Reactions of Co-ordinated Nitriles. Part II.[1] Nickel(II)- and Cobalt(II)-promoted Hydrolysis of 2-Cyano-8-hydroxyquinoline

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Base hydrolysis of 2-cyano-8-hydroxyquinoline to the corresponding carboxamide has been studied spectrophotometrically; $k_{OH} = 4{\cdot}85 \times 10^{-3}$ l mol^{-1} s^{-1} at 45 °C and $I = 1{\cdot}0$M. The hydrolysis is strongly promoted by nickel(II), cobalt(II), and copper(II). Thus the 1 : 1 complex of nickel(II) and 2-cyano-8-hydroxyquinoline undergoes base hydrolysis 2×10^5 times faster than the uncomplexed substrate at 45 °C. Activation parameters for the uncatalysed base hydrolysis are $\Delta H^‡ = 13{\cdot}4 \pm 0{\cdot}5$ kcal mol^{-1} and $\Delta S^‡ = -27$ cal K^{-1} mol^{-1}; corresponding values for the metal-promoted reactions are $\Delta H^‡ = 14{\cdot}2 \pm 0{\cdot}5$ kcal mol^{-1}, $\Delta S^‡ = -0{\cdot}8$ cal K^{-1} mol^{-1} [nickel(II)] and $\Delta H^‡ = 14{\cdot}3 \pm 0{\cdot}1$ kcal mol^{-1}, $\Delta S^‡ = -3$ cal K^{-1} mol^{-1} [cobalt(II)]. The substantial rate acceleration is due to an entropy effect alone and possible mechanisms for the reaction are considered.

RECENTLY there has been considerable interest in the hydrolysis of nitriles in the co-ordination sphere of metal ions. Breslow *et al.*[2] first showed that hydrolysis of 2-cyano-1,10-phenanthroline to the corresponding amide is strongly promoted by metal ions such as Cu^{II}, Ni^{II}, and Zn^{II}. Base hydrolysis of the nickel(II) complex was 10^7 times faster than that of the uncomplexed substrate. The entire rate acceleration was accounted for by the change in $\Delta S^‡$. Somewhat similar effects have been observed for base hydrolysis of 2-cyanopyridine to the corresponding carboxamide. In this case rate accelerations of 10^9 occurred with the nickel(II) complex.[3] In the presence of tris[(hydroxymethyl)amino]methane (Tris) and copper(II) or nickel(II) the product obtained was not the expected pyridine-2-carboxamide but 2-(2′-pyridyl)-4,4-di(hydroxymethyl)-Δ^2-isoxazoline, (I),[4] which presumably arises as a result of formation of a mixed-ligand complex.

A number of studies have also been made of reactions

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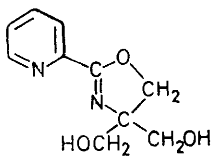
[1] Part I, K. B. Nolan and R. W. Hay, *J.C.S. Dalton*, 1974, 914.

[2] R. Breslow, R. Fairweather, and J. Keana, *J. Amer. Chem. Soc.*, 1967, **89**, 2135.

[3] R. Breslow, 'Bioinorganic Chemistry,' *Adv. Chem. Ser.*, no. 100, ed. R. F. Gould, Amer. Chem. Soc., p. 25; R. W. Hay and A. Mudie, unpublished work.

[4] R. Breslow and M. Schmir, *J. Amer. Chem. Soc.*, 1971, **93**, 4960.

