The Kinetics of Base Hydrolysis of *trans*-Dichlorotetrakis(alkylamine)-rhodium(III) Ions †

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The observed pseudo-first-order rate constants for the base hydrolysis of the series of complexes *trans*-$[Rh(NH_2R)_4Cl_2]^+$ (R = H, Me, Et, or Pr^n) have been found to depend on hydroxide ion according to $k_{obs.} = k_1 + k_2[OH^-]$. The k_1 term is believed to be the aquation pathway which is operative in the bromide interchanges of these complexes, whereas the k_2 term corresponds to the S_N1(c.b.) (conjugate base) mechanism. Values of the activation parameters for the base hydrolysis have also been determined and are discussed in relation to the results for similar rhodium(III), cobalt(III), and chromium(III) complexes. It is concluded that in complexes of this type rhodium(III) is less able to participate in π bonding than are cobalt(III) and chromium(III).

Earlier work [1] on the kinetics of base hydrolysis of the series of complexes of the type chloropentakis(alkylamine)rhodium(III) showed that the complexes underwent base hydrolysis by the S_N1(c.b.) (conjugate base) mechanism [2] and that the relative rates along the series of complexes were controlled by steric factors so that there was a gradual increase in rate as the amine was changed from ammonia to n-propylamine. The increase in rate was due to a decrease in the activation enthalpy along the series and was consistent with the dissociative character of the mechanism. We have now studied the base hydrolysis of the series of complexes *trans*-dichlorotetrakis(alkylamine)-rhodium(III) to see whether they undergo base hydrolysis by the S_N1(c.b.) mechanism and to determine what factors affect the relative rates of reaction along the series. Previous work [3–5] on the base hydrolysis of amine complexes of rhodium(III), where the leaving group was not *trans* to an amine nitrogen bearing an ionisable hydrogen, showed that these complexes were far less susceptible to base hydrolysis than those where the leaving group was *trans* to a nitrogen bearing an ionisable hydrogen. This was thought to be due to the inability of rhodium(III) to form an effective π bond with the co-ordinated amido-group in the five-co-ordinate intermediate. If the present series of complexes undergo base hydrolysis *via* the S_N1(c.b.) mechanism then a comparison of the rate parameters for the base hydrolysis of this series of complexes with those for the base hydrolysis of chloropentakis(alkylamine)rhodium(III) will afford a means of quantitatively assessing the effect on the leaving chloride of being *trans* to a chloride in one case and *trans* to a primary amine in the other. In both cases the leaving chloride is surrounded by the same four *cis* ligands.

Experimental

Materials.—The complex ions *trans*-$[Rh(NH_2R)_4Cl_2]^+$ (R = H, Me, Et, or Pr^n) were prepared as their chloride salts by the literature methods [6,7] and their purity was confirmed by the excellent agreement between their measured electronic spectra and literature data. All the solutions of reagents used were prepared from the anhydrous solids.[1]

Kinetic Studies.—The kinetics of the reactions were studied using the instrumentation mentioned previously [1] by measuring absorbance changes in the electronic spectra of the reaction mixtures in the region 255—260 nm where the absorbance of the reaction mixtures decreased as the reaction proceeded. However, during the course of the reactions of the complexes with R = Me, Et, and Pr^n at high temperatures and hydroxide ion concentrations the solutions tended to darken and in some cases a precipitate formed in the cell. For these reactions the value of the absorbance at infinite time, A_∞, was obtained by an extrapolation of the absorbance *vs.* time data. Pseudo-first-order rate constants were obtained either by plotting $\ln(A_t - A_\infty)$ *vs.* time or by using the Guggenheim method.[8] In all the reactions the plots were linear for several half-lives. The statistical treatment of the results was similar to that described previously.[1,4]

For the complexes with R = H, Me, and Et, the ionic strength of the reaction mixture was maintained at 1.0 mol dm^{-3} with sodium perchlorate. However, the complex with R = Pr^n was not sufficiently soluble in perchlorate medium so that the ionic strength of the reaction mixture containing this complex was maintained with sodium chloride at 1.0 mol dm^{-3}. Comparisons of the spectra at infinite time of the reaction mixtures which contained chloride with those containing no chloride showed them to be identical, thus indicating that the base hydrolysis had gone to completion in all cases and that the possible back reaction involving replacement of the hydroxo-ligands by chloride could be ignored.

