

Mercury(II) Assisted Acid and Base Hydrolysis of Chloroaminocobalt(III) Complexes containing Aniline and Toluidine Ligands

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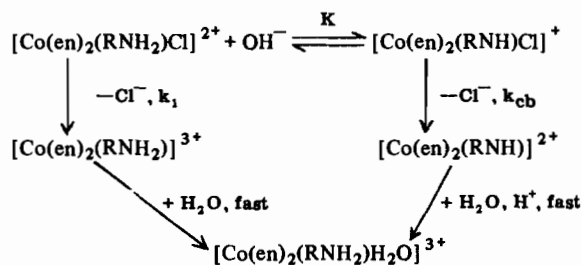
It is now well established that rates of acid hydrolysis of halogenocobalt(III) complexes are markedly enhanced in the presence of halide abstractors such as Hg^{II} [1]. This behaviour has been explained in terms of rapid pre-equilibrium formation of a halogeno-bridged complex, $-\text{Co}^{\text{III}}-\text{X}-\text{Hg}^{\text{II}}$ (formation constant K^1) which then reacts in a rate determining dissociative process (rate constant k) through loss of the good leaving group HgX^+ (better leaving group than X^- in the unpromoted reaction). These reactions usually follow second order kinetics, rate = $kK^1[\text{Hg}^{\text{II}}][\text{complex}]$, although departures from a simple first order dependence on $[\text{Hg}^{\text{II}}]$ have in some instances been reported [2]. Base hydrolysis of halogenoaminocobalt(III) complexes, involving dissociative activation steps with X^- departing (rate constant k_{cb}) from the amido conjugate base (formation constant K) [3], should also be susceptible to catalysis by Hg^{II} . However these reactions (rate = $k_{\text{cb}}K[\text{OH}^-][\text{complex}]$) are normally carried out at $\text{pH} > 7$ and are much too slow to investigate under the acidic conditions required for the existence of Hg^{II} [4]. Recent reports have described base hydrolysis reactions which are sufficiently fast to observe in acidic solutions ($\text{pH} < 3$) [5, 6]. The enhanced reactivity of the cobalt(III) systems described therein is due to the presence in the complexes of relatively acidic (large K) aniline-derived ligands (estimated to be 10^5 -fold more acidic than coordinated aliphatic amines). These reactive substrates afford an opportunity to investigate the effect of Hg^{II} on rates of base hydrolysis of halogenocobalt(III) complexes.

The complexes *cis*- $[\text{Co}(\text{en})_2(\text{RNH}_2)\text{Cl}]\text{Cl}_2$ ($\text{R} = \text{C}_6\text{H}_5$, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, *m*- $\text{CH}_3\text{C}_6\text{H}_4$; en = 1,2-diaminoethane) were prepared by literature methods [5], the purity of each complex was checked by C, H, N microanalysis and the *cis* configuration in each case was established by a combination of electronic, i.r. and n.m.r. spectroscopic methods. Kinetics of hydrolysis reactions were investigated spectrophotometrically by following absorbance changes at 550

nm ($\text{R} = \text{C}_6\text{H}_5$), 450 nm ($\text{R} = \textit{p}\text{-CH}_3\text{C}_6\text{H}_4$) and 448 nm ($\text{R} = \textit{m}\text{-CH}_3\text{C}_6\text{H}_4$) on a Unicam SP 8-100 spectrophotometer. The reaction solution (4 cm cells) contained $\text{Hg}(\text{NO}_3)_2$ dissolved in HClO_4 (or HNO_3 if the complex was difficult to dissolve in HClO_4) and an appropriate amount of NaClO_4 (or NaNO_3) to raise the ionic strength to 0.1 mol dm^{-3} . Hg^{II} solutions were standardised by an EDTA substitution titration [7] using PAN indicator and Cu^{II} -EDTA complex.