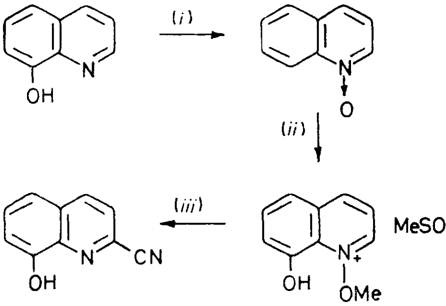
of nitriles in the co-ordination sphere of cobalt(III).[1,5-7] Pinnell *et al.* reported [5] that aromatic nitriles co-ordinated to penta-amminecobalt(III) are rapidly hydrolysed by base to give corresponding nitrogen-bonded carboxamido-complexes. Rate enhancements of 2×10^6 were observed in these reactions. Buckingham *et al.*[6] recently found similar effects with aliphatic nitriles; thus base hydrolysis of acetonitrile to acetamide was promoted by a factor of 2×10^6 on co-ordination to $[Co(NH_3)_5]^{3+}$. A number of papers dealing with synthetic applications of metal-ion-promoted hydrolysis of nitriles have also been published.[8-10] In the present paper we report a kinetic study of nickel(II)- and cobalt(II)-promoted hydrolysis of 2-cyano-8-hydroxyquinoline to the corresponding carboxamide.



(I)

EXPERIMENTAL

2-Cyano-8-hydroxyquinoline was prepared by the reactions outlined in Scheme 1, essentially as Krasavin *et al.*[11] Crude 8-hydroxy-1-methoxyquinolinium methyl sulphate [11] (18 g) dissolved in water (40 cm^3) was added over a 2 h period to a cold stirred solution of sodium cyanide (9·2 g) in water (40 cm^3). The pH of the resulting mixture was adjusted to 4·5 with glacial acetic acid and the crude product was filtered off and thoroughly washed with water. After drying, the product was recrystallised twice from acetonitrile giving yellow plates, m.p. 135 °C (lit.,[11] 134·5—135·5 °C) (Found: C, 70·45; H, 3·7; N, 16·6. Calc. for $C_{10}H_6N_2O$: C, 70·55; H, 3·55; N, 16·5%). Absorption spectrum: (*a*) in 0·01M-sodium hydroxide,* $\lambda_{max.}$ 270 (ε $3{\cdot}9 \times 10^4$), 347·5 (ε $2{\cdot}7 \times 10^3$), and 414 nm (ε $3{\cdot}5 \times 10^3$ dm^3 mol^{-1} cm^{-1}); (*b*) pH 6·3 (neutral molecule), $\lambda_{max.}$ 253·5 nm (ε $5{\cdot}4 \times 10^4$ dm^3 mol^{-1} cm^{-1}).



SCHEME 1 (*i*), H_2O_2; (*ii*), Me_2SO_4; (*iii*), KCN

2-Carboxamido-8-hydroxyquinoline hydrate was prepared by hydrolysis of 2-cyano-8-hydroxyquinoline with potassium hydroxide solution.[11] Recrystallisation from acetone-water (1 : 1) gave iridescent brown plates, m.p. 212 °C (lit.,[11] 214—215 °C) (Found: C, 58·2; H, 5·0; N, 13·7. Calc. for $C_{10}H_{11}N_2O_3$: C, 58·2; H, 4·9; N, 13·6%).

' Hepes ' (*N*-2-hydroxyethylpiperazine-*N'*-2-ethanesulphonic acid) was a B.D.H. biochemical reagent, and 2,6-dimethylpyridine was purified by distillation. All other chemicals were AnalaR grade.

Kinetic Measurements.—The hydrolysis of the nitrile and its nickel(II) and cobalt(II) complexes was followed spectrophotometrically on a Gilford 2400S instrument. Uncatalysed hydrolyses were monitored by the following method. A solution of the appropriate reaction mixture (3·0 cm^3) in a 1 cm silica cell was equilibrated in the cell compartment for *ca.* 25 min. The reaction was then initiated by injecting into the cell contents 10 µl of a solution of 2-cyano-8-hydroxyquinoline in ethanol and monitored at 398·5 nm, an isosbestic point for conversion of the amide to the carboxylate.