Results

The spectroscopic changes during the base hydrolysis of all four complexes were accompanied by sets of isosbestic points whose positions for a given reaction were independent of the hydroxide ion concentration. The products of the reaction were identified as the corresponding *trans*-dihydroxo-complexes by the close similarity of their electronic spectra with those reported [9] for *trans*-$[Rh(NH_3)_4(OH)_2]^+$ and *trans*-$[Rh(NH_2R)_4(OH)_2]^+$ (R = Me and Et).[10] A summary of the spectroscopic changes is given in Table 1.

Values of the observed rate constants for base hydrolysis at various temperatures and hydroxide ion concentrations for the four complexes are given in Tables 2—5. The pseudo-first-order rate constants were found to depend on hydroxide ion concentrations according to $k_{obs.} = k_1 + k_2[OH^-]$.

Discussion

All of the complexes studied here undergo base hydrolysis according to the two-term rate law $-d[\text{complex}]/dt = (k_1 + k_2[OH^-])[\text{complex}]$. A summary of the rate parameters for the base hydrolysis of all four compounds is given in Table 6; also included in the Table are the rate parameters for the halide interchanges of these complexes.[6,7] The two-term rate law observed for these complexes has also been observed

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† *Non-S.I. unit employed:* 1 cal = 4.184 J.

Table 1. Spectroscopic changes accompanying the base hydrolysis of the complex ions *trans*-$[Rh(NH_2R)_4Cl_2]^+$ (R = H, Me, Et, or Pr^n)

Complex	Final spectrum $\lambda_{max.}$/nm		$\varepsilon_{max.}$/$dm^3\ mol^{-1}\ cm^{-1}$		Isosbestic points λ/nm	
trans-$[Rh(NH_3)_4Cl_2]^+$	[a] 350	303	135	150	398	369
	[b] 347	303	96	120	—	—
trans-$[Rh(NH_2Me)_4Cl_2]^+$	[a] 350	300	116	133	398, 315, 290, 272	
	[c] 352	302	102	133		
trans-$[Rh(NH_2Et)_4Cl_2]^+$	[a] 345	290	94	110	400	325
	[c] 355	302	120	158		
trans-$[Rh(NH_2Pr^n)_4Cl_2]^+$	[a] 350(sh)	280	143	150	399	327

[a] This work, θ_c = 80 °C. [b] Ref. 9, θ_c = 25 °C. [c] Ref. 10, θ_c = 80 °C.

Table 2. Kinetic data for the reaction of *trans*-$[Rh(NH_3)_4Cl_2]^+$ with hydroxide. [Rh] = 4×10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3} ($NaClO_4$)

θ_c/°C	$[OH^-]$/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}	10^5k_1*/s^{-1}	10^5k_2*/$dm^3\ mol^{-1}\ s^{-1}$
68	0.2	2.46, 2.22	2.13 ± 0.06	1.01 ± 0.10
	0.25	2.41		
	0.6	2.71, 2.66		
	1.0	3.17, 3.15		
77	0.2	6.06	5.36 ± 0.11	3.88 ± 0.17
	0.4	7.03		
	0.75	8.24		
	1.0	9.23		
85	0.2	14.2, 13.2	11.0 ± 0.6	14.0 ± 0.9
	0.6	20.3		
	0.8	21.6		
	1.0	25.5, 24.6		

