The Base Catalysed Hydrolysis of *trans*-Dichlorobis-(1,2-diaminoethane)-cobalt(III) and -(1,3-diaminopropane)cobalt(III) Cations: Rate-limiting Proton Transfer

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The base hydrolysis of *trans*-$[Co(en)_2Cl_2]^+$ (en = 1,2-diaminoethane) has been re-examined over the temperature range 5—45 °C. The plot of ln (k_{OH}/T) *vs.* T^{-1} is curved above 25 °C indicating a change towards rate-limiting deprotonation at higher temperatures. The rate constants for the base hydrolysis of *trans*-$[Co(tn)_2Cl_2]^+$ [tn = trimethylenediamine (1,3-diaminopropane)] are *ca.* 20 times greater than those for the $(en)_2$ complex in the range 5—10 °C but the temperature dependence suggests that deprotonation is rate-limiting even at the lowest temperatures studied.

The base catalysed aquation (base hydrolysis) of octahedral cobalt amine complexes involves the deprotonation, by hydroxide, of a suitably placed amine group (rate constant, k_1/dm^3 mol^{-1} s^{-1}) to generate a dissociatively labile amido species which can either be reprotonated by water (rate constant, k_{-1}/s^{-1}) or dissociate (rate constant, k_2/s^{-1}) to give a short-lived five-co-ordinate intermediate that is consumed by reaction with water.[1] For the reaction $[CoL_5X]^{z+} + OH^- \longrightarrow [CoL_5(OH)]^{z+} + X^-$, the rate law is: $-d[CoL_5X^{z+}]/dt = k_{OH}[CoL_5X^{z+}][OH^-]$ (plus a contribution from the uncatalysed aquation). When there are n equivalent amine protons equation (1) applies (a somewhat more complicated

$$k_{OH} = nk_1k_2/(k_{-1} + k_2) \qquad (1)$$

expression is required when there are non-equivalent labilising nitrogens). In general, proton transfer is rapid compared to the hydrolysis and therefore reversible, *i.e.* $k_{-1} \gg k_2$, and equation (1) reduces to equation (2); occasionally a substrate is found in

$$k_{OH} = nk_1k_2/k_{-1} \qquad (2)$$

which $k_2 \gtrsim k_{-1}$ and in the limit this gives equation (3), *i.e.* deprotonation becomes rate-limiting.[2] Compounds of the

$$k_{OH} = nk_1 \qquad (3)$$

type *trans*-$[Co(N_4)X_2]^+$ (X = Cl or Br; N_4 is any combination of monodentate, bidentate, or quadridentate amine ligands that will occupy four co-ordination sites) frequently fall into this category. For example, when N_4 = (*RS*)-[3] or (*RR*)-1,9-diamino-3,7-diazanonane,[4] $k_{-1}/k_2 \leqslant 0.05$ at 0 °C; N_4 = (*RRSS*)-cyclam, k_{-1}/k_2 = 1.0 at 3 °C;[5] N_4 = (*RRRR*)-cyclam, $k_{-1}/k_2 \ll 1$;[6] $N_4 = (en)_2$, $4 < k_{-1}/k_2 < 10$ at 0 °C.[3,†]

It has been of interest to look at the features that determine the value of the ratio k_{-1}/k_2 and to examine the consequences of exchanging from one limit to the other.[2] Since the reprotonation and dissociation processes are likely to have different enthalpies of activation, a system where $k_{-1}/k_2 \sim 1$ at the centre of the temperature range studied can be transferred from one limit to the other by an adequate change of temperature. Such a change will lead to a curved Eyring plot [ln (k_{OH}/T) *vs.* T^{-1}]. This has been observed in the base hydrolysis of *trans*-$[Co\{(RRSS)\text{-cyclam}\}Cl_2]^+$.[5] Although the studies of proton exchange in *trans*-$[Co(en)_2Cl_2]^+$ indicated that k_{-1} was less than one order of magnitude greater than k_2 at 0 °C,[3] there was no mention in the literature relating to the well studied base hydrolysis of this substrate[7] of any curvature in the Eyring plot. We have therefore re-examined the kinetics of this reaction at higher temperatures using stopped-flow techniques and report our results in this paper. For comparison we also report the kinetics of the base hydrolysis of *trans*-$[Co(tn)_2Cl_2]^+$.