Nickel(II)- and cobalt(II)-promoted hydrolyses were monitored at 347 and 274 nm respectively. In the latter reaction scrupulous precautions were taken to exclude dioxygen from the system. Buffered cobalt(II) solutions were thoroughly flushed with nitrogen and transferred to the spectrophotometer cells under a nitrogen atmosphere. Hydrolysis of the cobalt(II)–nitrile complex ($\lambda_{max.}$ 275 nm, ε $4{\cdot}9 \times 10^4$ dm^3 mol^{-1} cm^{-1}) gave initially the cobalt(II)–amide complex ($\lambda_{max.}$ 276 nm, ε $3{\cdot}2 \times 10^4$ dm^3 mol^{-1} cm^{-1}), which subsequently underwent a further slow reaction (presumably hydrolysis to the carboxylate). As a result, stable infinity readings were not obtained, and the first-order rate constants reported were determined from computer-extrapolated infinity plots using data collected over the first two reaction half-lives. The program used was of the generalised least-squares type based on the Letagrop programs of Sillén,[12] and was operated on an ICL 1430 computer. First-order rate constants for nickel(II)-promoted and uncatalysed reactions were obtained from plots of log $(A_\infty - A_t)$ against time. No evidence of general base catalysis by buffer species was observed in the metal-ion promoted reactions. Two-fold variations in the concentration of 2,6-dimethylpyridine [nickel(II)-promoted hydrolysis] and ' Hepes ' [cobalt(II)-promoted hydrolysis] had no effect on the reaction rates.

Hydroxide-ion activities were obtained from pH measurements on a Radiometer 26 pH meter using the following values of pK_w: 13·997 (25); 13·680 (35); and 13·396 (45 °C).[13] Hydroxide-ion concentrations were then calculated using molar activity coefficients (γ) obtained from the Davies equation (1).

$$-\log \gamma = Az_1z_2\{[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})] - 0{\cdot}2I\} \qquad (1)$$

The product of base hydrolysis of the nickel(II)–nitrile complex was isolated as follows. The nitrile and nickel(II) (1 : 1) were dissolved in dioxan–water at 45 °C and the pH

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* 1M = 1 mol dm^{-3}.

[5] D. Pinnell, G. B. Wright, and R. B. Jordan, *J. Amer. Chem. Soc.*, 1972, **94**, 6104.

[6] D. A. Buckingham, F. R. Keene, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1973, **95**, 5649.

[7] D. A. Buckingham, B. M. Foxman, A. M. Sargeson, and A. Zanella, *J. Amer. Chem. Soc.*, 1972, **94**, 1007.

[8] K. Sakai, T. Ito, and K. Watanabe, *Bull. Chem. Soc. Japan*, 1967, **40**, 1660.

[9] S. Komiya, S. Suzuki, and K. Watanabe, *Bull. Chem. Soc. Japan*, 1971, **44**, 1440; K. Watanabe, S. Komiya, and S. Suzuki, *ibid.*, 1973, **46**, 2792.

[10] P. F. D. Barnard, *J. Chem. Soc.* (*A*), 1969, 2140.

[11] I. A. Krasavin, V. M. Dziomko, and Y. P. Radin, *Metody Policheniya Khim., Reactivov i Preparatov*, 1965, **13**, 68, 94.

[12] L. G. Sillén, *Acta Chem. Scand.*, 1962, **16**, 159; 1964, **18**, 1085.

[13] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' 2nd edn., Butterworths, London, 1959.

adjusted to 8·0 (pH meter). It was found that 2·0 ± 0·1 mole of sodium hydroxide per mole of nitrile were required to attain this pH. Careful acidification of an aqueous suspension of the yellow nickel complex which precipitated resulted in liberation of the monohydrate of 2-carboxamido-8-hydroxyquinoline, identical (m.p. and i.r. spectrum) with an authentic sample.[11]

