Kinetics of Base Hydrolysis of Cationic Dichlororhodium(III) Complexes containing Two Substituted Ethylenediamine Ligands

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The kinetics of base hydrolysis of complexes of the type *trans*-$[Rh(L–L')_2Cl_2]^+$ (L–L' = en, men, sdmen, udmen, trimen, or tetmen) † have been studied and found, with the exception of the complex with L–L' = tetmen, to depend on $[OH^-]$. For the complexes with L–L' = en or udmen the observed pseudo-first-order rate constant is given by $k_{obs.} = k_1 + k_2[OH^-]$ for hydroxide-ion concentrations up to 1.0 mol dm^{-3}, whereas no $[OH^-]$-dependent term occurs for the complex with L–L' = tetmen over the same range of $[OH^-]$. The activation parameters for the base hydrolysis of the complexes with L–L' = en, udmen, or tetmen have been determined and are discussed in relation to literature data for the base-hydrolysis reactions of similar amine chlororhodium(III) complexes and some analogous cobalt(III) complexes.

In recent years a number of kinetic studies on the base hydrolysis of various amineanionorhodium(III) complexes have been reported.[1,2] One feature to emerge from these earlier results was that in those complexes which exhibited pH-dependent rates of base hydrolysis the leaving ligand was *trans* to an amine nitrogen bearing an ionisable proton. Complexes such as *trans*-$[Rh(NH_3)_4Cl]^+$ and *trans*-$[Rh(L–L)_2Cl_2]^+$ (L–L = en, mbd, or rbd) which did not possess this feature were found to undergo base hydrolysis to give the dihydroxo-complexes at a rate which was apparently independent of pH.[1c] Poë and Vuik,[2] however, have recently shown that the base-hydrolysis kinetics of the complexes *trans*-$[Rh(en)_2(OH)X]^+$ and *trans*-$[Rh(en)_2X_2]^+$ (X = Cl, Br, or I) all follow a rate law with an $[OH^-]$-dependent term, although the latter is quite small. Extensive studies on similar aminehalogenocobalt(III) complexes have shown that the rates of base hydrolysis exhibit a very large pH dependence and there is considerable evidence that these reactions occur primarily *via* a $S_N1(CB)$ mechanism.[3] It has been suggested [1c,4] that this difference in behaviour of cobalt(III) and rhodium(III) aminehalogeno-complexes arises because the ability of Rh^{III} to form a π bond with the co-ordinated amide group in the conjugate base is less than that of Co^{III}. There is also evidence [1c,4] that the pK_a of amine groups in complexes in which they are *trans* to a halide is lower than in complexes lacking this feature and this could contribute to the base-hydrolysis behaviour of the rhodium(III) complexes.

As an extension of our earlier work on the halide-interchange reactions of *trans*-dichlorobis(*N*-methyl-substituted ethylenediamine)rhodium(III) complexes [5] we have examined the base-hydrolysis kinetics of these and of the parent complex *trans*-$[Rh(en)_2Cl_2]^+$ over a wide range of $[OH^-]$ and we compare our results with those obtained previously for other aminechlororhodium(III) complexes and analogous cobalt(III) complexes.

EXPERIMENTAL

Materials.—All the complexes were prepared by published methods.[5-7] Their electronic spectra were in good agreement with those reported previously.[5,7] Solutions of sodium perchlorate and sodium bromide were prepared by dissolving the required amount of anhydrous salt in distilled water. Anhydrous sodium perchlorate was obtained by dehydrating the corresponding monohydrate (B.D.H.) at *ca.* 200 °C. Solutions of sodium hydroxide were prepared by dissolving AnalaR sodium hydroxide in distilled water, and diluted portions of this solution were standardised against 0.1N hydrochloric acid (prepared from B.D.H. concentrated volumetric solution). The buffer solutions were prepared using analytical grade reagents as follows: pH 9.08, 0.1 mol dm^{-3} H_3BO_3 + 0.1 mol dm^{-3} $Na_2[B_4O_7]$; pH 12.17, 0.1 mol dm^{-3} $Na_2[HPO_4]$ + 0.1 mol dm^{-3} Na[OH]. The pH of these media at 20 °C were measured using a model 23A direct-reading pH meter (Electronic Instruments Ltd.), calibrated with fresh standard buffer solutions prepared from buffer tablets (Burroughs Wellcome Ltd.). No correction was applied for the change in pH of a buffer with increase in temperature.