Experimental

Preparations and Reagents.—*trans*-Dichlorobis(1,2-diaminoethane)cobalt(III) chloride was prepared by the method of Bailar and Rollinson[8] and converted to the nitrate by adding ammonium nitrate to a concentrated aqueous solution. The green crystals were filtered off, washed with ice-cold dilute NH_4NO_3 solution and then ice-cold water, ethanol, and diethyl ether and air dried (Found: C, 15.4; H, 5.05; N, 22.2. $C_4H_{16}Cl_2CoN_5O_3$ requires C, 15.4; H, 5.15; N, 22.4%).

trans-Dichlorobis(1,3-diaminopropane)cobalt(III) chloride was prepared from anhydrous cobalt chloride and 1,3-diaminopropane by the method of Bailar and Work[9] (Found: C, 22.9; H, 6.30; N, 18.0. $C_6H_{20}Cl_3CoN_4$ requires C, 23.0; H, 6.45; N, 17.9%).

Buffers in the pH range 8—9 were prepared using Tris [tris(hydroxymethyl)aminomethane] and HCl. Solutions containing Tris (50.0 cm^3, 0.10 mol dm^{-3}) and the appropriate amount of 0.10 mol dm^{-3} hydrochloric acid were made up to 100.0 cm^3 by adding 0.10 mol dm^{-3} solutions of $NaNO_3$ in order to ensure a constant ionic strength of 0.050 mol dm^{-3}. The pH of the buffer solution was measured at the temperature of the kinetics experiments using a Radiometer PHM 26 pH meter and glass electrode calibrated against the primary standards (0.050 mol dm^{-3} potassium hydrogenphthalate and 0.10 mol dm^{-3} sodium tetraborate) at the same temperature and ionic strength. The hydroxide concentration was calculated from the equation $[OH^-] = 10^{(\log K_w^{I,T} + pH)}$, where $K_w^{I,T}$ is the ionic product of water at the ionic strength and temperature of the kinetics experiments, calculated from the literature values of K_w at $I = 0$ and temperature[10] and the appropriate activation coefficients.[11]

All other reagents were AR grade.

Kinetics.—Fast reactions were followed spectrophotometrically using a Hi-Tech stopped-flow spectrophotometer, the photon multiplier output being digitalised by an A/D converter

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† Abbreviations: cyclam = 1,4,8,11-tetra-azacyclotetradecane, en = 1,2-diaminoethane, tn = trimethylenediamine (1,3-diaminopropane); 2,3,2-tet was used for 1,9-diamino-3,7-diazanonane in refs. 3 and 4.

designed by A. Griffiths and J. Cant of Johnson Matthey plc and processed with a Research Machines 380Z minicomputer using software written by Dr. A. Treadgold. Equal volumes of complex and NaOH solution were mixed, the concentration of sodium hydroxide used being at least ten times greater than that of the complex in order to ensure first-order kinetics.

The reactions in buffer solution were followed in the thermostatted cell compartment of a Perkin-Elmer 554 u.v.–visible spectrophotometer; the reagents, apart from the complex, were brought to the reaction temperature and the reaction then initiated by adding a small weighed amount of the complex which dissolved rapidly. Repetitive scans over the range 280—360 nm for the slower reactions showed no isosbestic points but were consistent with a single stage of reaction (*i.e.*, at any wavelength the change of absorbance was first order and the rate constant independent of wavelength). Faster reactions were followed at a single wavelength, 310 nm.