RESULTS AND DISCUSSION

In basic solution 2-cyano-8-hydroxyquinoline was hydrolysed to the corresponding carboxamide which subsequently underwent hydrolysis to the dianion of 2-carboxy-8-hydroxyquinoline. Base hydrolysis of the nitrile was studied in isolation by monitoring the reaction at 398·5 nm, the isosbestic point for conversion of the amide to the carboxylic acid. Rate data obtained in this manner are summarised in Table 1. In 1·0M-sodium hydroxide, $k_{obs} = 4\cdot80 \times 10^{-3}$ s^{-1} giving a value of $k_{OH} = 4\cdot85 \times 10^{-3}$ l mol^{-1} s^{-1} (corrected for volume expansion) at 45 °C. The hydrolysis of the carboxamide was studied under the same conditions by monitoring the increase in absorbance at 360 nm. The value of k_{obs} (in 1·0M-sodium hydroxide) was $2\cdot02 \times 10^{-4}$ s^{-1} at 45 °C, so that at this temperature hydrolysis of the carboxamide is some 24 times slower than that of the nitrile. The temperature dependence of the nitrile hydrolysis was studied at the additional temperatures of 25 and 35 °C (Table 1). For uncatalysed base hydrolysis, $\Delta H^{\ddagger} = 13\cdot4 \pm 0\cdot5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27$ cal K^{-1} mol^{-1} at 308 K.* The large negative entropy of activation is expected for a base hydrolysis of this type where two molecules come together in the transition state.

TABLE 1

Base hydrolysis of 2-cyano-8-hydroxyquinoline to give the carboxamide in 1·0M-sodium hydroxide solutions

θ_c/°C	10^3k_{obs}/s^{-1} *	10^3k_{OH}/l mol^{-1} s^{-1}
25·0	1·11	1·11
35·0	2·48	2·48
45·0	4·80	4·85 †

$\Delta H^{\ddagger} = 13\cdot4 \pm 0\cdot5$ kcal mol^{-1}
$\Delta S^{\ddagger} = -27$ cal K^{-1} mol^{-1} at 308 K

Substrate concentration, $3\cdot2 \times 10^{-4}$M; k_{OH} is defined as $k_{obs}/[OH^-]$.

* Average of duplicate runs. † Rate constant corrected for volume expansion of the reaction medium.

The pK_a (phenolic hydroxyl group) of the ligand was determined spectrophotometrically as 8·73 ± 0·03 at 25 °C and I = 0·01M (Table 2). The cyano-group in the 2-position of the quinoline ring is strongly electron withdrawing and leads to a significant increase in acidity of the hydroxyl group compared with that of 8-hydroxyquinoline (pK_a 9·81 at 25 °C and $I \longrightarrow 0$). Thus, although the electron-withdrawing cyano-group leads to a lower basicity for the nitrogen donor, the effect is partially compensated by increased acidity of the phenolic group. As a result 2-cyano-8-hydroxyquinoline retains good chelating properties.

Nickel(II)-*promoted Hydrolysis.*—At pH 6·86 and a ligand concentration of $1\cdot7 \times 10^{-4}$M, essentially constant values of k_{obs} were found when the concentration of nickel(II) was varied from $5\cdot25 \times 10^{-4}$ to $2\cdot63 \times 10^{-3}$M (Table 3). The zero-order dependence on the metal-ion concentration at metal : ligand ratios in excess of 3 : 1 confirms that the ligand is fully complexed under these conditions presumably as a 1 : 1 complex, [NiL]$^+$ (L$^-$ = 2-cyanoquinolin-8-olate). Rate constants obtained at a nickel(II) concentration of $2\cdot63 \times 10^{-3}$M (metal : ligand = 15·5 : 1) as a function of pH are also shown in Table 3. Values of k_{OH} (= $k_{obs}/[OH^-]$) were sensibly constant, confirming a first-order dependence on the hydroxide-ion concentration. The 1 : 1 nickel(II) complex underwent base hydrolysis some 2×10^5 times faster than did 2-cyanoquinolin-8-olate. The rate acceleration was somewhat less than the figure of 10^7 reported for nickel(II)-promoted hydrolysis of 2-cyano-1,10-phenanthroline.[1] It is possible that this lower rate acceleration is due to electrostatic effects. The 2-cyanoquinoline-8-olate complex has a single positive charge while the analogous phenanthroline complex carries a dipositive charge. In reactions involving negatively charged nucleophiles rate differences of 10^2 would not be unexpected.

