Concerted *E2* Mechanism for the Base Hydrolysis of *cis*-[$CoCl_2$(cyclen)]$^+$†

By ROBERT W HAY* and PAUL R NORMAN
(*Chemistry Department, University of Stirling, Stirling* FK9 4LA)

Summary Evidence is presented in support of a concerted *E2* mechanism for the base hydrolysis of *cis*-[$CoCl_2$(cyclen)]$^+$ (cyclen = 1,4,7,10-tetra-azacyclododecane) in which cleavage of the N–H and Co–Cl bonds occurs synchronously to give a five-co-ordinate intermediate without the intervention of a six-co-ordinate conjugate base.

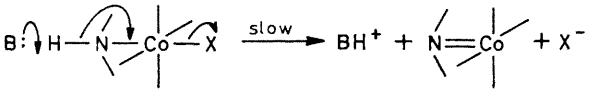
THE base hydrolysis of halogeno-amine complexes of cobalt(III) has occupied a central area in the study of inorganic reaction mechanisms for many years [1] Much evidence[1] now supports the view that the rapid hydrolysis of acido–aminecobalt(III) complexes in basic solution is due to the generation of a dissociatively labile amido species, as initially suggested by Garrick [2] This $S_N1(CB)$ mechanism may be summarised as in equation (1), where AH is the

† Abbreviations used throughout the paper are cyclen = 1,4,7,10-tetra-azacyclododecane, trien = 1,8-diamino-3,6-diazaoctane, 2,3,2-tet = 1,9-diamino-3,7-diazanonane, en = 1,2-diaminoethane, cyclam = 1,4,8,11-tetra-azacyclotetradecane

metal complex, A^- is the amido conjugate base, and B is hydroxide ion. Normally ligand loss from the conjugate

$$AH + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^- + BH^+ \quad (1)$$
$$\downarrow k_2$$
products

base is the rate-determining step. However, in recent years a number of examples of general base catalysis have been observed.[3-5] For general base catalysis to occur $k_2 >> k_r[BH^+]$ where B represents any base in solution. The observation of general base catalysis is consistent with rate-determining-proton transfer in which deprotonation of AH becomes rate limiting. General base catalysis is also consistent with a concerted mechanism (2) in which proton



(2)

transfer and cleavage of the Co–X bond occur synchronously. 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.

We present evidence in support of a concerted (*E*2) mechanism in the base hydrolysis of *cis*-$[CoCl_2(cyclen)]^+$.† For aquation of *cis*-$[CoCl_2(cyclen)]^+$, k_{aq} at 25 °C is $4{\cdot}5 \times 10^{-3}$ s^{-1} with $\Delta H^{\ddagger} = 78$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = -21$ J K^{-1} mol^{-1} in 0·1 mol dm^{-3} HNO_3.‡ For the series of complexes *cis*-$[CoCl_2(L)]^+$ where L = α-trien,§ en_2,§ cyclen, and cyclam§ the aquation rates at 25 °C vary by a factor of *ca.* 10^2, owing almost exclusively to minor changes in $\Delta H^{\ddagger}$ ($\Delta S^{\ddagger}$ is effectively constant at −21 to −25 J K^{-1} mol^{-1}).

Base hydrolysis of *cis*-$[CoCl_2(cyclen)]^+$ is extremely rapid with $k_{OH} = 2{\cdot}1 \times 10^7$ dm^3 mol^{-1} at 25 °C and $I = 0{\cdot}1$ mol dm^{-3}, the highest rate constant reported for a dichloro-complex of a saturated macrocycle. The activation parameters for base hydrolysis are $\Delta H^{\ddagger} = 53$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = +73$ J K^{-1} mol^{-1}. These 'low' activation parameters are consistent with a mechanism involving rate-determining deprotonation of the substrate.[4] Base hydrolysis is subject to general base catalysis by formate ion, with $k_B = 2{\cdot}3 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} at 25 °C. An approximate value of the Bronsted β-coefficient is 0·7 (calculated from k_{OH} and k_B). This value is similar to the $\beta = 0{\cdot}67$ reported[4] for *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$. Rate determining substrate deprotonation is also confirmed by the observation of a primary isotope effect $k^H_{OH}/k^D_{OH} = 1{\cdot}6$ where k^H_{OH} relates to the *N*-protiocomplex and k^D_{OH} to the *N*-deuteriocomplex. This value compares well with the isotope effects of 1·7 and 1·5 reported[4] for the *RR*(*SS*) and *RS* isomers of *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$.

For base hydrolysis of *cis*-$[CoBr_2(cyclen)]^+$, $k_{OH} = 1{\cdot}9 \times 10^8$ dm^3 mol^{-1} s^{-1} ($k_{aq} = 8{\cdot}2 \times 10^{-3}$ s^{-1}) at 25 °C and $I = 0{\cdot}1$ mol dm^{-3}. The ratio $k^{Br}_{OH}/k^{Cl}_{OH} = 9$ at 25 °C. The marked dependence on the leaving group excludes a stepwise $S_N1(CB)$ mechanism in which substrate deprotonation is rate-determining. However, the data are fully consistent with a synchronous *E*2¶ mechanism.

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‡ The activation parameters reported by Y. Hung and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 4971, *i.e.*, $\Delta H^{\ddagger} = 56{\cdot}5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -100$ J K^{-1} mol^{-1} are markedly different from those reported for other *cis*-dichlorotetramine complexes (footnote §). The substantial negative entropy of activation is inconsistent with a dissociative mechanism which is expected for these reactions. Our own results indicate good agreement with the reported value of k_{aq} at 25 °C but very poor agreement with the rate constants at higher temperatures, leading to a marked difference in the activation parameters.

§ For values of k_{aq} and activation parameters, see E. Campi, J. Ferguson, and M. L. Tobe, *Inorg. Chem.*, 1970, **9**, 1781.

¶ Such a mechanism is best described as an elimination. It is similar in character to the classical *E*2 mechanism of organic chemistry, see, for example, E. Baciocchi, *Acc. Chem. Res.*, 1979, **12**, 430. Strong evidence in support of π-stabilization of a conjugate base has recently been reported: P. Comba and W. Marty, *Helv. Chim. Acta*, 1980, **63**, 693.

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