Results

The base hydrolysis of *trans*-$[Co(en)_2Cl_2]^+$ takes place in two stages giving a mixture of the *cis*- and *trans*-$[Co(en)_2(OH)_2]^+$ cations. At the hydroxide concentrations used in this work the second stage is some 3—4 orders of magnitude slower than the first[7] and can be ignored. At temperatures below 50 °C the background uncatalysed aquation is far too slow to interfere with the stopped-flow technique which requires that, within the time required to prepare each experiment (*ca.* 30 min), the substrate does not undergo significant reaction. The system is therefore ideal for a study of the base hydrolysis at elevated temperature with an unambiguous knowledge of $[OH^-]$ provided as excess NaOH. Although the base catalysed hydrolysis of the *trans*-$[Co(tn)_2Cl_2]^+$ cation appears to follow a similar course, the 10^3-fold increase in lability towards uncatalysed solvolysis[12] rules out the use of the stopped-flow technique and makes it necessary to work in buffer solution at low temperatures. Even under the most favourable conditions the background aquation makes a significant contribution to the overall reaction and reliable data could not be collected above 10 °C.

The absorbance changes are consistent with a single first-order spectrophotometric process in both cases. However, in the diaminoethane complex it is known that the loss of the second chloride is at least three orders of magnitude slower under the conditions of the experiment and the reaction being followed is as in equation (4), whereas at pH 8—9 the uncatalysed

$$trans\text{-}[Co(en)_2Cl_2]^+ + OH^- \longrightarrow trans\text{-}[Co(en)_2(OH)Cl]^+ + Cl^- \quad (4)$$

solvolytic processes will make a much greater contribution to the overall reaction. Although the rate constants have never been obtained, it is unlikely that reaction (5) is slower than the

$$trans\text{-}[Co(tn)_2(OH)Cl]^+ + H_2O \longrightarrow [Co(tn)_2(OH)_2]^+ + H^+ + Cl^- \quad (5)$$

uncatalysed aquation of the dichloro species and the clean single spectrophotometric change observed leads to the conclusion that the second stage is very much faster than the first. Nevertheless, the loss of the first chloride is rate-determining and the observed rate constants relate to this process.

The first-order rate constants, $k_{obs.}$, which were obtained from a linear least-squares analysis of the plot of ln $(A_t - A_\infty)$ *vs.* t, where A_t and A_∞ are the absorbances of the reacting solution at time t and after eight half-lives, respectively, are collected in the Table. At the lower temperatures (< 25 °C), the rate constants (each of which is the average of two or three independent runs with agreement generally better than ±2%) were measured at a number of hydroxide concentrations and plots of $k_{obs.}$ *vs.* $[OH^-]$ were linear, passing through the origin for the $(en)_2$ complex but with a finite intercept for the $(tn)_2$ species. Slopes $(= k_{OH})$ and intercepts where relevant are also collected in the Table. At temperatures above 25 °C the kinetics was measured

Table. Rate constants for the base catalysed aquation of the *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(tn)_2Cl_2]^+$ cations*

(*a*) *trans*-$[Co(en)_2Cl_2]^+$

T/°C	$[OH^-]$/mol dm^{-3}	$k_{obs.}$/s^{-1}	k_{OH}/dm^3 mol^{-1} s^{-1}
5.0	0.0250	2.33	
	0.0275	3.26	
	0.0500	4.50	90.8 ± 0.2
10.0	0.0250	4.13	
	0.0375	6.26	
	0.0500	8.30	167 ± 2
15.0	0.0250	7.55	
	0.0375	11.3	
	0.0500	15.3	310 ± 6
20.0	0.0250	13.0	
	0.0375	18.7	
	0.0500	26.8	552 ± 55
25.0	0.0125	11.6	928
	0.0500	46.0	920
30.0	0.0125	20.3	1 620
35.0	0.0125	29.4	2 350
37.5	0.0125	38.4	3 070
40.0	0.0125	46.5	3 720
42.5	0.0125	60.8	4 860
45.0	0.0125	67.9	5 430

(*b*) *trans*-$[Co(tn)_2Cl_2]^+$

T/°C	pH	$10^6[OH^-]$/ mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
5.0	8.77	1.6	7.04
	8.87	2.0	8.54
	8.97	2.5	9.3
	9.07	3.2	10.3
	9.17	4.0	11.9
	9.27	5.0	14.2
	9.37	6.3	16.3
	9.47	7.9	19.6
	9.57	10.0	24.1

$k_{OH} = (1.96 \pm 0.03) \times 10^3$ dm^3 mol^{-1} s^{-1}
$k_{aq} = (4.2 \pm 0.2) \times 10^{-3}$ s^{-1}

T/°C	pH	$10^6[OH^-]$/ mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
10.0	8.67	2.0	14.6
	8.87	3.2	18.6
	8.97	4.0	20.0
	9.07	5.0	22.5
	9.17	6.3	26.2
	9.26	7.8	30.5

$k_{OH} = (2.67 \pm 0.09) \times 10^3$ dm^3 mol^{-1} s^{-1}
$k_{aq} = (9.5 \pm 0.4) \pm 10^{-3}$ s^{-1}

* [Complex] = 1.0×10^{-3} mol dm^{-3}, I = 0.050 mol dm^{-3} ($NaNO_3$).