TABLE 2

Determination of pK_a of 2-cyano-8-hydroxyquinoline at 25 °C and I = 0·01M *

pH	A (414 nm)	pK_a
6·3 (phosphate)	0·053	
8·065	0·181	8·75
8·290	0·252	8·73
8·495	0·343	8·70
8·770	0·451	8·72
9·040	0·563	8·72
9·290	0·625	8·73
12 (NaOH)	0·809	
		Mean 8·73 ± 0·03

* Measurements made using Tris and borate buffers described by D. D. Perrin, *Austral. J. Chem.*, 1963, **16**, 572.

TABLE 3

Nickel(II)-promoted hydrolysis of 2-cyano-8-hydroxyquinoline at I = 0·1M and 45 °C (2,6-dimethylpyridine buffer), using a ligand concentration of $1\cdot7 \times 10^{-4}$M

(*a*) Nickel(II) dependence at pH 6·86

[Ni^{II}]/M	10^4k_{obs}/s^{-1}
$5\cdot25 \times 10^{-4}$	3·25
$1\cdot31 \times 10^{-3}$	3·33
$2\cdot63 \times 10^{-3}$	3·45

(*b*) pH Dependence at a nickel(II) concentration of $2\cdot63 \times 10^{-3}$M *

pH	10^4k_{obs}/s^{-1}	$10^7[OH^-]$/M	$10^{-2}k_{OH}$/ l mol^{-1} s^{-1}
6·27	0·872	0·971	8·98
6·54	1·77	1·81	9·78
6·86	3·45	3·78	9·13
7·18	6·97	7·89	8·83
7·60	19·4	20·8	9·33
			Mean 9·2 ± 0·4

* All solutions were $2\cdot63 \times 10^{-3}$M in Ni(ClO$_4$)$_2$ and $2\cdot0 \times 10^{-2}$M in 2,6-dimethylpyridine. The supporting electrolyte was NaClO$_4$.

Temperature-dependence studies of the nickel(II)-promoted base hydrolysis (Table 5) give $\Delta H^{\ddagger} = 14\cdot2 \pm$

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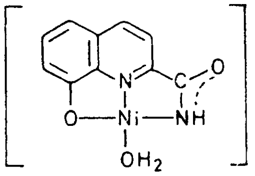
* 1 cal = 4·184 J.

0·5 kcal mol^{-1} and $\Delta S^{\ddagger} = -0{\cdot}8 \pm 2$ cal K^{-1} mol^{-1} at 308 K. As values of $\Delta H^{\ddagger}$ for both promoted and unpromoted reactions were the same within experimental error, the entire rate acceleration is due solely to the more positive contribution of the entropy term.

Cobalt(II)-*promoted Hydrolysis*.—The cobalt(II)-promoted hydrolysis was followed by monitoring the increase in absorbance at 274 nm. A subsequent slow reaction of the cobalt(II)–amide complex was observed (presumably hydrolysis to the carboxylate). Such a reaction, however, did not occur in the presence of nickel(II). It is probable that the carboxamide complex with nickel(II) occurs as the deprotonated species (II) at the pH values of the measurements, while deprotonation does not occur with cobalt(II) until higher pH values are reached. The deprotonated species (II) would be expected to be inert to base hydrolysis, and hence a subsequent reaction was not observed in the presence of nickel(II).


(II)

At a ligand concentration of 4×10^{-5}M and cobalt(II) concentrations of $2{\cdot}0 \times 10^{-3}$—$8{\cdot}0 \times 10^{-3}$M essentially constant values of k_{obs} were obtained at pH 6·89. The zero-order dependence on the metal-ion concentration at metal : ligand ratios in excess of 12 : 1 confirms that the ligand is fully complexed under these conditions (Table 4).

