Evidence for the Conjugate-base Mechanism for the Base Hydrolysis of Some Cobalt(III) Amine Complexes

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THE mechanism of base hydrolysis of octahedral complexes has been the subject of much discussion.[1] Although bimolecular (S_N2)[2] and ion-pair interchange (S_NIP)[3] mechanisms have been suggested, the general consensus of opinion is in favour of the conjugate-base mechanism, originally proposed by Garrick,[4] in which the base removes a proton from the amine ligand in a pre-equilibrium to form a substitutionally labile amido-complex, *e.g.*,

$$[Co(NH_3)_5X]^{2+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(NH_3)_4NH_2X]^+ + H_2O \tag{1}$$

$$[Co(NH_3)_4NH_2X]^+ \xrightarrow{k_2} [Co(NH_3)_4NH_2]^{2+} + X^- \tag{2}$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \longrightarrow [Co(NH_3)_4NH_2\,H_2O]^{2+} \tag{3}$$

$$[Co(NH_3)_4NH_2\,H_2O]^{2+} \longrightarrow [Co(NH_3)_5OH]^{2+} \tag{4}$$

Steps 3 and 4 are very much faster than 1 and 2. In certain cases, nucleophiles other than water can enter at stage 3,[5] and it has been suggested that there are occasions when the solvolysis of the conjugate base (steps 2 and 3) can be bimolecular.[6] If the processes in step 1 are much faster than those in step 2, proton exchange will be much faster than base hydrolysis and the latter would be subject to specific base catalysis. This is indeed true for the chloropentammine complexes[7] where k_{exchange}: $k_{\text{base hydrolysis}}$ is 10^5—10^6:1 but the rates approach one another more closely for unipositive complexes and in the not very labile *trans*-[Co en$_2$ F$_2$]$^+$ the ratio becomes 15 : 1.[7,8]

The base hydrolysis of *trans*-[Co cyclam Cl$_2$],$^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane), is unusually fast (k at 25° = $6{\cdot}7 \times 10^4$ l.sec.$^{-1}$ mole^{-1})[9] but the rate of proton exchange is usual for an amine complex with a single positive charge[10] and so it seemed possible to use this system to distinguish between the three mechanisms. We therefore took a solution of *trans*-[Co D$_4$-cyclam Cl$_2$]$^+$ (D$_4$-cyclam = *NN'N''N'''*-tetradeuteriocyclam) in 0·01N-HCl and combined it, in a fast mixing apparatus,[11] with a cold aqueous solution of 2,6-dimethylpiperidine such that the pH and ionic strength of the mixture were 10·5 and 0·05 *M*, respectively. When *ca.* 30% of the complex had reacted, the mixture was acidified with strong perchloric acid and the unreacted *trans*-dichloro-complex was precipitated as its insoluble perchlorate. The filtrate was then warmed with concentrated hydrochloric acid whereby the reaction product was also converted into the insoluble *trans*-dichloro-perchlorate and precipitated. From the relative intensities of the N–H and N–D stretching absorptions (at 3200 and 2380 cm.$^{-1}$ respectively) it will be seen (Figure 1) that both samples retain a considerable amount of their deuterium. The extent of label transfer indicated is *ca.* 20% exchanged in the unreacted substrate, and *ca.* 40% exchanged for the recovered product. A blank experiment using *trans*-[Co D_4-cyclam OH Cl]$^+$ showed no exchange under the same conditions. A similar treatment of the substitutionally more labile *trans*-[Co cyclam Br_2^+] indicated that, although the amount of exchange in the unreacted material was less, that in the recovered product was still about 40%.