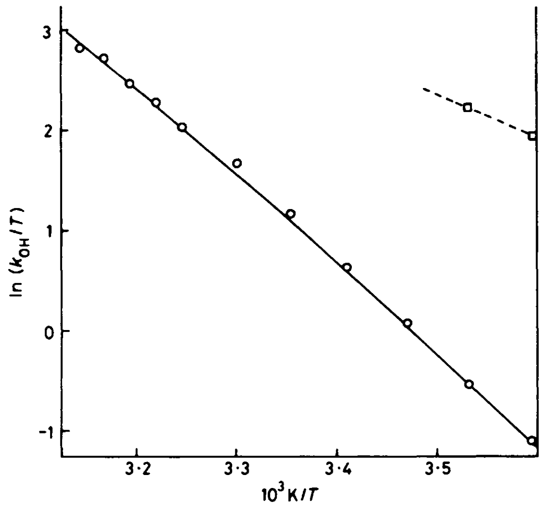

Figure. Plot of ln (k_{OH}/T) *vs.* T^{-1} for the base hydrolysis of *trans*-[Co(en)$_2$Cl$_2$]$^+$ (○) and *trans*-[Co(tn)$_2$Cl$_2$]$^+$ (□). The curve for the diaminoethane complex is calculated using $\Delta H^{\ddagger}_1$ = 44 kJ mol^{-1}, $\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}$ = 40 kJ mol^{-1}, $k_2 = k_{-1}$ at 47 °C, and k_{OH} = 167 dm^3 mol^{-1} s^{-1} at 10.0 °C

at a single [OH$^-$] and the value of k_{OH} listed is simply $k_{obs.}$/[OH$^-$]. The Eyring plots are shown in the Figure.

Discussion

The earliest studies of the base hydrolysis were carried out by primitive flow techniques[7,13] over the temperature range 0—25 °C using equal concentrations of complex and NaOH, no attempt being made to hold the ionic strength constant. The rate constants reported were some three times greater than the values found in this work but the difference is too large to be accounted for by ionic strength variation. The Eyring plot was linear with an activation energy of 23 kcal mol^{-1} (*ca.* 96 kJ mol^{-1}). A more recent study in buffer solution[3] (pH ~ 8) also gives rate constants greater than those reported in this work even after correcting for the fact that the values of K_w used in the original calculation were appropriate for $I = 0$ rather than the ionic strength used (not quoted but probably *ca.* 0.050 mol dm^{-3}), but the differences are not so great. There is no systematic curvature of the Eyring plot but the scatter of the points is large. The stopped-flow study that we now report, in which the sodium hydroxide concentration is sufficiently large to ensure first-order kinetics, the subsequent stages of the reaction are too slow to interfere, and the temperature control is efficient, offers the most reliable results so far.