$\Delta H_1^\ddagger = 22.8 \pm 0.5$ kcal mol^{-1} $\Delta S_1^\ddagger = -13.2 \pm 1.5$ cal $K^{-1}\ mol^{-1}$
$\Delta H_2^\ddagger = 36.8 \pm 1.2$ kcal mol^{-1} $\Delta S_2^\ddagger = 26.2 \pm 3.3$ cal $K^{-1}\ mol^{-1}$

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

Table 3. Kinetic data for the reaction of *trans*-$[Rh(NH_2Me)_4Cl_2]^+$ with hydroxide. [Rh] = 1.6×10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3} ($NaClO_4$)

θ_c/°C	$[OH^-]$/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}	10^5k_1*/s^{-1}	10^5k_2*/$dm^3\ mol^{-1}\ s^{-1}$
60	0.5	0.602	0.238 ± 0.010	0.722 ± 0.014
	0.6	0.667		
	0.7	0.739		
	0.8	0.821, 0.817		
	0.9	0.885		
72	0.25	2.40, 2.35	1.19 ± 0.07	4.94 ± 0.11
	0.3	2.64		
	0.5	3.84, 3.65		
	0.75	5.00, 4.81		
	1.0	6.12, 6.06		
80	0.25	7.50	3.55 ± 0.42	17.0 ± 0.7
	0.35	9.80		
	0.5	11.67, 12.62		
	0.6	13.73		
	0.7	15.2, 15.45		
	0.75	16.38		

$\Delta H_1^\ddagger = 30.8 \pm 0.7$ kcal mol^{-1} $\Delta S_1^\ddagger = 8.0 \pm 1.9$ cal $K^{-1}\ mol^{-1}$
$\Delta H_2^\ddagger = 36.2 \pm 0.2$ kcal mol^{-1} $\Delta S_2^\ddagger = 26.4 \pm 0.6$ cal $K^{-1}\ mol^{-1}$

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

previously for the base hydrolysis of similar chloro–amine rhodium(III) complexes containing chelating ligands like ethylenediamine (en).[4,5,11] The k_1 term can be identified with the pathway for aquation which is known to operate in the bromide interchanges of these complexes, reactions (1)—(3). In this reaction the chloride is replaced in a slow rate-determining step by water and this is then followed either by a faster replacement of this water by bromide if it is the bromide interchange, reaction (2), or a rapid proton exchange if it is the base hydrolysis, reaction (3). Replacement of the second chloride follows a similar pathway but at a faster rate thus making replacement of the first chloride rate-determining. A comparison of the rate parameters determined here for the

$$trans\text{-}[Rh(NH_2R)_4Cl_2]^+ + H_2O \xrightarrow{\text{slow}} trans\text{-}[Rh(NH_2R)_4Cl(H_2O)]^{2+} + Cl^- \quad (1)$$

$$trans\text{-}[Rh(NH_2R)_4Cl(H_2O)]^{2+} \xrightarrow{\text{Br,fast}} trans\text{-}[Rh(NH_2R)_4ClBr]^+ + H_2O \quad (2)$$

$$\xrightarrow{OH^-\text{,fast}} trans\text{-}[Rh(NH_2R)_4Cl(OH)]^+ + H_2O \quad (3)$$

Table 4. Kinetic data for the reaction of *trans*-$[Rh(NH_2Et)_4Cl_2]^+$ with hydroxide. [Rh] = 3 × 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3} ($NaClO_4$)

θ_c/°C	$[OH^-]$/mol dm^{-3}	$10^5k_{obs.}/s^{-1}$	10^5k_1*/s^{-1}	10^5k_2*/dm^3 mol^{-1} s^{-1}
70	0.2	2.51	0.91 ± 0.25	6.78 ± 0.35
	0.4	3.51		
	0.6	4.78		
	0.8	6.08		
	1.0	7.72, 7.97		
81	0.2	10.33	3.76 ± 1.26	32.91 ± 1.9
	0.4	16.86		
	0.6	23.92, 23.03		
	0.7	25.58		
	0.8	32.28		
	1.0	35.83		
87	0.2	23.0, 23.0	4.58 ± 2.20	83.7 ± 3.1
	0.4	40.0		
	0.6	49.3, 51.9, 53.8		
	0.8	69.0		
	0.9	80.1, 83.9		
	1.0	89.2, 89.8		

