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Kinetics of Cyclisation of 2-Cyanobenzamidopentaamminecobalt(III)

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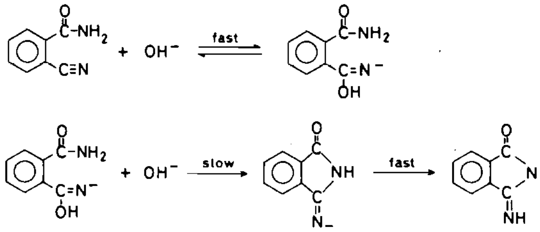
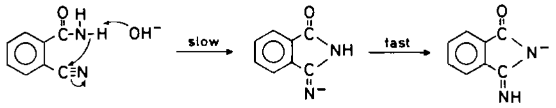
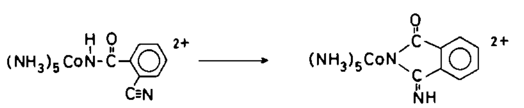
The cyclisation of *o*-cyanobenzamide to 3-imino-isoindolin-1-one is known to be catalyzed by alkali [1]. A kinetic study of this reaction in 87% ethanol showed that the reaction was second order in hydroxide ion and the following mechanism was suggested [2].



This mechanism was disputed by Butler [3] who demonstrated that the reaction was first-order in hydroxide ion in water and postulated the following scheme



We have studied the kinetics of the base-catalysed reaction below



where the pentaamminecobalt(III) moiety is coordinated to the amido nitrogen. We were interested in determining what effect the metal might have on the reaction and hoped that the mechanistic ambiguities referred to above could be cleared up.

Experimental

Standard sodium hydroxide solutions were prepared in 1.0 *M* $LiClO_4$ by dilution of a standard 1.0 *M* NaOH solution. The concentration of base in these solutions was determined by titration with standard HCl. The preparation and characterization of the starting complex, 2-cyanobenzamidopentaamminecobalt(III), and the product, $(NH_5)_5Co(2\text{-imino-isoindolin-1-one-2-yl})^{2+}$, has been described [4].

TABLE I. Cyclization of 2-Cyanobenzamidopentaamminecobalt(III). [a]

T, °C	$[OH^-]$, *M*	k_{obsd}, s^{-1}
25.6	0.0100	0.00788
	0.0200	0.0165
	0.0300	0.0267
	0.0400	0.0304
	0.0500	0.0407[b]
	0.0500	0.0410[c]
	0.100	0.098, 0.099
	0.200	0.200, 0.220
	0.300	0.330, 0.327
34.6	0.0500	0.102, 0.104
	0.100	0.239
	0.300	0.820
43.6	0.0500	0.207
	0.200	1.30
	0.300	2.02

[a] $[Co(III)] = 5 \times 10^{-5}$; I = 1.0 *M* ($LiClO_4$); λ = 300 nm. [b] Beckman Acta CIII. [c] Durrum stopped-flow.

Kinetic data were gathered on a Beckman Acta CIII spectrophotometer and a Durrum stopped-flow spectrophotometer. Rate constants were obtained under pseudo-first-order conditions from plots of $\log(A_t - A_\infty)$ *vs.* time where A_t and A_∞ are the absorbancies at time t and after the reaction was complete.

Results and Discussion

The kinetic data are gathered in Table I. Clearly, in the range $[OH^-] = 0.010–0.30$, the reaction is first order in hydroxide ion. These data lead to a second order rate constant of 1.13 ± 0.03 M^{-1} s^{-1} at 25.6 °C and from a transition state plot of the data in Table I one obtains $\Delta H^{\neq} = 18.3 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\neq} = +3 \pm 6$ cal mol^{-1} deg^{-1}.

The reaction was also studied as a function of ionic strength and these data are given in Table II. As expected for the reaction of an anion and a cation the observed rate constant decreases with increasing ionic strength. Furthermore, a plot of $\log(k_{obsd}/[OH^-])$ *vs.* $[I^{1/2}/(1 + I^{1/2}) - 0.20\ I]$ [5] gave a straight line with slope -2.4 ± 0.3 and intercept, log

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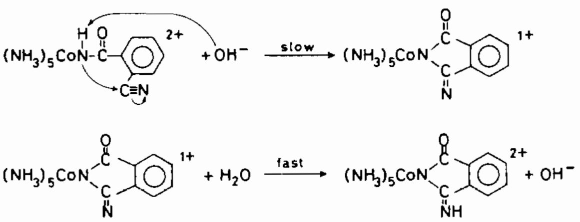
TABLE II. Cyclization of 2-Cyanobenzamidopentaamminecobalt(III) at Variable Ionic Strength.[a]

$[OH^-]$, M	I, M	k_{obsd}, s^{-1}
0.0100	0.010	0.0754, 0.0693
0.0100	0.020	0.0619
0.0100	0.040	0.0513
0.0100	0.060	0.0412
0.0100	0.080	0.0408
0.0100	0.10	0.0330, 0.0357

[a] T = 25.6 °C; I maintained with $LiClO_4$.

k_0 = 1.08. The slope represents the charge product of the reactants and k_0 the rate constant in the limit of zero ionic strength.

A mechanism consistent with the above is given below.



This mechanism is similar to that given in scheme 2 except that it is the second proton on the amide nitrogen that is being removed. Presumably the metal stabilizes the dianion so as to facilitate nucleophilic attack on the neutral cyano group. Butler [3] found a rate constant of 11–12 M^{-1} s^{-1} at 25 °C and low ionic strength for the cyclisation reaction. Our extrapolated value of k_0 (see Table II) is 11 M^{-1} s^{-1} at I = 0 indicating that similar mechanisms operate.

This requires that the pK_a of the second amido proton in the complex be similar to the pK_a of the first proton in the free amide. The acidity of coordinated amides is known to increase by >16 orders of magnitude over the free amides [6] and this enhanced acidity may lead to the above requirement. The cyclization in both the complex and free ligand appears then to be controlled by the favourable geometry of the amide and cyano groups. It is somewhat surprising that no term independent of $[OH^-]$ was found in the rate law since coordinated amides are known to be very effective nucleophiles [7].

A mechanism incorporating hydroxide addition to the cyano group followed by attack of coordinated amide seems improbable since attack at a group which is negatively charged by a nucleophile is highly improbable (see scheme 1).

Acknowledgements

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