Kinetic Studies.—The reactions were studied by observing absorbance changes in the electronic spectrum either by scanning the whole spectrum at known time intervals or by following the reaction at a constant wavelength. Electronic spectra were recorded on a Unicam SP 800 spectrophotometer fitted with a constant-wavelength attachment and a thermostatted cell block capable of holding cells of up to 10 mm path length. It was possible to control the temperature of the cell block to better than ±0.25 °C. The reaction mixtures were maintained in the thermostatted cells throughout the reaction. The wavelengths at which the base-hydrolysis reactions were monitored in the constant-wavelength experiments were as follows:

Complex	λ/nm
trans-$[Rh(en)_2Cl_2]^+$	253 [a]
trans-$[Rh(men)_2Cl_2]^+$	345 [b]
trans-$[Rh(udmen)_2Cl_2]^+$	360,[b] 260 [a]
trans-$[Rh(sdmen)_2Cl_2]^+$	350 [b]
trans-$[Rh(trimen)_2Cl_2]^+$	285 [a]
trans-$[Rh(tetmen)_2Cl_2]^+$	300 [a]

[a] Absorbance decreasing with time. [b] Absorbance increasing with time.

Substitution of bromide for chloride in *trans*-$[Rh(udmen)_2Cl_2]^+$ was monitored by observing the increase in absorbance at 295 nm.

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† Abbreviations used throughout this paper are: en = ethylenediamine; men = *N*-methylethylenediamine; sdmen = *NN'*-dimethylethylenediamine; udmen = *NN*-dimethylethylenediamine; trimen = *NNN'*-trimethylethylenediamine; tetmen = *NNN'N'*-tetramethylethylenediamine; een = *N*-ethylethylenediamine; rbd = *rac*-butane-2,3-diamine; mbd = *meso*-butane-2,3-diamine.

The ionic strength of all reaction mixtures prepared using sodium hydroxide solutions was adjusted to 1.0 mol dm^{-3} by addition of Na[ClO$_4$]. Pseudo-first-order rate constants were obtained in the usual manner by plotting $\log_{10}(A_t - A_\infty)$ or $\log_{10}(A_\infty - A_t)$ against time. In nearly all cases the plots were linear for more than three half-lives, but a few reactions in the buffered solutions were followed for less than one half-life, due to the slowness of the reaction (*cf.* Table 1). Final absorbance values (A_∞) were measured after allowing the reaction to proceed for $\geqslant 10\ t_{\frac{1}{2}}$. For the very slow reactions A_∞ was obtained after heating the stoppered cell, containing the partially reacted solution, on a steam-bath until the absorbance no longer changed with time; the final absorbance was then measured at the temperature of the kinetic run. Final spectra were likewise recorded at the temperatures of the kinetic runs.

For all the reactions where solutions of Na[OH] were used, the observed rate constants quoted are the average of at least three separate determinations. Values of k_1 and k_2 in the expression $k_{\text{obs.}} = k_1 + k_2[\text{OH}^-]$, and their uncertainties (standard deviations), were obtained by a linear least-squares analysis of the data at that particular temperature. Activation parameters together with their uncertainties were estimated, using these values of k_1 and k_2, by one linear least-squares analysis of the dependence of $\ln(k_1/T)$ and $\ln(k_2/T)$ on $1/T$, the uncertainties in the logarithmic quantities being derived from the uncertainties in k_1 and k_2. The usual assumption was made that no error existed in the temperature.

RESULTS

Base Hydrolysis of trans-[Rh(L–L')$_2$Cl$_2$]$^+$ (L–L' = *men, sdmen, udmen, trimen, or tetmen*) *in Buffer Solutions.*—The pseudo-first-order rate constants for the reactions of these complexes in buffer solutions of pH 9.08 and 12.17 at 80 °C are given in Table 1. Comparison of the electronic spectra of the products of these reactions with the spectrum of *trans*-[Rh(en)$_2$(OH)$_2$]$^+$ (see below)[2,7c] indicates that the overall hydrolysis reaction is (1). The positions of the maxima for the dihydroxo-complexes shift generally to longer wavelength with increasing *N*-methylation of the ligand, as found for the dichloro-complexes.

TABLE 1

Rate constants and final spectra for the base hydrolysis of *trans*-[Rh(L–L')$_2$Cl$_2$]$^+$ in buffered solution at 80 °C

			Final spectrum	
L–L'	pH	$10^5\ k_{\text{obs.}}$/ s^{-1}	$\lambda_{\text{max.}}$/nm	$\varepsilon_{\text{max.}}$/ dm^3 mol^{-1} cm^{-1}
en [a]	8.9	4.2		
	9.9	4.4		
	12.7	5.1		
men	9.08	0.69 [b]	338	149
	12.17	13.8	291	152
sdmen	9.08	0.3 [b]	345 (sh)	142
	12.17	28	304	157
udmen	9.08	1.8	355 (sh)	126
	12.17	25	325	135
trimen	9.08	7.9	380 (sh)	112
	12.17	105	329	203
tetmen	9.08	62	358	156
	12.17	63	335 (sh)	150