At temperatures below 25 °C, the Eyring plot is essentially linear but a significant curvature can be observed at the higher temperatures (Figure). Unfortunately the increase in the rate of the uncatalysed solvolysis does not allow enough time to set up the stopped-flow experiments and it was not possible to collect reliable data for k_{OH} at temperatures significantly above 45 °C. The region where the upper limit ($k_2 \gg k_{-1}$) is reached and the curvature ceases is therefore inaccessible and an independent evaluation of $\Delta H^{\ddagger}_1$ is ruled out. Any attempt to analyse the ln (k_{OH}/T) *vs.* T^{-1} plot in terms of optimum values for $\Delta H^{\ddagger}_1$, $\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}$, and k_{-1}/k_2, as was carried out successfully for *trans*-[Co(cyclam)Cl$_2$]$^+$,[5] is not worthwhile, even with a computer guided curve-fitting program. While the value for $\Delta H^{\ddagger}_1 + \Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}$ is reasonably well defined by the tangent to the Eyring plot (= 84 ± 2 kJ mol^{-1}) and the temperature at which $k_{-1} = k_2$ has to be 47 ± 3 °C, $\Delta H^{\ddagger}_1$ can be varied between 30 and 50 kJ mol^{-1} without significant deviation of the experimental and calculated values. Nevertheless, the uncertainty can be narrowed by taking account of the isotopic exchange experiment of Marangoni *et al.*[3] From an analysis of the relationship between the fraction of reaction completed, F_R, and the fraction of protons exchanged in the unreacted material, N_u, it could be shown that, at 0 °C, $4 < k_{-1}/k_2 < 10$, the wider error limits being due, in part, to the errors in the measurements but mainly to the inability to correct for the isotope effects due to working with the deuteriated substrate in H$_2$O. Consequently $20 < \Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1} < 40$ kJ mol^{-1}. The solid curve in the Figure is calculated using the following data: $k_{-1} = k_2$ at 47 °C, $\Delta H^{\ddagger}_1$ = 44 kJ mol^{-1}, $\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}$ = 40 kJ mol^{-1} and is made to pass through the experimental value for k_{OH} at 10 °C. The higher value for $\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}$ was chosen in order to keep $\Delta H^{\ddagger}_1$ within the range of values found in the literature for $\Delta H^{\ddagger}_1$ determined directly from the kinetics of proton exchange.

Not only does the great uncatalysed solvolytic lability of the *trans*-[Co(tn)$_2$Cl$_2$]$^+$ cation[12] prevent the stopped-flow technique being used it also rules out a study of the base hydrolysis reaction over a wide range of temperature. At temperatures much above 10 °C the uncatalysed aquation dominates the overall reaction and, because of the difficulties in following reactions with $t_{\frac{1}{2}} < 5$ s, it becomes impossible to vary [OH$^-$] sufficiently to obtain reliable values for k_{OH}. Studies were therefore only carried out at 5 and 10 °C and while k_{OH} for the (tn)$_2$ complex is *ca.* 20 times greater than that for the (en)$_2$ complex, this enhanced reactivity does not approach the factor of *ca.* 1 500 found in the uncatalysed reaction.[12] Although it would be unsatisfactory to use the slope of the line joining two points 5 °C apart to obtain a reliable value for $\Delta H^{\ddagger}_{OH}$ for the base hydrolysis (38 kJ mol^{-1}) it is quite clear that whatever the precise value, it must be about one-half of that for the (en)$_2$ complex within the same range of temperature. It seems reasonable to suggest that the greater lability of the (tn)$_2$ complex should be reflected by a large increase in k_2, the rate constant for the dissociation of the conjugate base. This would have the effect of tipping the balance completely to the point where $k_2 \gg k_{-1}$ so that $k_{OH} = 8k_1$ and $\Delta H^{\ddagger}_{OH} = \Delta H^{\ddagger}_1$. Under these circumstances the values of k_1 for the (tn)$_2$ complex, 245 and 332 dm^3 mol^{-1} s^{-1} at 5.0 and 10.0 °C respectively, do not differ greatly from those of the (en)$_2$ complex (120 and 170 dm^3 mol^{-1} s^{-1} respectively, using the parameters of the calculated curve in the Figure). The difference in the reactivity of the *trans*-[Co(en)$_2$Cl$_2$]$^+$ and *trans*-[Co(tn)$_2$Cl$_2$]$^+$ cations towards aquation, whether base catalysed or not, is very similar to that observed between the *RRSS* and *RRRR* isomers of the *trans*-[Co(cyclam)Cl$_2$]$^+$ cation[5,6,14] and is presumably due to the same cause, *i.e.* the much greater ability of the more labile species to form the trigonal-bipyramidal geometry required in the five-co-ordinate intermediate. This has already been proposed by Couldwell and House[15] to account for the high reactivity of the *trans*-[Co(tn)$_2$Cl$_2$]$^+$ complex.

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