The Kinetics of Base Hydrolysis of Chloropentakis(alkylamine)-rhodium(III) Ions †

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The kinetics of the base hydrolysis of the complex ions $[Rh(NH_2R)_5Cl]^{2+}$ (R = Me, Et, or Pr^n) have been studied and values of the rate constants and activation parameters determined. For all the complexes the observed first-order rate constants were found to be proportional to the hydroxide ion concentration and to increase as the size of the amine, RNH_2, increased. The increase in the rate constant was found to arise from a small but steady decrease in the activation enthalpy for the complexes and this is thought to be consistent with a S_N1(c.b.) mechanism (c.b. = conjugate base) where steric effects alone are the most important factor in controlling the difference in the rates of these reactions.

In a previous publication [1] the kinetics of the bromide interchange of the chloropentakis(alkylamine)rhodium(III) ions, $[Rh(NH_2R)_5Cl]^{2+}$ (R = H, Me, Et, or Pr^n) were reported. No obvious trends in the values of the rate constants or activation parameters were found and it was concluded that the kinetic behaviour of these complexes in this reaction were best described by an associative interchange (I_a) mechanism.[2] Studies [3-5] of the base hydrolysis of a number of complexes of rhodium(III) of the type *trans*-$[Rh(L-L)_2Cl_2]^+$, where L–L was a chelate such as ethylenediamine (en), revealed that these complexes could undergo reactions *via* a S_N1 (c.b.) [6] mechanism (c.b. = conjugate base), or *D*(c.b.), using the nomenclature of Langford and Gray.[2] In view of the dissociative character of the S_N1 (c.b.) mechanism it seemed of interest to study the base hydrolysis of the chloropentakis(alkylamine)-rhodium(III) ions to discover whether they reacted *via* the S_N1(c.b.) mechanism and if they did, what would be the effect on the rate parameters of varying the size of the alkyl group, R, along the series R = H, Me, Et, or Pr^n. A similar study has been reported for the corresponding complexes of Co^{III} [7] and Cr^{III},[8] thus a comparison of the kinetics of base hydrolysis for the three metal ions can be made.

Experimental

Materials.—The complex ions $[Rh(NH_2R)_5Cl]^{2+}$ (R = Me, Et, or Pr^n) were prepared as their chloride salts by the published method.[1] Their electronic spectra were in agreement with those reported previously.[1] Solutions of sodium perchlorate were prepared from the anhydrous salt. Standard solutions of sodium hydroxide were prepared by dissolving AnalaR sodium hydroxide in distilled water, and diluted portions of this solution were standardised against 0.1 mol dm^{-3} hydrochloric acid.

Kinetic Studies.—The kinetics of the reactions were studied by observing absorbance changes in the electronic spectrum of the reaction mixture either by scanning the whole spectrum at known time intervals or by following absorbance changes at a fixed wavelength. Electronic spectra were recorded on a Unicam SP800 spectrophotometer fitted with a constant wavelength attachment and a thermostatted cell block capable of holding cells up to 10 mm path length. It was possible to control the temperature of the cell block to better than ±0.1 °C. The wavelengths at which the reactions were monitored in the constant wavelength experiments were in the region 230—247 nm (absorbance decreasing).

For the complexes with R = Me and Et, the ionic strength of the reaction mixture was maintained at 1.0 mol dm^{-3} with sodium perchlorate. However, the solubility of the complex with R = Pr^n was not sufficient in this medium so the ionic strength of the reaction mixture was maintained at 0.5 mol dm^{-3} with sodium perchlorate.

Pseudo-first-order rate constants were obtained in the usual manner by a linear least-squares plot of $\ln(A_t - A_\infty)$ *vs.* time; in all the reactions the plots were linear for several half-lives. The values of the observed rate constant quoted are the average of at least three separate determinations. Values of k_2 in the expression $k_{obs.} = k_2[OH^-]$ and their standard deviations, together with the activation parameters and their standard deviations, were obtained by a linear least-squares analysis of the data as described previously.[4]

Results

The spectroscopic changes during the base hydrolysis of the three complexes were accompanied by sets of clean isosbestic points whose positions did not vary with hydroxide ion concentration. The products of the reactions were identified as the corresponding hydroxy complexes by the similarity in their electronic spectra with that reported [9] for $[Rh(NH_3)_5(OH)]^{2+}$ and the reported spectra [10] of $[Rh(NH_2R)_5(OH)]^{2+}$ (R = Me, Et, or Pr^n). Swaddle [11] has also shown that the products of the reactions between hydroxide ion and the two complex ions $[Rh(NH_2R)_5Cl]^{2+}$ (R = H or Me) are the corresponding ions $[Rh(NH_2R)_5(OH)]^{2+}$. The spectroscopic changes accompanying these reactions are summarized in Table 1.