[a] Ref. 1*c*; final spectra not reported. [b] Reaction followed for less than one half-life.

$$trans\text{-}[\text{Rh(L–L}')_2\text{Cl}_2]^+ + 2[\text{OH}]^- \xrightarrow{\text{H}_2\text{O}} trans\text{-}[\text{Rh(L–L}')_2(\text{OH})_2]^+ + 2\text{Cl}^- \quad (1)$$

Base Hydrolysis of trans-[Rh(L–L')$_2$Cl$_2$]$^+$ (L–L' = *en, udmen, or tetmen*) *in Solutions of Sodium Hydroxide.*—During the course of the reaction of *trans*-[Rh(en)$_2$Cl$_2$]$^+$ with 1.0 mol dm^{-3} hydroxide the absorption maximum at 406 nm, characteristic of the dichloro-complex, decreased in intensity while two new maxima at 335 ($\varepsilon_{\text{max.}}$ 157) and 290 nm ($\varepsilon_{\text{max.}}$ 170 dm^3 mol^{-1} cm^{-1}) appeared. These changes were accompanied throughout by a set of isosbestic points at 387 and 280 nm. However, the spectroscopic changes accompanying the reaction were found to vary with the hydroxide concentration; thus with 0.2 mol dm^{-3} hydroxide the absorption maxima of the product were at 342 ($\varepsilon_{\text{max.}}$ 113) and 294 nm ($\varepsilon_{\text{max.}}$ 142 dm^3 mol^{-1} cm^{-1}), while the accompanying isosbestic points were at 388 and 290 nm.

These spectroscopic changes were similar to those observed by Poë and Vuik[2c] who were able to show that although reaction (2) occurred it was accompanied by some

$$trans\text{-}[\text{Rh(en)}_2\text{Cl}_2]^+ + 2[\text{OH}]^- \xrightarrow{\text{H}_2\text{O}} trans\text{-}[\text{Rh(en)}_2(\text{OH})_2]^+ + 2\text{Cl}^- \quad (2)$$

trans ⟶ *cis* isomerisation. The extent of this isomerisation was dependent on the concentration of hydroxide ion used so that the variation of the spectroscopic changes with hydroxide concentration for reaction (2) could be ascribed to varying degrees of *trans* ⟶ *cis* isomerisation.

TABLE 2

Kinetic data for the reaction of *trans*-[Rh(en)$_2$Cl$_2$]$^+$ with hydroxide. [Rh] = 1.6 × 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3} with sodium perchlorate

θ_c/°C	[OH$^-$]/mol dm^{-3}	$10^5 k_{\text{obs.}}$/s^{-1}	$10^5 k_1$*/s^{-1}	$10^5 k_2$*/dm^3 mol^{-1} s^{-1}
70.5	0.1	1.81	1.62 ± 0.03	1.87 ± 0.04
	0.25	2.07, 2.11		
	0.5	2.59, 2.49		
	0.6	2.74		
	0.75	3.09, 3.00		
	1.0	3.47, 3.50, 3.49		
80.5	0.1	5.92, 6.08	5.13 ± 0.1	7.98 ± 0.1
	0.2	6.72, 6.60		
	0.5	9.00, 9.13		
	0.75	11.10, 11.25		
	0.9	12.30, 12.30		
	1.0	13.11, 13.25, 12.95		
89	0.2	17.8, 18.2	13.70 ± 1.03	24.10 ± 1.14
	0.3	20.7		
	0.5	26.0, 28.6		
	0.75	31.1, 30.3, 31.7		
	0.9	35.4		
	1.0	37.9, 38.1, 37.8		

$\Delta H_1^{\ddagger} = 27.8 \pm 0.4$ kcal mol^{-1}, $\Delta S_1^{\ddagger} = 0.2 \pm 1.0$ cal K^{-1} mol^{-1}, $\Delta H_2^{\ddagger} = 33.5 \pm 0.6$ kcal mol^{-1}, $\Delta S_2^{\ddagger} = 17.0 \pm 1.2$ cal K^{-1} mol.

* Derived from $k_{\text{obs.}} = k_1 + k_2[\text{OH}^-]$.

Values of the observed rate constant at various temperatures and hydroxide-ion concentration are given in Table 2. These pseudo-first-order rate constants were found to vary with hydroxide-ion concentration according to $k_{\text{obs.}} = k_1 + k_2[\text{OH}^-]$.