$\Delta H_1^‡$ = 23.7 ± 5.7 kcal mol^{-1} $\Delta S_1^‡$ = −12.7 ± 16.3 cal K^{-1} mol^{-1}
$\Delta H_2^‡$ = 35.4 ± 1.2 kcal mol^{-1} $\Delta S_2^‡$ = 25.2 ± 3.4 cal K^{-1} mol^{-1}

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

Table 5. Kinetic data for the reaction of *trans*-$[Rh(NH_2Pr^n)_4Cl_2]^+$ with sodium hydroxide. [Rh] = 1.5 × 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3} (NaCl)

θ_c/°C	$[OH^-]$/mol dm^{-3}	$10^5k_{obs.}/s^{-1}$	10^5k_1*/s^{-1}	10^5k_2*/dm^3 mol^{-1} s^{-1}
70	0.5	6.28, 7.33	2.77 ± 0.86	8.16 ± 1.2
	0.6	7.98, 7.32		
	0.75	8.44, 9.46		
	0.8	9.5		
	0.9	9.88		
80	0.25	18.8	9.14 ± 2.1	33.7 ± 3.1
	0.5	25.4, 25.6		
	0.75	35.0, 31.3		
	0.9	39.9, 41.5		
88	0.3	56.2	17.4 ± 3.8	131 ± 5
	0.5	84.4		
	0.6	91.5		
	0.7	113		
	0.8	123		
	0.9	137		
	1.0	146		

$\Delta H_1^‡$ = 24.6 ± 2.4 kcal mol^{-1} $\Delta S_1^‡$ = −7.9 ± 6.7 cal K^{-1} mol^{-1}
$\Delta H_2^‡$ = 37.1 ± 2.5 kcal mol^{-1} $\Delta S_2^‡$ = 30.4 ± 7.1 cal K^{-1} mol^{-1}

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

k_1 step with those obtained for the bromide interchange show them to be very similar thus confirming the assignment of the k_1 term to the aquation pathway. The trends in the values of the rate parameters for the aquation of these complexes were previously concluded to indicate that the kinetic behaviour was best accounted for by an associative interchange (I_a)[7,12] mechanism.

The hydroxide ion dependent term, k_2, is associated with the S_N1(c.b.) mechanism[2] which is outlined below; and this mechanism leads to the observed rate law (7) provided $K[OH^-] \ll 1$.

$$trans\text{-}[Rh(NH_2R)_4Cl_2]^+ + OH^- \xrightleftharpoons{K,\ fast} trans\text{-}[Rh(NH_2R)_3(NHR)Cl_2] + H_2O \quad (4)$$

$$trans\text{-}[Rh(NH_2R)_3(NHR)Cl_2] \xrightarrow{k,\ slow} [Rh(NH_2R)_3(NHR)Cl]^+ + Cl^- \quad (5)$$

$$[Rh(NH_2R)_3(NHR)Cl]^+ + H_2O \xrightarrow{fast} trans\text{-}[Rh(NH_2R)_4Cl(OH)]^+ \quad (6)$$

$$Rate = kK[trans\text{-}Rh(NH_2R)_4Cl_2{}^+][OH^-] \quad (7)$$

As for the aquation pathway, replacement of the second chloride by hydroxide is faster than that of the first so that the replacement of the first chloride is rate-determining. Further confirmation that the hydroxide ion dependent pathway corresponds to the S_N1(c.b.) mechanism is provided by the values of the activation enthalpies and entropies. These values are *ca.* 36 kcal mol^{-1} for $\Delta H_2^‡$ and *ca.* 27 cal K^{-1} mol^{-1} for $\Delta S_2^‡$. Entropies of activation of this magnitude are considered[4,13] typical for complexes of this type reacting *via* the the S_N1(c.b.) mechanism. Similarly, Poë and Vuik[14] have shown that the activation parameters for a whole range of reactions of rhodium(III) complexes lie on an isokinetic plot