Results and Discussion

High reactivity in base hydrolysis of cobalt(III) amine complexes may arise from the presence in the complexes of relatively acidic amine ligands or from the production of very labile amido conjugate bases. The former situation was first encountered by Nanda *et al.* [5], who observed parallel acid/base hydrolysis reactions ($k_{\text{obs}} = k_1 + k_{\text{cb}}K[\text{OH}^-]$) in the complexes *cis*- $[\text{Co}(\text{en})_2(\text{RNH}_2)\text{Cl}]^{2+}$ over the pH range 1-3 (scheme 1).

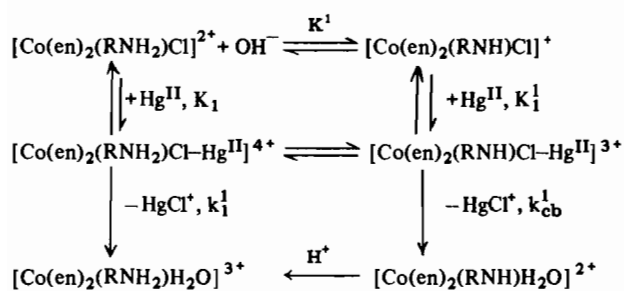


Scheme 1

As mentioned in the introduction base hydrolysis of halogenoaminocobalt(III) complexes should, like acid hydrolysis, be accelerated by Hg^{II} . Indeed base hydrolysis should be the more susceptible of the two reactions to catalysis by Hg^{II} since (with reference to scheme 2, where the solution equilibria in the presence of Hg^{II} are summarised) (a) Cl^- in the unipositively charged amido conjugate base should be a better bridging ligand than Cl^- in the dipositively charged substrate ($K_1^1 > K_1$) and (b) cobalt(III)-leaving group bond breaking should occur with greater ease in the binuclear intermediate carrying the lower positive charge ($k_{\text{cb}}^1 > k_1^1$) [8].

Kinetics of hydrolysis of the complexes *cis*- $[\text{Co}(\text{en})_2(\text{RNH}_2)\text{Cl}]^{2+}$ in the presence of Hg^{II} were investigated under conditions similar to those used for the uncatalysed reactions (50°C , $\text{pH} < 3$). Applying steady state conditions to bridged complexes and assuming that $K_1[\text{Hg}^{\text{II}}]$ and $K_1^1[\text{Hg}^{\text{II}}]$ are both much less than 1, leads to the rate expression

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Scheme 2

$$\text{rate} = k_2 [\text{Hg}^{\text{II}}] [\text{Co(en)}_2(\text{RNH}_2)\text{Cl}]^{2+}$$

where

$$k_2 = k_1^1 K_1 + k_{\text{cb}}^1 K_1^1 K^1 [\text{OH}^-]$$

for the reactions in scheme 2. Each reaction was investigated under pseudo first order conditions at constant Hg^{II} and OH^- concentrations. Values of k_{obs} ($= k_2 [\text{Hg}^{\text{II}}]$) and k_2 at various Hg^{II} and OH^- concentrations are collected in Table I. In accordance with the derived rate expression, plots of k_2 versus $[\text{OH}^-]$ are linear and at low pH k_2 values become pH

independent. A comparison between the results in Table I and those for the uncatalysed systems [5] indicates that in solutions containing $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ Hg}^{\text{II}}$ hydrolysis rates are enhanced 100-fold. In addition the slopes of plots of k_{obs} versus $[\text{OH}^-]$ (at constant $[\text{Hg}^{\text{II}}]$) for the Hg^{II} promoted reactions are much larger than the corresponding slopes for the uncatalysed reactions, indicating that rates of base hydrolysis are markedly enhanced by Hg^{II} . Values of $k_{\text{cb}}^1 K_1^1 K^1$ (third order rate constant for Hg^{II} -promoted base hydrolysis) and $k_1^1 K_1$ (second order rate constant for Hg^{II} -promoted acid hydrolysis) were calculated from the slopes and intercepts respectively of the linear sections in the k_2 versus $[\text{OH}^-]$ plots. These values are listed in Table II along with the first order rate constants for acid hydrolysis (k_1) and the second order rate constants for base hydrolysis ($k_{\text{cb}} K$) of the complexes in the absence of Hg^{II} (data from [5]). These results indicate that while both acid and base hydrolysis reactions are markedly accelerated in the presence of Hg^{II} the latter reaction is the more sensitive of the two to catalysis. In solutions containing $1.0 \text{ mol dm}^{-3} \text{ Hg}^{\text{II}}$ rates of acid