The reactions of *trans*-[Rh(udmen)$_2$Cl$_2$]$^+$ and *trans*-[Rh(tetmen)$_2$Cl$_2$]$^+$ with hydroxide were characterised by changes in the electronic spectra consistent with the formation of the *trans*-dihydroxo-complexes {final spectra: $\lambda_{max.}$ 355(sh) and 325, $\varepsilon_{max.}$ 114 and 125 for *trans*-[Rh(udmen)$_2$(OH)$_2$]$^+$; $\lambda_{max.}$ 358 and 335 (sh) nm, $\varepsilon_{max.}$ 157 and 148 dm^3 mol^{-1} cm^{-1} for *trans*-[Rh(tetmen)$_2$(OH)$_2$]$^+$}. Both reactions were accompanied by sets of clear isosbestic points {for *trans*-[Rh(udmen)$_2$Cl$_2$]$^+$ and [OH]$^-$ at 404 and 332, and for *trans*-[Rh(tetmen)$_2$Cl$_2$]$^+$ and [OH]$^-$ at 448, 394, 372, and 337 nm}. These spectroscopic changes did not vary with the hydroxide concentration between 0.1 and 1.0 mol dm^{-3}. The rate of reaction of *trans*-[Rh(tetmen)$_2$Cl$_2$]$^+$ with hydroxide was independent of the hydroxide-ion concentration up to [OH$^-$] = 1.0 mol dm^{-3} (Table 3). However, the reaction of *trans*-[Rh(udmen)$_2$Cl$_2$]$^+$ with hydroxide was found to follow a rate law similar to that for *trans*-[Rh(en)$_2$Cl$_2$]$^+$ (Table 4), although the value of k_1 in this case was very small compared with k_2 so that accurate values of k_1 could not be obtained from the intercepts of plots of $k_{obs.}$ against [OH$^-$]. Values of k_1 were obtained in this case by studying the reaction of the complex with bromide at an ionic strength of 1.0 mol dm^{-3}. Changes in the electronic spectra accompanying this reaction are consistent with the formation of the *trans*-dibromo-species ($\lambda_{max.}$ 465 nm, $\varepsilon_{max.}$ 134 dm^3 mol^{-1} cm^{-1}) and are attended by isosbestic points at 438 and 392 nm. The observed rate constants (Table 5) were independent of the bromide concentration up to 1.0 mol dm^{-3}.

TABLE 3

Kinetic data for the reaction of *trans*-[Rh(tetmen)$_2$Cl$_2$]$^+$ with hydroxide. [Rh] = 1.6 × 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3} with sodium perchlorate

$\frac{\theta_c}{°C}$	$\frac{[OH^-]}{mol\ dm^{-3}}$	$\frac{10^5 k_{obs.}}{s^{-1}}$
59	1.0	6.62, 6.58
69	1.0	21.2, 20.2
80	0.01	78.8, 77.8
	0.1	70.4, 72.5
	0.5	70.9, 74.0
	1.0	69.0, 70.3

$\Delta H^‡$ = 25.5 ± 0.2 kcal mol^{-1}, $\Delta S^‡$ = −1.2 ± 0.2 cal K^{-1} mol^{-1}.

TABLE 4

Kinetic data for the reaction of *trans*-[Rh(udmen)$_2$Cl$_2$]$^+$ with hydroxide. [Rh] = 8 × 10^{-4} mol dm^{-3}, I = 1.0 mol dm^{-3} with sodium perchlorate

$\frac{\theta_c}{°C}$	$\frac{[OH^-]}{mol\ dm^{-3}}$	$\frac{10^4 k_{obs.}}{s^{-1}}$	$\frac{10^4 k_2\ *}{dm^3\ mol^{-1}\ s^{-1}}$
70	0.2	1.06	6.33 ± 0.09
	0.3	1.96	
	0.4	2.50	
	0.6	3.76	
	0.7	4.29	
	1.0	6.62	
80	0.2	4.37	22.1 ± 0.2
	0.4	9.22	
	0.5	11.3	
	0.8	17.5	
	1.0	22.4	
88.5	0.05	3.45	61.1 ± 0.6
	0.1	7.27	
	0.3	18.35	
	0.5	30.4	
	0.7	43.9	

$\Delta H_2^‡$ = 29.5 ± 0.1 kcal mol^{-1}, $\Delta S_2^‡$ = 12.6 ± 0.2 cal K^{-1} mol^{-1}

* Derived from $k_{obs.} = k_1 + k_2[OH^-]$; k_1 was too small to be determined by extrapolation and was therefore obtained from data for halide interchange (*cf.* Table 5).