TABLE 4

Cobalt(II)-promoted hydrolysis of 2-cyano-8-hydroxyquinoline at I = 0·1M and 45 °C (Hepes buffer), using a ligand concentration of $4{\cdot}1 \times 10^{-5}$M

(*a*) Cobalt(II) dependence at pH 6·89

10^3[Co^{II}]/M	$10^4 k_{obs}$/s^{-1}
2·0	1·05
4·0	1·03
8·0	1·10

(*b*) pH Dependence at a cobalt(II) concentration of 2×10^{-3}M *

pH	$10^4 k_{obs}$/s^{-1}	10^6[OH$^-$]/M	$10^{-2} k_{OH}$/ l mol^{-1} s^{-1}
6·89	1·05	0·404	2·50
7·08	1·72	0·627	2·74
7·44	3·95	1·44	2·74
7·69	6·30	2·55	2·47
8·02	13·1	5·46	2·40
			Mean 2·6 ± 0·2

* All solutions were 2×10^{-3}M in Co(NO$_3$)$_2$ and 10^{-2}M in 'Hepes.' The supporting electrolyte was KCl.

Within the pH range 6·89—8·02 values of k_{obs}/[OH$^-$] were constant, again showing a first-order dependence on hydroxide-ion concentration for the metal-ion promoted reaction. The mean value of k_{OH} was $(2{\cdot}6 \pm 0{\cdot}2) \times 10^2$ l mol^{-1} s^{-1} at 45·0 °C and I = 0·1M. Base hydrolysis of the 1 : 1 cobalt(II) complex is thus 5×10^4 faster than that of the anionic form of the ligand. The data in the latter part of Table 5 give $\Delta H^{\ddagger} = 14{\cdot}3 \pm 1{\cdot}0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3 \pm 4$ cal K^{-1} mol^{-1} at 308 K. Thus the rate enhancement exhibited in the cobalt(II)-promoted process is also due primarily to a more positive entropy of activation.

TABLE 5

Temperature dependence of the nickel(II)- * and cobalt(II)-promoted reactions †

(*a*) Nickel(II) at I = 0·108M

θ$_c$/°C	pH	$10^4 k_{obs}$/ s^{-1}	10^6[OH$^-$]/ M	$10^{-2} k_{OH}$/ l mol^{-1} s^{-1}
25·0	7·97	1·97	1·20	1·64
35·0	7·82	6·61	1·80	3·67
45·0	7·66	19·0	2·39	7·97

$\Delta H^{\ddagger} = 14{\cdot}2 \pm 0{\cdot}5$ kcal mol^{-1}
$\Delta S^{\ddagger} = -0{\cdot}8$ cal K^{-1} mol^{-1} at 308 K

(*b*) Cobalt(II) at I = 0·108M

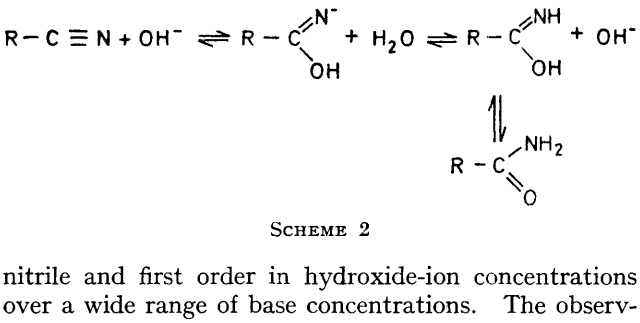
θ$_c$/°C	pH	$10^4 k_{obs}$/ s^{-1}	10^6[OH$^-$]/ M	$10^{-2} k_{OH}$/ l mol^{-1} s^{-1}
25·0	8·00	0·697	1·30	0·536
35·0	7·87	2·32	2·02	1·15
45·0	7·77	8·40	3·07	2·74

$\Delta H^{\ddagger} = 14{\cdot}3 \pm 1{\cdot}0$ kcal mol^{-1}
$\Delta S^{\ddagger} = -3{\cdot}0$ cal K^{-1} mol^{-1} at 308 K

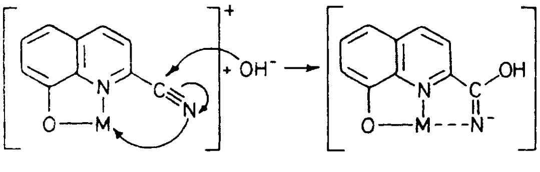
* Solutions were $2{\cdot}63 \times 10^{-3}$M in Ni(ClO$_4$)$_2$ and 4×10^{-2}M in 2,6-dimethylpyridine. The substrate concentration was $2{\cdot}1 \times 10^{-4}$M; supporting electrolyte, NaClO$_4$. † Solutions were $1{\cdot}6 \times 10^{-3}$M in Co(NO$_3$)$_2$ and 10^{-2} in 'Hepes.' The substrate concentration was $4{\cdot}1 \times 10^{-5}$M; supporting electrolyte, KCl.