Table 6. Kinetic data for the base hydrolysis of *trans*-$[Rh(NH_2R)_4Cl_2]^+$ (R = H, Me, Et, or Pr^n)

Complex	$10^9k_1{}^a/s^{-1}$	$\Delta H_1{}^‡$/kcal mol^{-1}	$\Delta S_1{}^‡$/cal K^{-1} mol^{-1}	$10^9k_2{}^a$/dm^3 mol^{-1} s^{-1}	$\Delta H_2{}^‡$/kcal mol^{-1}	$\Delta S_2{}^‡$/cal K^{-1} mol^{-1}
trans-$[Rh(NH_3)_4Cl_2]^+$	155 [b]	22.8 ± 0.5	−13.2 ± 1.5	3.42	36.8 ± 1.2	26.2 ± 3.3
	127 [c]	24.1 ± 0.4	−9.2 ± 1.1	—	—	—
trans-$[Rh(NH_2Me)_4Cl_2]^+$	9.06 [b]	30.8 ± 0.7	8.0 ± 1.9	10.4	36.2 ± 0.2	26.4 ± 0.6
	7.67 [d]	29.2 ± 1.0	2.30 ± 2.3	—	—	—
trans-$[Rh(NH_2Et)_4Cl_2]^+$	43.7 [b]	23.7 ± 5.7	−12.7 ± 16.3	22.0	35.4 ± 1.2	25.2 ± 3.4
	59.5 [d]	24.5 ± 0.7	−9.4 ± 2.1	—	—	—
trans-$[Rh(NH_2Pr^n)_4Cl_2]^+$	106.9 [e]	24.6 ± 2.4	−7.9 ± 6.7	17.1	37.1 ± 2.5	30.4 ± 7.1
	67.7 [d]	24.9 ± 3.3	−7.8 ± 9.3	—	—	—

[a] Rate parameters are derived from the equation $k_{obs.} = k_1 + k_2[OH^-]$; k_1 and k_2 at 25 °C, calculated from the activation parameters. [b] This work, I = 1.0 mol dm^{-3} ($NaClO_4$). [c] Data taken from ref. 6, ionic strength variable. [d] Data taken from bromide interchange (ref. 7), I = 0.2 mol dm^{-3} ($NaClO_4$). [e] This work, I = 1.0 mol dm^{-3} (NaCl).

which covers a mechanistic range from S_N1(c.b.) to S_N1(i.p.) (ion pair) and possibly as far as S_N2. Values of the activation parameters for the reactions reported here lie in the region of the isokinetic plot assigned to the S_N1(c.b.) mechanism and are well separated from that region considered to represent the S_N1(i.p.) mechanism where the values of both $\Delta H_2{}^‡$ and $\Delta S_2{}^‡$ are smaller.