TABLE 5

Kinetic data for the reaction of *trans*-[Rh(udmen)$_2$Cl$_2$]$^+$ with bromide. [Rh] = 5 × 10^{-4} mol dm^{-3}, I = 1.0 mol dm^{-3} with sodium perchlorate

$\frac{\theta_c}{°C}$	$\frac{[Br^-]}{mol\ dm^{-3}}$	$\frac{10^6 k_{obs.}}{s^{-1}}$
71	1.0	8.34, 8.60, 8.94
82	0.5	33.2
	1.0	31.7, 29.9
90	1.0	77.2

$\Delta H^‡$ = 28.0 ± 0.5 kcal mol^{-1}, $\Delta S^‡$ = −0.7 ± 1.2 cal K^{-1} mol^{-1}

DISCUSSION

All the complexes employed in the present work, with the exception of that with L–L′ = tetmen, undergo base hydrolysis at a rate which is dependent on the hydroxide-ion concentration. In two cases the two-term rate law $-d[complex]/dt = (k_1 + k_2[OH^-])$ [complex] has been established and it seems very probable that the same rate law will apply for all the other complexes. A rate law of this form has been found previously for the base hydrolysis of a few other complexes of rhodium(III),[1a,b,2] and is also often found for base hydrolysis of cobalt(III) amine complexes.[3] A summary of the activation parameters for the base-hydrolysis reactions of *trans*-[Rh(L–L′)$_2$Cl$_2$]$^+$, together with those for some other rhodium(III) complexes for which this two-term rate law has been observed, is given in Table 6. Also included in the Table are the parameters for the acid and base hydrolysis of three analogous cobalt(III) complexes.

The k_1 term in the above two-term rate law, which represents the major contribution to the hydrolysis rate at low hydroxide-ion concentrations, can be explained as corresponding to the path for aquation [reaction (3)],

$$trans\text{-}[Rh(L\text{–}L')_2Cl_2]^+ + H_2O \longrightarrow trans\text{-}[Rh(L\text{–}L')_2Cl(H_2O)]^{2+} + Cl^- \quad (3)$$

which also appears to be operative in the halide interchanges of complexes of this type.[1c,5,8] In the latter case this step is normally followed by rapid anation of the aqua-complex by the incoming halide; a similar sequence of events then occurs for replacement of the second chloride but at a greater rate so that replacement of the first chloride is rate determining. In the k_1 path for the reactions considered here the hydroxide ion simply serves to drive the equilibrium over to the corresponding hydroxo-complex so that replacement of the first chloride is still rate determining. Thus, in the case of the reaction of *trans*-[Rh(udmen)$_2$Cl$_2$]$^+$ with hydroxide, where k_1 in the two-term rate law could not be determined directly because of its very small value relative to k_2, we have calculated the activation parameters for the k_1 path from kinetic data for the replacement of chloride by bromide in this complex (Table 6).

The hydroxide-ion-concentration-dependent k_2 path for base hydrolysis probably corresponds to attack by

TABLE 6

Kinetic data for the base hydrolysis of some rhodium(III) and cobalt(III) complexes *

Complex	10^5k_1 / s^{-1}	$\Delta H_1^‡$ / kcal mol^{-1}	$\Delta S_1^‡$ / cal mol^{-1} K^{-1}	k_2 / dm^3 mol^{-1} s^{-1}	$\Delta H_2^‡$ / kcal mol^{-1}	$\Delta S_2^‡$ / cal mol K^{-1}	Ref
trans-$[Rh(en)_2Cl_2]^+$	4.88 [a,b]	27.8 ± 0.4	0.2 ± 1.0	7.26×10^{-5} [a]	33.5 ± 0.6	17.0 ± 1.2	This work
trans-$[Rh(udmen)_2Cl_2]^+$	2.51 [a,c]	28.0 ± 0.5	−0.7 ± 1.2	221×10^{-5} [a]	29.5 ± 0.1	12.6 ± 0.2	This work
trans-$[Rh(tetmen)_2Cl_2]^+$	70.0 [a,d]	25.5 ± 0.2	−1.2 ± 0.2				This work
trans-$[Rh(en)_2Br_2]^+$	1.79 [e]	25.8 ± 0.3	−3.2 ± 1.0	1.68×10^{-5} [e]	33.5 ± 0.6	20.3 ± 1.8	2*c*
trans-$[Rh(en)_2I_2]^+$	38.4 [f]	24.4 ± 0.1	−1.3 ± 0.4	18.1×10^{-5} [f]	31.2 ± 0.7	17.7 ± 2.2	2*c*
trans-$[Rh(en)_2Cl(OH)]^+$	91.4 [g]	25.14 ± 0.15	−0.67 ± 0.46	33.7×10^{-5} [g]	25.84 ± 0.70	−0.49 ± 2.10	2*a*,*b*
trans-$[Rh(en)_2Br(OH)]^+$	141.9 [h]	25.99 ± 0.19	1.91 ± 0.57	36.5×10^{-5} [h]	25.08 ± 1.30	−3.11 ± 3.88	2*a*,*b*
trans-$[Rh(en)_2I(OH)]^+$	62.2 [i]	27.81 ± 0.18	5.01 ± 0.52	27.8×10^{-5} [i]	29.34 ± 0.85	7.93 ± 2.48	2*a*,*b*
$[Rh(NH_3)_5Cl]^{2+}$	0.015 [j]	22.2	−15.3	10.9×10^{-5} [j]	27.5	15.6	1*a*,14
$[Rh(NH_3)_5Br]^{2+}$	0.0063 [j]	24.4	−9.6	9.6×10^{-5} [j]	29.5	22.1	1*a*,14
$[Rh(NH_3)_5I]^{2+}$	0.00195 [j]	26.7	−4.2	2.3×10^{-5} [j]	31.8	27.0	1*a*,14
trans-$[Co(en)_2Cl_2]^+$	3.1 [j]	27.5	13.1	3.2×10^{3} [j]	22.6	33.3	11, 12, 14
trans-$[Co(men)_2Cl_2]^+$	1.6 [j]	26.5	8.4	1.2×10^{4} [j]	23.3	38.3	12—14
trans-$[Co(een)_2Cl_2]^+$	9.6 [j]	27.5	15.4	1.6×10^{4} [j]	22.6	36.5	12—14