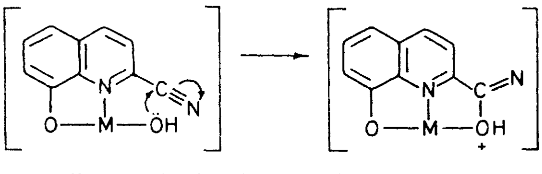
The reaction was also catalysed by both zinc(II) and copper(II). In the former case the formation constant of the zinc–nitrile complex was appreciably lower than those for the corresponding nickel(II) and cobalt(II) derivatives. Attempts to increase the zinc(II) : nitrile ratio to achieve full complexation of the substrate were frustrated due to precipitation of zinc(II) hydroxide. A kinetic investigation of base hydrolysis of the copper(II)–nitrile complex in aqueous solution was also prevented due to its very low solubility in water. A limited study of the copper(II)-promoted reaction using *NN*-dimethylformamide (5% v/v) in water as solvent indicated a rate acceleration of 10^7—10^8.

Mechanistic Considerations.—Base hydrolysis of nitriles is considered to occur by the mechanism shown in Scheme 2. The reaction is generally first order in the nitrile and first order in hydroxide-ion concentrations over a wide range of base concentrations. The observation that the nickel(II)- and cobalt(II)-promoted hydrolyses of 2-cyano-8-hydroxyquinoline are first order in the hydroxide-ion concentration and are not susceptible


SCHEME 2

to general base catalysis is consistent with either of two general mechanisms:[2] (*a*) nucleophilic attack of external hydroxide ion on the complexed substrate (' bound substrate–free nucleophile ') [equation (1)]; or (*b*) attack of co-ordinated hydroxide on the complexed substrate (' bound substrate–bound nucleophile ') [equation (2)]. Here M = $\mathrm{Co^{II}}$ or $\mathrm{Ni^{II}}$ and co-ordinated water molecules are not included for the sake of clarity.


(1)


(2)

It has been suggested[2] that mechanism (*a*) applies in the case of 2-cyano-1,10-phenanthroline. In case (*a*) involving external attack, the reaction scheme can be represented as in equations (3) and (4) and the rate

$$\mathrm{M{-}OH_2^+} + \mathrm{OH^-} \xrightarrow{k_1} \text{products} \qquad (3)$$

$$\mathrm{M{-}OH^0} + \mathrm{OH^-} \xrightarrow{k_2} \text{products} \qquad (4)$$

expression takes the form (5), where $\mathrm{M{-}OH_2^+}$ and

$$\text{Rate} = k_1[\mathrm{M{-}OH_2^+}][\mathrm{OH^-}] + k_2[\mathrm{M{-}OH^0}][\mathrm{OH^-}] \qquad (5)$$

$\mathrm{M{-}OH^0}$ represent the aqua- and hydroxo-forms of the complex ($\mathrm{M{-}OH_2^+} \overset{K_a}{\rightleftharpoons} \mathrm{M{-}OH^0} + \mathrm{H^+}$). Thus we obtain equation (6). For mechanism (*b*), involving intra-

$$k_{\mathrm{obs}} = k_1K_{\mathrm{w}}[\mathrm{OH^-}] + k_2K_{\mathrm{a}}[\mathrm{OH^-}]^2/(K_{\mathrm{w}} + K_{\mathrm{a}}[\mathrm{OH^-}]) \qquad (6)$$