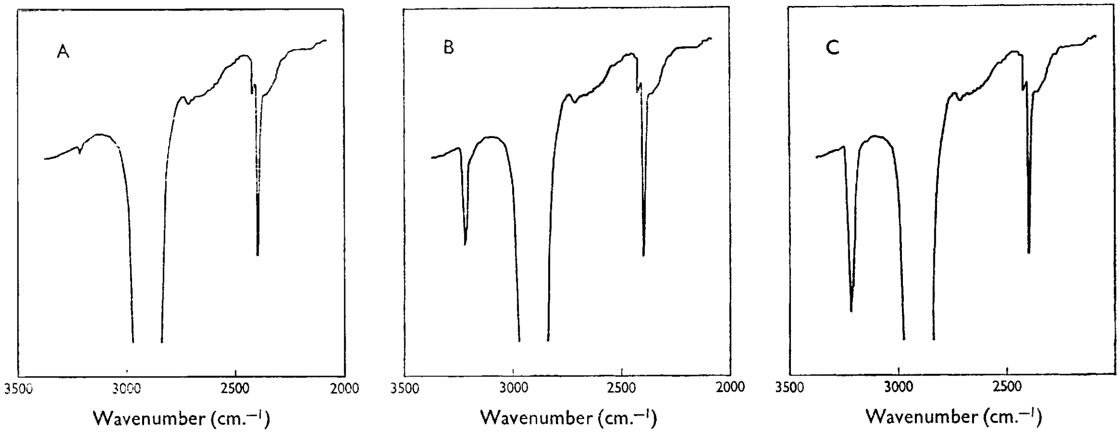

FIGURE 1. *Infrared spectra of Nujol mulls of trans*-[CoD_4-cyclam Cl_2]ClO_4

(A) as initially prepared,

(B) recovered unreacted from a 2,6-dimethylpiperidine–HNO_3 buffer at pH 10·5,

(C) regenerated from the product of base hydrolysis of (A)

The extra exchange in the product must therefore take place as it is being formed and is fully consistent with the S_N1CB mechanism. In the alternative mechanisms, base hydrolysis and proton exchange are in no way connected and therefore the extra exchange should not be observed under these circumstances. The data in Figure 1 indicate that step 1 is no longer an equilibrium and k_{-1} and k_2 are of similar magnitude. Thus, this reaction should be subject to a measure of general base catalysis,[12] whereas the S_NIP and S_N2 mechanisms require a specific first-order dependence on [OH^-]. The rate of base hydrolysis of *trans*-[Co cyclam Cl_2]$^+$ was measured in two different buffer systems. Holding the ionic strength and the buffer ratio (hence the pH) constant, the rate was found to increase significantly with the concentration of base, (Figure 2). The base does not enter the complex.

The reaction with the ionic base, azide, leads initially to the formation of *trans*-[Co cyclam OH N_3]$^+$. In unbuffered solution the rate law is of

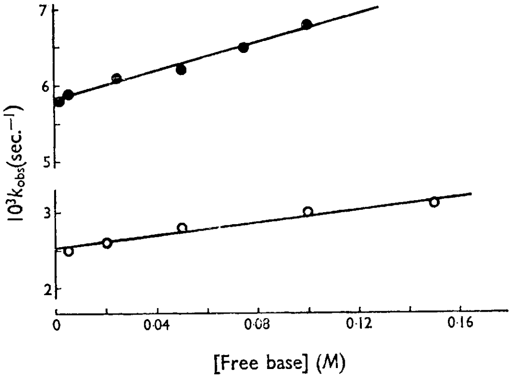

FIGURE 2. *First-order rate constants for the base hydrolysis of trans*-[Co cyclam Cl_2]$^+$ *as a function of free base concentration.*

● = 2,6-dimethylpyridine; buffer ratio [B]/[BH^+] = 1·33; pH = 6·95; temperature = 25·0°; ionic strength = 0·075*M*.

○ = pyridine; buffer ratio = 1; pH = 5·26; ionic strength = 0·2*M*; temperature = 49·2°.

the form, Rate = $(k[N_3^-]^{\frac{1}{2}} + k'[N_3^-])$ [complex] and only the first term can be ascribed to a hydroxide dependence.

This represents the first kinetic demonstration of the S_N1CB mechanism for base hydrolysis in aqueous solution.

(*Received, December 8th,* 1967; *Com.* **1317.**)

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