* Rate parameters in the Table are derived from the equation $k_{obs.} = k_1 + k_2[OH^-]$.

[a] 80 °C. [b] *cf.* Aquation results at $I = 0.2$ mol dm^{-3}, $k(80\ °C) = 4.4 \times 10^{-5}\ s^{-1}$, $\Delta H^‡ = 24.8 \pm 0.6$ kcal mol^{-1}, $\Delta S^‡ = -8.7 \pm 1.6$ cal K^{-1} mol^{-1}; [8b] *cf.* ref. 2*c*, $\Delta H_1^‡ = 26.6 \pm 0.6$ kcal mol^{-1}, $\Delta S_1^‡ = -5.1 \pm 1.8$ cal K^{-1} mol^{-1}, $\Delta H_2^‡ = 35.1 \pm 1.4$ kcal mol^{-1}, $\Delta S_2^‡ = 21.0 \pm 4.1$ cal K^{-1} mol^{-1}. [c] Derived from bromide-interchange results (Table 5), *cf.* at $I = 0.2$ mol dm^{-3}, k (80 °C) $= 2.50 \times 10^{-5}\ s^{-1}$.[5] [d] *cf.* Bromide-interchange results, at $I = 0.2$ mol dm^{-3}, k (80 °C) $= 56 \times 10^{-5}\ s^{-1}$, $\Delta H^‡ = 25.4 \pm 0.7$ kcal mol^{-1}, $\Delta S^‡ = -1.92 \pm 2.1$ cal K^{-1} mol^{-1}.[5] [e] 60.4 °C. [f] 59.6 °C. [g] 75.75 °C. [h] 78.94 °C. [i] 81 °C. [j] 25 °C.

$[OH]^-$ *via* a $S_N1(CB)$ mechanism.[3a] Thus the sequence of events can be represented by the following scheme, taking the bis(ethylenediamine) complex as representative. A similar sequence of events will follow for the

$$\textit{trans}\text{-}[Rh(en)_2Cl_2]^+ + [OH]^- \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \textit{trans}\text{-}[Rh(en)(en-H)Cl_2] + H_2O \quad (4)$$

$$\textit{trans}\text{-}[Rh(en)(en-H)Cl_2] \xrightarrow{\text{slow}} [Rh(en)(en-H)Cl]^+ + Cl^- \quad (5)$$

$$[Rh(en)(en-H)Cl]^+ + H_2O \xrightarrow{\text{fast}} [Rh(en)_2Cl(OH)]^+ \ (\textit{cis}?\ ^{2b,c}) \quad (6)$$

replacement of the second chloride but at a greater rate, thus making replacement of the first chloride rate determining. Reaction (4) is usually written as an equilibrium with constant K and if reaction (5) has a rate constant k then the full rate law for this path becomes

$$\text{Rate} = \frac{kK[\text{complex}][OH^-]}{1 + K[OH^-]} \quad (7)$$

(7) which reduces to the observed rate law (8) if $K[OH^-] \ll 1$. The presence of intermediates of the

$$\text{Rate} = kK[\text{complex}][OH^-] \quad (8)$$

type postulated in this mechanism during the base hydrolysis of a variety of cobalt(III) complexes has been demonstrated by competition experiments,[9] and Panunzi and Basolo[1d] have reported a study of the competition of $[N_3]^-$ or $[NO_2]^-$ for the intermediates formed in the base hydrolysis of *cis*-$[Rh(en)_2(NO_2)X]^+$ and *trans*-$[Rh(en)_2(NMeH_2)X]^{2+}$ (X = Cl, Br, or I), the results of which were consistent with a $S_N1(CB)$ mechanism of the type described above.