Values of the observed rate constants at various temperatures and hydroxide ion concentrations for the base hydrolysis of the three complex ions are given in Tables 2—4. In all cases the pseudo-first-order rate constants were found to vary with hydroxide ion concentration according to $k_{obs.} = k_2[OH^-]$.

Discussion

All the complexes studied here undergo base hydrolysis at a rate that is directly proportional to both the complex and hydroxide ion concentration. This form of rate law has been observed previously for a few other complexes of rhodium(III) [11-13] and is frequently found for the base hydrolysis of cobalt(III) amine complexes [14] and corresponds to attack by hydroxide ion *via* a S_N1(c.b.) mechanism.[6] This mechanism is outlined in equations (1)—(3) and the full rate law for this path is (4), which reduces to the observed rate law (5) if $K \ll 1$.

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† Presented in part at the Royal Society of Chemistry, International Conference on the Mechanisms of Reactions in Solution, University of Kent, Canterbury, July 1982.

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

Table 1. Spectroscopic changes accompanying the base hydrolysis of the complexes $[Rh(NH_2R)_5Cl]^{2+}$ (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
$[Rh(NH_3)_5Cl]^{2+}$	[a] 321 (124), 278 (108)	
$[Rh(NH_2Me)_5Cl]^{2+}$	[b] 326 (198), 277 (180)	347, 294, 278, 256
	[c] 336 (141), 286 (133)	
$[Rh(NH_2Et)_5Cl]^{2+}$	[b] 325 (189), 275 (172)	348, 298, 277, 257
	[c] 340 (163), 285 (158)	
$[Rh(NH_2Pr^n)_5Cl]^{2+}$	[b] 335 (159), 277 (169)	349, 301, 277, 257
	[c] 344 (157), 285 (139)	

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

Table 2. Kinetic data for the reaction of $[Rh(NH_2Me)_5Cl]^{2+}$ with hydroxide ($[Rh] = 4 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} with sodium perchlorate)

θ_c/°C	$[OH^-]$/ mol dm^{-3}	$10^5k_{obs.}/s^{-1}$	10^5k_2 */ dm^3 mol^{-1} s^{-1}
5	0.25	1.50, 1.60	6.50 ± 0.04
	0.5	3.30, 2.90	
	0.75	5.30, 4.90, 5.10	
	0.9	5.40, 6.30, 6.10	
15	0.25	8.60, 9.00	36.0 ± 2.3
	0.5	18.0, 17.2	
	0.75	30.4, 25.2	
	1.0	36.9	
24	0.25	41.7, 36.2	145 ± 12.5
	0.5	76.0, 64.3	
	0.75	105, 104	
	1.00	140	

$\Delta H^\ddagger = 26.3 \pm 0.3$ kcal mol^{-1}
$\Delta S^\ddagger = 16.9 \pm 1.4$ cal K^{-1} mol^{-1}

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

Table 3. Kinetic data for the reaction of $[Rh(NH_2Et)_5Cl]^{2+}$ with hydroxide ($[Rh] = 3.0 \times 10^{-4}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} with sodium perchlorate)

θ_c/°C	$[OH^-]$/ mol dm^{-3}	$10^5k_{obs.}/s^{-1}$	10^5k_2 */ dm^3 mol^{-1} s^{-1}
10	0.1	2.80	34.7 ± 3.8
	0.3	9.70	
	0.5	16.5	
	0.7	27.3, 26.2	
	0.8	29.5	
	1.0	36.3	
20.5	0.3	58.3	198 ± 9.8
	0.4	74.8	
	0.5	96.2	
	0.6	123	
	0.7	148	
29.5	0.1	80.0, 70.0	682 ± 55
	0.2	123, 133	
	0.3	193, 185	
	0.4	285, 250	
	0.5	340, 375	
	0.6	415, 408	

$\Delta H^\ddagger = 25.5 \pm 0.9$ kcal mol^{-1}
$\Delta S^\ddagger = 15.8 \pm 3.0$ cal K^{-1} mol^{-1}