An inspection of the activation parameters for the k_2 term for the four complexes studied here reveals no apparent trends, Table 6. This is in contrast to the values for the base hydrolysis of the complexes $[Rh(NH_2R)_5Cl]^{2+}$ (R = H, Me, Et, or Pr^n) where it was found [1] that the activation enthalpies decreased along the series from R = H to R = Pr^n due to the dominance of steric effects. That no such trend is observed for the complexes *trans*-$[Rh(NH_2R)_4Cl_2]^+$ (R = H, Me, Et, or Pr^n) suggests either that both steric and solvational differences along the series are very small or that the differences are significant but because of the opposite trends produced by the two effects along the series, *i.e.* the complex with R = Pr^n is most sterically congested and least solvated, they cancel each other. Values of the activation entropies should reflect any differences in solvation, *i.e.* electrostriction, along the series but these values show little variation. It would thus appear that solvation effects are fairly constant along the series; a similar conclusion was reached for the complexes $[Rh(NH_2R)_5Cl]^{2+}$. For the series *trans*-$[Rh(NH_2R)_4Cl_2]^+$ (R = H, Me, Et, or Pr^n), the position of the first spin-allowed ligand-field band shows little variation [7] so that any differences in the rates of base hydrolysis arising from differences in the loss of ligand-field stabilisation energy as the chloride leaves the complex will be small. Similarly the value of $\varepsilon_{max.}$ for this band in the series of complexes *trans*-$[Rh(NHR_2)_4Cl_2]^+$ does not increase along the series R = H to R = Pr^n which is in contrast to the increase in $\varepsilon_{max.}$ observed for this band in the series $[Rh(NH_2R)_5Cl]^{2+}$, R = H to Pr^n. An increase in the value of $\varepsilon_{max.}$ for the first spin-allowed ligand-field band in rhodium(III) complexes containing bulky or sterically rigid ligands has been explained as arising from ground-state distortion.[15] The absence of such an increase in $\varepsilon_{max.}$ for the present series of complexes can thus be taken to indicate that the complexes are less sterically strained with little or no difference in the steric effects along the series. Thus for the *trans* series of complexes it is probable that both steric and solvation differences along the series are small hence giving rise to fairly constant values for the activation enthalpies and entropies.

The spectroscopic changes during the reactions of these complexes were accompanied by isosbestic points whose positions were independent of hydroxide ion concentration; similarly the final spectrum of the product for a given reaction was independent of the hydroxide ion concentration, thus suggesting that no *trans*→*cis* isomerisation had occurred. This contrasts with the observation of *trans*→*cis* isomerisation in the base hydrolysis of *trans*-$[Rh(en)_2Cl_2]^+$ which was rationalised [5] in terms of the very strong *trans* σ-bond-weakening effect of the amido-group which resulted in the formation of a trigonal-bipyramidal intermediate with the amido-group in the trigonal plane, so as to strengthen the bond between the rhodium and the amido-group without greatly weakening the other rhodium–nitrogen bonds. Isomerisation would result in the formation of *cis*-$[Rh(NH_2R)_4(OH)_2]^+$ and although these complexes would be more sterically strained than the corresponding *trans* isomers, they probably cannot be discounted on steric grounds as the synthesis of *cis*-$[Rh(NH_3)_4(OH)_2]^+$ has been reported [16] together with its electronic spectrum [9,16] which was, however, sufficiently different from that of the *trans* isomer as to indicate that any *trans*→*cis* isomerisation in this case was very small. A similar retention of stereochemistry was reported [4] for the base hydrolysis of the complex *trans*-$[Rh(udmen)_2Cl_2]^+$ (udmen = *NN*-dimethylethylenediamine), where again isomerisation cannot be discounted on steric grounds since the *cis* isomer has been synthesised.[17] The base hydrolysis of the complexes *trans*-$[Rh(NH_2R)_4Cl_2]^+$ (R = Me, Et, or Pr^n) was accompanied by some decomposition at high temperature and hydroxide ion concentration, and this might indicate that some isomerisation was occurring during the reaction but that the intermediate decomposed before isomerisation was complete. However, the decomposition could also be due to the *trans* bond-weakening effect of the amido-group resulting in a weakening of the amine Rh–N bond *trans* to the amido-group. The lack of isomerisation suggests therefore that the reaction proceeds through a square-pyramidal intermediate.