Evidence for the operation of a $S_N1(CB)$ mechanism is provided by the observation that the complex *trans*-$[Rh(tetmen)_2Cl_2]^+$ shows no hydroxide-ion concentration-dependent term in its base-hydrolysis kinetics up to a hydroxide-ion concentration of 1.0 mol dm^{-3}. This complex possesses no *N*-bonded ionisable protons and hence this reaction path is not available.

trans ⟶ *cis* Isomerisations in reactions of rhodium(III) species are in general uncommon.[1c,d,10] However, Poë and Vuik[2c] in their study of the base hydrolysis of *trans*-$[Rh(en)_2Cl_2]^+$ showed that some isomerisation to *cis*-$[Rh(en)_2(OH)_2]^+$ had occurred. They also pointed out that the isomerisation occurred in the first stage of the reaction, *i.e.* the replacement of the first chloride by hydroxide. An estimate of the extent of isomerisation was made by converting the products of the reaction, the dihydroxo-complexes, into the dichloro-complexes by treatment with an excess of HCl and then measuring the absorption spectra of the mixtures. Knowing the absorption spectra of pure *trans*- and *cis*-$[Rh(en)_2Cl_2]^+$, they were able to calculate that *ca.* 100% isomerisation occurs with the $[OH^-]$-dependent path. It is interesting to note that replacement of the first chloride in *trans*-$[Co(en)_2Cl_2]^+$ by hydroxide proceeds with >95% retention of configuration, whereas the further reaction of *trans*-$[Co(en)_2Cl(OH)]^+$ with $[OH]^-$ gives almost exclusively *cis*-$[Co(en)_2(OH)_2]^+$.[11]

Our spectroscopic observations on the base hydrolysis of *trans*-$[Rh(en)_2Cl_2]^+$ are in agreement with those of Poë and Vuik. The spectroscopic changes accompanying the reactions of *trans*-$[Rh(udmen)_2Cl_2]^+$ and *trans*-$[Rh(tetmen)_2Cl_2]^+$ with hydroxide were independent of the hydroxide concentration which would indicate that no *trans* ⟶ *cis* isomerisation was occurring. For the complex *trans*-$[Rh(tetmen)_2Cl_2]^+$ this is perhaps not surprising since there is no $[OH^-]$-dependent term in the rate law and also the bulky tetmen complex may be prevented on steric grounds from forming the *cis* isomer; no such steric constraints can apply to the complex with udmen since both isomers have been characterised.[5] However, if any isomerisation is occurring it will not affect the results reported here for replacement of the first chloride by hydroxide.

The activation parameters for the base hydrolysis of *trans*-$[Rh(L-L')_2Cl_2]^+$ (L–L = en or udmen) reveal that in both cases $\Delta H_2^{\ddagger} > \Delta H_1^{\ddagger}$ and $\Delta S_2^{\ddagger}$ is more positive than $\Delta S_1^{\ddagger}$. The unimportance of the k_2 term for the complex with L–L′ = en relative to that for the complex with L–L′ = udmen can be seen to be due to the larger value of $\Delta H_2^{\ddagger}$ in the former case which is only partly offset by the slightly more positive value of $\Delta S_2^{\ddagger}$. The lower value of $\Delta H_2^{\ddagger}$ for the *NN*-dimethylethylenediamine complex than that for the ethylenediamine species is probably a reflection of the general trend, observed for the base hydrolysis of cobalt(III) amine complexes, that increasing *N*-alkyl substitution leads to an increase in the value of *K* for equilibria of type (4) (above) and hence to an increased rate for $[OH^-]$-dependent base hydrolysis.[4] The enhanced steric repulsion resulting from an increase in the degree of *N*-alkylation would further reinforce such an effect.

