# A Concerted Mechanism for the Base Hydrolysis of some Cobalt(III) Complexes (E2 Hydrolysis)

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The base hydrolysis of halo-amine complexes of cobalt(III) has occupied a central area in the study of inorganic reaction mechanisms for many years [1]. It is now well established that the rapid hydrolysis of acido-amine–cobalt(III) complexes in basic solution is due to the generation of a dissociatively labile amido species, in accordance with the mechanism first proposed by Garrick [2]. The $S_N1(CB)$ mechanism (1) is supported by much experimental evidence [1], and may be summarised,

$$AH + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^- + BH^+$$
$$\downarrow k_2 \qquad (1)$$
$$\text{products}$$
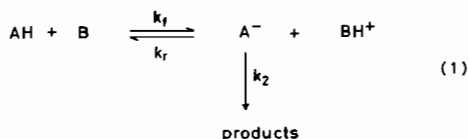
where AH is the metal complex, A^- is the amido conjugate base and B is hydroxide ion. Normally ligand loss from the conjugate base is the rate-determining step, however, in recent years a number of examples of general base catalysis have been described [3–5]. For general base catalysis to be observed $k_2 \gg k_r[BH^+]$, where B represents any base in solution. If k_{obs} is the observed first order rate constant at constant pH, then the rate expression is given by $k_{obs} = k_{aq} + k_{OH}[OH^-] + k_B[B]$ where k_{aq} is the first-order rate constant for aquation and k_B is the second order rate constant for general base catalysis. The observation of general base catalysis rather than specific base catalysis is consistent with rate determining proton transfer in which deprotonation of AH becomes rate limiting. In the case of specific base catalysis, ligand loss from A^- is rate determining. The concentration of A^- is a function of the pH (*i.e.* hydroxide ion concentration) of the solution. If deprotonation becomes rate limiting, any base in solution becomes effective in the proton transfer step. The observation of general base catalysis is also consistent with a concerted mechanism which may be represented,
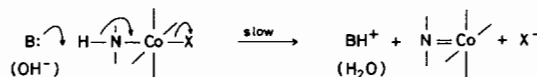

in which proton transfer and cleavage of the Co–X bond occurs synchronously. The purpose of the present paper is to consider the evidence for the occurrence of the concerted mechanism.

As an approximate guide, reactions with $k_{OH} > 5 \times 10^4\ M^{-1}\ s^{-1}$ at 25 °C appear to be subject to general base catalysis and in addition display 'low' values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$. The 'low' activation parameters result from the change in rate-determining step from halide loss to proton loss or to a synchroniety of the two. For $S_N1(CB)$ reactions the estimated value of $\Delta S^\ddagger$ is *ca.* +140 $JK^{-1}\ mol^{-1}$ with $\Delta H^\ddagger$ values of *ca.* 100 $JK^{-1}\ mol^{-1}$ [6]. In cases where proton transfer becomes rate limiting $\Delta H^\ddagger$ is 50 to 70 $kJ\ mol^{-1}$ with low positive values of $\Delta S^\ddagger$ of +33 to +70 $JK^{-1}\ mol^{-1}$ [1, 3–5].

For a stepwise mechanism involving slow proton transfer, cleavage of the metal–halogen bond occurs after the rate determining step, while for a concerted mechanism cleavage occurs in the rate determining step. A reaction which displays a dependence on the leaving group and is subject to general base catalysis must therefore be concerted.

Table I summarises the available data for reactions which have been shown to be subject to general base catalysis or have values of k_{OH} which make it highly probable that such catalysis will be observed. All the reactions listed show a dependence on the leaving group with K_{OH}^{Br}/k_{OH}^{Cl} ratios of 2–3. In addition the activation parameters differ quite markedly on variation of the leaving group; this effect would not occur if a stepwise slow proton transfer was involved, as the activation parameters would be independent of the leaving group. A concerted process in which removal of a proton from an N–H group and displacement of the leaving group from cobalt occur simultaneously is in full accord with the experimental observations. Such a mechanism is best described as an elimination, and it is similar in character to the classical E2 elimination mechanism (2) of organic chemistry [9]. Substitution takes place by an elimination–addition pathway and does not involve
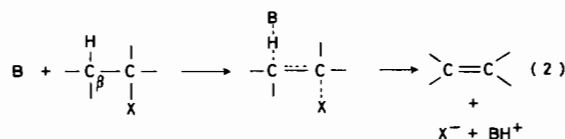
a six-coordinate amido intermediate. The addition pathway can be considered as a direct reversal of the elimination pathway,

TABLE I. Rate Constants (25 °C) and Activation Parameters for the Base Hydrolysis of Some Halo-Amine Complexes of Cobalt(III).

Complex[a]	k_{OH}[b] $(M^{-1} s^{-1})$	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	Ref.
trans-[CoL$_a$(NCS)Cl]$^+$	1.7×10^5 [c]	53	+33	5
trans-[CoL$_a$(NCS)Br]$^+$	3.9×10^5 [c]	57	+54	5
trans-[CoL$_b$(NCS)Cl]$^+$	2.5×10^4 [c]	68	+67	5
trans-[CoL$_b$(NCS)Br]$^+$	9.8×10^4 [c]	54	+33	5
trans-[CoL$_a$(Cl)$_2$]$^+$	7.8×10^8	–	–	7
trans-[CoL$_a$(Br)$_2$]$^+$	1.9×10^9	–	–	7
trans-[CoL$_c$(Cl)$_2$]$^+$	8.5×10^7	–	–	8
trans-[CoL$_c$(Br)$_2$]$^+$	$\sim 1 \times 10^9$	–	–	8

[a]L$_a$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene(trans[14]diene); L$_b$ = C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (tet *a*); L$_c$ = 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene. [b]For the S$_N$1 (CB) mechanism, values of k_{OH}^{Br}/k_{OH}^{Cl} are *ca.* 6 (Ref. 10). [c]General base catalyses confirmed.

Acknowledgement

References

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