molecular attack by co-ordinated hydroxide ion, the reaction scheme may be represented as in equation (7),

$$\mathrm{M{-}OH_2^+} \overset{K_a}{\rightleftharpoons} \mathrm{M{-}OH^0} + \mathrm{H^+} \xrightarrow{k_i} \text{products} \qquad (7)$$

in which case rate = $k_i[\mathrm{M{-}OH^0}]$ and it can readily be shown that equation (8) is applicable. Equations (6)

$$k_{\mathrm{obs}} = k_iK_{\mathrm{a}}[\mathrm{OH^-}]/(K_{\mathrm{w}} + K_{\mathrm{a}}[\mathrm{OH^-}]) \qquad (8)$$

and (8) have similar forms indicating a plateau region in plots of k_{obs} against pH when significant concentrations of $\mathrm{M{-}OH^0}$ are present and $k_2 < k_1$. In principle it might be possible to resolve some of the mechanistic ambiguities of these reactions by measurements at high pH, since absolute values of the constants obtained might shed some light on the problem. However, in the case of nickel(II) at least, this was not possible owing to precipitation of nickel(II) hydroxide in solutions above pH 8·5 when nickel(II) concentrations exceeded $1{\cdot}5 \times 10^{-3}$M.

The acid dissociation constants of the aqua-ions $[\mathrm{Co(H_2O)_6}]^{2+}$ and $[\mathrm{Ni(H_2O)_6}]^{2+}$ are 8·9 and 10·6 mol $\mathrm{l^{-1}}$ respectively.[14] The present complexes carry a single positive charge and it would therefore be expected that the $\mathrm{p}K_{\mathrm{a}}$ values would be somewhat greater than those for the aqua-ions. (In the case of intramolecular hydroxide attack, the function $k_{\mathrm{obs}}/[\mathrm{OH^-}]$ will only remain constant provided that no more than *ca.* 10% of the complex is in the hydroxo-form, as only under these conditions will the concentration of M–OH be proportional to $[\mathrm{OH^-}]$.) It could be argued that, since ionisation constants of the cobalt(II) and nickel(II) complexes probably differ by *ca.* 2 $\mathrm{p}K_{\mathrm{a}}$ units, hydrolysis by mechanism (*b*) does not occur since similar catalytic effects are observed with both metal ions.

For base hydrolysis of 2-cyanoquinolin-8-olate $\Delta H^\ddagger = 13{\cdot}4 \pm 0{\cdot}5$ kcal $\mathrm{mol^{-1}}$ and $\Delta S^\ddagger = -27$ cal $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ at 308 K. These values are comparable to those for base hydrolysis of other nitriles, *e.g.* $\Delta H^\ddagger = 15{\cdot}1$ kcal $\mathrm{mol^{-1}}$ and $\Delta S^\ddagger = -20$ cal $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ for 2-cyano-1,10-phenanthroline.[2] For both these reactions the catalytic effects of metal ions is due to a more positive $\Delta S^\ddagger$. Similar observations have been made for many other metal-promoted reactions.[15] Bimolecular reactions have $\Delta S^\ddagger$ values in the range −5 to −15 cal $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$.[16] The entropy of activation is extremely sensitive to solvent effects. The orientation of solvent molecules around charges, or developing charges, results in a negative entropy change and the effect may be as large or larger than that resulting from the molecularity of the reaction. The more positive values of $\Delta S^\ddagger$ in the promoted reactions can be partially rationalised in terms of desolvation arising from charge neutralisation in the metal complex–hydroxide ion transition state.

For steric reasons, bonding of the cyano-group to the metal ion cannot occur in the initial state of the reaction. It therefore appears that the transition state must involve bonding of the developing imino-anion to the metal ion, possibly resulting in displacement of a co-ordinated water molecule. The metal ion can be regarded as ' solvating ' the developing negative charge on the nitrogen atom of cyano-group. These effects would lead to more positive entropies of activation and thus account for the observed rate accelerations.

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[15] See, for example, D. A. Buckingham, J. MacB. Harrowfield, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1974, **96**, 1726.

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