the nickel–amine bond and enhances the reactivity of the octahedral species. It is worth noting that the use of more hindered pyridines, such as 2-benzyl- and 2-isopropyl-pyridine, was not possible because of the high rate of the reactions, which were complete within the response time of the apparatus (0.6 µs).

The absence of large deviations from linearity for leaving groups differing in size and aromatic properties as greatly as pyridine, piperidine, and morpholine indicates that these factors do not affect the lability of the leaving group to a significant extent. A plot of $\log k_1$ against $\log K$ [where K is the equilibrium constant for the overall reaction (1)] was linear with a gradient of -0.43 (Figure 2). Kinetic and thermodynamic data are therefore correlated through the linear free-energy relation (l.f.e.r.) $\log k_1 = a + b \log K$, where $a = 5.93 \pm 0.16$ and $b = -0.43 \pm 0.05$. It is interesting to note that in this case the points referring to the reaction with 2Me-py and 2,4Me$_2$-py do not show any deviation from the linear plot. This means that steric effects due to these two amines exert the same influence both on the rate constants and the equilibrium constants of the reactions.

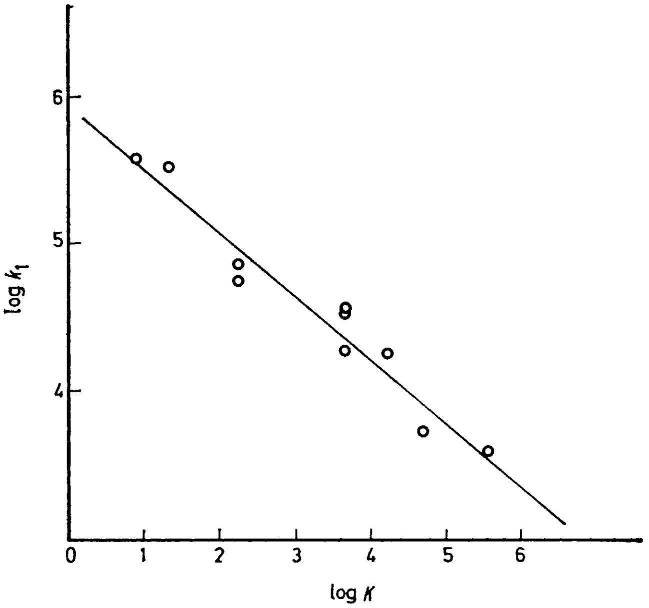

FIGURE 2 Linear free-energy relation between $\log k_1$ and $\log K$

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[10] L. Sacconi, G. Lombardo, and P. Paoletti, *J. Chem. Soc.*, 1958, 848.

Linear free-energy relations have often been applied to octahedral substitution reactions;[11] a l.f.e.r. of gradient *ca.* 1 is expected for a dissociative mechanism,[12] whereas a gradient of *ca.* 0.5 implies an I_a mechanism.[11,13] This conclusion is true as long as two conditions are fulfilled: (*i*) the transition state must be nearly the same for the series of reactions compared; (*ii*) the values of the equilibrium and rate constants which are correlated must both refer to the same step of the reaction. In the present case, however, neither of these conditions is fulfilled. The transition state may be very different from one base to another depending on the nature of the amine still bound to the nickel atom. Furthermore, the values of log k_1, which refer to the rate of release of one amine molecule, are compared with the values of log K which refer to the formation of the octahedral adduct implying the addition of two molecules of base. Clearly no mechanistic conclusions can be drawn from the value of the gradient (−0.5) for the l.f.e.r. here applied.

The activation parameters are consistent with the mechanism proposed, the activation entropies being usually large and positive. It may be noted that the values both of the activation enthalpy and of the activation entropy are about the same in the series of reactions examined, apart from those associated with the reactions with 2Me-py and 2,4Me_2-py which are less positive. The differences between the two sets of values may be due to different contributions of solvation to the activation parameters associated with the reactions. The activated complex is less polar than the reactants (owing to the removal of the partial charges generated in the nickel–amine bond); therefore the passage from reactant to transition state is associated with a release of solvent molecules. In the case of the octahedral complexes with 2Me-py and 2,4Me_2-py, the reactant will be less solvated because of steric inhibition. As a result the smaller release of solvent molecules will lead to a smaller positive contribution to the overall activation entropy, and at the same time less energy will be required for the desolvation associated with the passage from reactant to transition state.

The values of $\Delta S^\ominus$ associated with reactions (1) are negative in each case, as expected for processes which take place with a decrease in the number of free particles. These values are strongly dependent on the nature of the amine. In comparison, the corresponding values of $\Delta H^\ominus$ vary to a much smaller extent. Variation of the thermodynamic stability of the octahedral complexes, as indicated by the values of $\Delta G^\ominus$ ranging from −1.1 to −7.5 kcal mol^{-1},* are therefore mainly due to the change in $\Delta S^\ominus$. This result is in agreement with that previously found by Sacconi *et al.*[10] who studied these reactions in benzene. A comparison of the thermodynamic values obtained in the two solvents shows that, although the stability of the complexes (represented by $\Delta G^\ominus$) is nearly the same in both solvents, the variations in $\Delta H^\ominus$ and $\Delta S^\ominus$ for the reactions in the solvent chlorobenzene are more negative than the analogous variations in benzene. This result may be interpreted by supposing that chlorobenzene has a stronger solvating action than benzene on the products of reaction (1), which are expected to be more polar than the reactants. The solvation of the products and the consequent decrease in the number of free molecules of solvent will affect both the value of $\Delta H^\ominus$ and that of $\Delta S^\ominus$, without altering considerably the stability ($\Delta G^\ominus$) of the complexes in the two solvents.

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* 1 cal = 4.184 J.

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