A comparison of the rate parameters for the hydroxide ion dependent pathway in the base hydrolysis of the complexes *trans*-$[Rh(NH_2R)_4Cl_2]^+$ with those for the series [1] $[Rh(NH_2R)_5Cl]^{2+}$ provides an opportunity to compare the effect on the leaving chloride of being *trans* to a chloride or *trans* to a nitrogen bearing an ionisable hydrogen. It is found that the series $[Rh(NH_2R)_5Cl]^{2+}$ react at a rate that is *ca.* 10^5 times faster, as measured by the rate constants at 25 °C, and this is due to the smaller activation enthalpy for this series, the difference being *ca.* 10 kcal mol^{-1}. However, the more favourable enthalpies of activation for the series $[Rh(NH_2R)_5Cl]^{2+}$ are slightly offset by the more positive values of the activation entropies for the series *trans*-$[Rh(NH_2R)_4Cl_2]^+$; the difference is *ca.* 12 cal K^{-1} mol^{-1}. An apparently similar comparison can be made by comparing the kinetic parameters for the *cis* and *trans* isomers of complexes of the type $[RhL^4Cl_2]^+$, where L^4 is a four-N-donor amine type ligand or ligands. Two examples for rhodium(III) complexes are the isomers of $[Rh(en)_2Cl_2]^+$ [3,4] and $[Rh(cyclam)Cl_2]^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane).[18,19] For the isomers of $[Rh(en)_2Cl_2]^+$ it was found that the *cis* isomer was the more reactive, the ratio of the rate constants for base hydrolysis at 25 °C was *ca.* 10^5; no activation parameters were available for the *cis* isomer. Similarly the *cis* isomer of $[Rh(cyclam)Cl_2]^+$ reacted more quickly, with the ratio of rate constants at 25 °C being *ca.* 10^6 and with the *cis* isomer having a smaller activation enthalpy, the difference in the activation enthalpies was 16 kcal mol^{-1}; the *trans* isomer had a more positive entropy of activation, the difference being 24 cal K^{-1} mol^{-1}. However, in these *cis* and *trans* isomers the leaving chloride is not in identical environments in that it is surrounded by different *cis* ligands in the two cases and there is no means of quantitatively allowing for this effect. A further difficulty when comparing the rates of base hydrolysis of the *cis* and *trans* isomers of $[Rh(cyclam)Cl_2]^+$ is that the nature of the configurations of the hydrogen on each of the four secondary nitrogens is not known and may be different in the two geometric isomers. It has been shown [20] in the case of the corresponding cobalt complexes that differences in the configuration of the hydrogens on the secondary nitrogens can give rise to differences in rates of reaction for the same geometric isomers. For the two series of complexes studied here the leaving chloride is surrounded by the same *cis* ligands, *i.e.* $(NH_2R)_4$, so that the effect of changing the group *trans* to the leaving chloride from chloride to NH_2R can be easily measured.

One difference that does exist between the two series of complexes is the net charge on the complexes; this difference is probably reflected only in the differences in the activation entropies. The series of complexes $[Rh(NH_2R)_5Cl]^{2+}$ are doubly charged and hence are more solvated than the corresponding *trans*-$[Rh(NH_2R)_4Cl_2]^+$ complexes. As a consequence, the doubly charged ions will experience a greater loss of entropy from electrostriction in the dissociative step to form the five-co-ordinate intermediate and should as a result have a less positive entropy of activation than that for the corresponding member of the series *trans*-$[Rh(NH_2R)_4Cl_2]^+$, as is indeed the case. There is also the statistical factor to allow for the fact that in one series there are two possible chlorides available for replacement. This will give an additional positive contribution to the entropy of activation for the series *trans*-$[Rh(NH_2R)_4Cl_2]^+$; however, the contribution is small (<2 cal K^{-1} mol^{-1}).