TABLE I. Kinetic Data for the Hg^{II} Assisted Acid and Base Hydrolysis of the Complexes $\text{Cis-}[\text{Co(en)}_2(\text{RNH}_2)\text{Cl}]^{2+}$ at 50°C .

R	$10^3 [\text{Hg}^{\text{II}}]$	$10^{12} [\text{OH}^-]$	$10^4 k_{\text{obs}}/\text{s}^{-1}$	$10^1 k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
C_6H_5	5.05	1.19	5.72	1.13	
		2.28	6.02	1.19	
	3.03	5.96	9.46	1.87	
		9.13	7.77	2.56	
		11.9	7.41	2.93	
$p\text{-CH}_3\text{C}_6\text{H}_4$	5.38	1.09	15.2	2.82	
		2.11	15.6	2.90	
		5.47	22.6	4.20	
	3.23	9.13	18.8	5.82	
		2.69	10.9	20.1	7.47
$m\text{-CH}_3\text{C}_6\text{H}_4$	5.38	1.09	11.8	2.19	
		2.11	12.4	2.30	
		5.47	17.6	3.27	
	3.23	9.13	15.9	4.92	
		2.69	10.9	14.8	5.50

TABLE II. Rate Constants for the Hg^{II} Assisted and Unassisted Acid ($k_1^1 K_1$, k_1) and Base ($k_{\text{cb}}^1 K_1^1 K^1$, $k_{\text{cb}} K$) Hydrolysis of the Complexes $\text{Cis-}[\text{Co(en)}_2(\text{RNH}_2)\text{Cl}]^{2+}$ at 50°C .

R	$10^2 k_1^1 K_1 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^{-10} k_{\text{cb}}^1 K_1^1 K^1 / \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	$10^6 k_1/\text{s}^{-1}$	$10^{-6} k_{\text{cb}} K / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
C_6H_5	8.39	1.79	7.01	1.15
$p\text{-CH}_3\text{C}_6\text{H}_4$	9.15	5.78	6.97	1.96
$m\text{-CH}_3\text{C}_6\text{H}_4$	10.02	4.17	6.43	1.12

^aThe second order rate constants $k_{\text{cb}} K$ were calculated from the constants $K_a k_2$ listed in ref. 5 using K_w value for water of 5.47×10^{-14} (50°C) [10] ($k_2 = k_{\text{cb}}, K_a = K K_w$).

hydrolysis are promoted by factors of 1.2×10^4 ($R = C_6H_5$), 1.3×10^4 ($R = p\text{-CH}_3C_6H_4$) and 1.6×10^4 ($R = m\text{-CH}_3C_6H_4$), while rates of base hydrolysis are promoted by factors of 1.6×10^4 ($R = C_6H_5$), 2.9×10^4 ($R = p\text{-CH}_3C_6H_4$) and 3.7×10^4 ($R = m\text{-CH}_3C_6H_4$). The greater sensitivity of the base hydrolysis reaction to catalysis falls in line with the prediction outlined earlier in this discussion.

Acknowledgement

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- 8 Although the hydrolysis of $cis\text{-}[\text{Co}(\text{en})_2(\text{C}_6\text{H}_5\text{NH}_2\text{Cl})]^{2+}$ in the presence of Hg^{II} has been investigated [9] rate data has been reported for 30 °C and the results have not been compared with those for the unpromoted reaction (studied at 50 °C [5]). In addition in some cases Hg^{II} concentrations did not exceed complex concentrations which, assuming that pseudo first order kinetics were observed throughout the reaction, implies that catalysis by HgCl^+ was also being observed and that this was equally as efficient as catalysis by Hg^{II} .
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