A consideration of the kinetic parameters for base hydrolysis of other complexes of rhodium(III) (Table 6) reveals that in the majority of cases $\Delta H_2^{\ddagger} > \Delta H_1^{\ddagger}$ and $\Delta S_2^{\ddagger}$ is more positive than $\Delta S_1^{\ddagger}$. Two apparent exceptions to this generalisation are the complexes *trans*-$[Rh(en)_2(OH)X]^+$ (X = Cl or Br) where $\Delta H_2^{\ddagger} \simeq \Delta H_1^{\ddagger}$, and the values for the entropy of activation are quite similar. Data for these complexes without a co-ordinated N–H group *trans* to the leaving halide do however lie on an isokinetic plot [2c] implying a similarity of mechanism, *i.e.* $S_N1(CB)$, although it was argued that, for those complexes where $\Delta H_2^{\ddagger} \simeq \Delta H_1^{\ddagger}$, $S_N1(IP)$ is a better description of the mechanism. Our data for the base hydrolysis of *trans*-$[Rh(L\text{–}L')_2Cl_2]^+$ (L–L′ = en or udmen) also lie on this isokinetic plot, lending further support to the $S_N1(CB)$ mechanism for these complexes. Furthermore, our data for the complex with L–L′ = en lie on a pseudo-isokinetic plot,[2c] although the data for L–L′ = udmen deviate significantly; the implication of this is, at present, not clear.

Data [11-13] for the base hydrolysis of some *N*-alkyl-substituted ethylenediamine complexes of cobalt(III) (Table 6) are interesting since they show that $\Delta H_1^{\ddagger} > \Delta H_2^{\ddagger}$ and that $\Delta S_2^{\ddagger}$ is more positive than $\Delta S_1^{\ddagger}$, so that $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ contribute in the same direction to the relative importance of the $[OH^-]$-dependent path for these complexes. The relative magnitudes of $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$ for the cobalt(III) complexes have been explained,[1c,4] on the basis of stabilisation of the five-co-ordinate conjugate-base intermediate by π bonding from the amide group to the metal, thus effectively lowering the activation energy for the k_2 path. The ability of rhodium(III) to form a π bond with the amide group is believed to be much less than that of cobalt(III) so that little, if any, stabilisation of the intermediate occurs and hence there is no appreciable lowering of the activation energy for this path.

Edwards *et al.*[14] have suggested that the value of $\Delta S_2^{\ddagger}$ for base hydrolysis gives a definite clue as to the mechanism. They argued that if a direct displacement mechanism were operative this would lead to values of $\Delta S_2^{\ddagger}$ of *ca.* −15 cal K^{-1} mol^{-1}.* However, for the $S_N1(CB)$ mechanism they suggested that $\Delta S_2^{\ddagger}$ was the sum of the entropy change for the equilibrium step [*e.g.* reaction (4) above] and that for the slow second step [*e.g.* reaction (5) above], and that the equilibrium was analogous to a neutralisation reaction (*i.e.* $[X_5\text{–}Rh\text{–}H_2O]^{n+} + [OH]^- \rightleftharpoons [X_5\text{–}Rh\text{–}OH]^{(n-1)+} + H_2O$), typical ΔS values for such a process being 18 and 10 cal K^{-1} mol^{-1} for $[Rh(OH_2)_6]^{3+}$ and $[Rh(NH_3)_5(OH_2)]^{3+}$ respectively. The slow step (5) involves charge separation as well as the formation of two particles from one and hence it should have a value for $\Delta S^{\ddagger}$ near to zero as found, for example, for the aquation of $[Co(NH_3)_5Y]^{2+}$ where Y is a large leaving group. Hence $\Delta S_2^{\ddagger}$ should be given approximately by ΔS for the equilibrium step (4). Using an average value for the entropy of neutralisation derived from values for a range of different types of complexes of various trivalent metal ions, they deduced that $\Delta S_2^{\ddagger}$ was *ca.* 34 cal K^{-1} mol^{-1}, which is indeed a good average value for $\Delta S_2^{\ddagger}$ in base hydrolysis of cobalt(III) amine complexes. However, the values of ΔS for the neutralisation of the two rhodium(III) complexes taken above as examples are significantly less than those for any of the other complexes considered, so that $\Delta S_2^{\ddagger}$ for base hydrolysis of rhodium(III) complexes is more likely to be between 10 and 18 cal K^{-1} mol^{-1}. The majority of the $\Delta S_2^{\ddagger}$ values in Table 6 either fall within this range or are closer to these values than to the value of *ca.* −15 cal K^{-1} mol^{-1} predicted for direct displacement. This observation can therefore be taken as adding further weight to the evidence in favour of the $S_N1(CB)$ mechanism. The two apparent exceptions are provided by the complexes *trans*-$[Rh(en)_2(OH)X]^+$ (X = Cl or Br)[2b] which show values for $\Delta S_2^{\ddagger}$ of −0.49 and −3.11 cal K^{-1} mol^{-1}, respectively. It seems unlikely that these complexes react by a significantly different mechanism and it has been suggested [2c] that they react by a $S_N1(IP)$ mechanism in which case the entropy of activation would be less positive.

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* Throughout this paper: 1 cal = 4.184 J.

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