The effect therefore of having the leaving chloride *trans* to a NH_2R as compared to being *trans* to a Cl is to increase the rate of base hydrolysis by a lowering of the activation enthalpy by *ca.* 10 kcal mol^{-1}. This result indicates that it is the amine *trans* to the Cl in the series $[Rh(NH_2R)_5Cl]^{2+}$ that ionises to form the amido-group, and that the greater rate of base hydrolysis in these complexes arises from the strong *trans* σ-bond-weakening effect of the amido-group in the conjugate base [2,5] which can only operate in this series of complexes. However, the fact that base hydrolysis *via* the S_N1(c.b.) mechanism does occur in the series *trans*-$[Rh(NH_2R)_4Cl_2]^+$ suggests that the amido-group can exert a weak *cis* effect.

Amine complexes of cobalt(III) are generally more susceptible to base hydrolysis than the corresponding rhodium(III) complexes. Thus many amine complexes of cobalt(III) which undergo base hydrolysis follow a similar two-term rate law [2,4,13] to that observed here for the series *trans*-$[Rh(NH_2R)_4Cl_2]^+$, but in the case of cobalt(III) complexes $\Delta H_2^‡ \lesssim \Delta H_1^‡$. Similarly a comparison of the rate parameters for the base hydrolysis of *cis* and *trans* isomers of $[Co(en)_2Cl_2]^+$ and of other similar complexes reveals no large difference in the rate constants or activation enthalpies. Although there have been no comparable studies reported on cobalt(III) complexes similar to the two series of complexes of rhodium(III) discussed here, it is interesting to note that *trans*-$[Co(NH_3)_4Cl_2]^+$ has a larger rate constant for base hydrolysis than does $[Co(NH_3)_5Cl]^{2+}$ and the activation enthalpy for the base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ is larger than that for *trans*-$[Co(en)_2Cl_2]^+$. The base hydrolysis of amine complexes of chromium(III) has not been as extensively studied as those of cobalt(III) but the complexes of chromium(III) that have been found to undergo base hydrolysis are believed to react *via* the S_N1(c.b.) mechanism.[13,21-24] A comparison of the rate parameters for these complexes of chromium(III) which are similar to the two series of rhodium(III) complexes discussed above reveals that there is no large difference in either the rate constant or activation enthalpy. Thus *cis*- and *trans*-$[Cr(en)_2Cl_2]^+$ undergo base hydrolysis with almost identical rate constants at 25 °C.[21,23,24] Also, $[Cr(NH_3)_5Cl]^{2+}$ undergoes base hydrolysis at 25 °C with a rate constant that is smaller by a factor of almost 20 than that of *trans*-$[Cr(en)_2Cl_2]^+$ and this is due to the larger activation enthalpy (*ca.* 3 kcal mol^{-1}), although the activation entropy for base hydrolysis of $[Cr(NH_3)_5Cl]^{2+}$ is more positive by *ca.* 7 cal K^{-1} mol^{-1}.[22,24]

The results for the cobalt(III) and chromium(III) complexes have been explained [2,3] as arising from the ability of cobalt(III) and chromium(III) to π bond with the amido-group in the transition state or the trigonal-bipyramidal five-co-ordinate intermediate. Although the site of deprotonation to form the active amido-group in these complexes is still uncertain, the position of the amido-group is less critical as it is possible to form a trigonal-bipyramidal intermediate with the amido-group in the trigonal plane, where it can π bond effectively with the cobalt or chromium irrespective of whether the initial position of the amido-group was *cis* or *trans* to the leaving group. The results presented here for the rhodium(III) complexes, where $\Delta H_2^‡ > \Delta H_1^‡$ for the series *trans*-$[Rh(NH_2R)_4Cl_2]^+$ and the considerably lower values of activation enthalpies for base hydrolysis of the complexes $[Rh(NH_2R)_5Cl]^{2+}$ compared to the corresponding values for the above complexes, can thus be interpreted as direct evidence for the reduced ability of rhodium(III) compared to cobalt(III) and chromium(III) to participate in π bonding in complexes of this type.

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Received 20*th June* 1983; *Paper* 3/1041