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

$$[Rh(NH_2R)_5Cl]^{2+} + OH^- \xrightleftharpoons{K,\ fast} [Rh(NH_2R)_4(NHR)Cl]^+ + H_2O \quad (1)$$

$$[Rh(NH_2R)_4(NHR)Cl]^+ \xrightarrow{k,\ slow} [Rh(NH_2R)_4(NHR)]^{2+} + Cl^- \quad (2)$$

$$[Rh(NH_2R)_4(NHR)]^{2+} + H_2O \xrightarrow{fast} [Rh(NH_2R)_5(OH)]^{2+} \quad (3)$$

$$\text{Rate} = \frac{kK[Rh(NH_2R)_5Cl^{2+}][OH^-]}{1 + K[OH^-]} \quad (4)$$

$$\text{Rate} = kK[Rh(NH_2R)_5Cl^{2+}][OH^-] \quad (5)$$

Few values of the acidities of co-ordinated ammonia or amines have been measured, although values of pK_a of 14.9,[15] 14,[16] and 17.7[17] for $[Co(en)_3]^{3+}$, $[Rh(NH_3)_6]^{3+}$, and $[Rh(NH_3)_5Br]^{2+}$ respectively have been reported, thus suggesting that the above equilibrium constant is normally small (the equilibrium constant is related to K_a of the complex by $K_a/K_w = K$). Also, the excellent linearity of the plots of $k_{obs.}$ *vs.* $[OH^-]$ up to a maximum concentration of 1.0 mol dm^{-3} {in the case of $[Rh(NH_2Pr^n)_5Cl]^{2+}$, the maximum concentration of hydroxide was 0.5 mol dm^{-3}} indicates the absence of appreciable ion pairing between the initial complex and perchlorate.[18]

A report by Reynolds and Hafezi[19] suggested that in the base hydrolysis of $[Co(NH_3)_5X]^{2+}$ (X = Cl, Br, NO_3, or Me_2SO) there was a significant contribution to the overall reaction from an interchange mechanism. More recent studies,[20] however, have established that the S_N1(c.b.) mechanism is the main pathway for base hydrolysis in complexes of this type, and that the lifetime of the five-co-ordinate intermediate is probably no longer than the time required for a few collisions in the encounter complex.

A summary of the activation parameters for the base hydrolysis of the compounds studied here together with the values for $[Rh(NH_3)_5Cl]^{2+}$ are given in Table 5. It can be seen that the rate constants increase steadily along the series R = H to R = Pr^n and this is due to a small but continuous decrease in the values of the activation enthalpies. This is consistent with the S_N1(c.b.) mechanism where, if steric effects alone are the most important factor controlling the differences in the rates of hydrolysis, the increasing steric strain in these complexes and subsequent relief on forming the five-co-ordinate intermediate in the dissociative step, reaction (2), on proceeding along the series from R = H to R = Pr^n is expected to be reflected in a parallel decrease in the activation enthalpies.

While a consideration of steric effects alone would appear to be sufficient to explain the variation of the rates of base hydrolysis, differences in solvational and electronic factors along the series should also be considered, although (as will be shown below) these are relatively minor and unimportant in these reactions.

The complex with R = Pr^n should be the least solvated of the series and consequently should have the smallest gain in solvation energy on forming a polar transition state as in the S_N1(c.b.) mechanism. Thus the complex with R = Pr^n should

Table 4. Kinetic data for the reaction of $[Rh(NH_2Pr^n)_5Cl]^{2+}$ with hydroxide ([Rh] = 8.0×10^{-4} mol dm^{-3}, I = 0.5 mol dm^{-3} with sodium perchlorate)

θ_c/°C	$[OH^-]$/ mol dm^{-3}	$10^5k_{obs.}$/s^{-1}	10^5k_2 *$/$ dm^3 mol^{-1} s^{-1}
6.9	0.35	16.5	48.9 ± 4.2
	0.40	18.8, 18.6	
	0.45	21.7, 20.4	
	0.50	25.3, 28.8	
15.7	0.1	19.1, 14.1	180 ± 19.6
	0.2	35.0	
	0.3	53.4, 53.7	
	0.4	77.8, 80.2	
24.8	0.1	71.2, 73.5	711 ± 46
	0.2	139	
	0.3	187, 193	
	0.34	253	
	0.38	292	
	0.4	293, 287	
	0.42	311	

$\Delta H^\ddagger$ = 24.2 ± 0.6 kcal mol^{-1}
$\Delta S^\ddagger$ = 12.9 ± 2.0 cal K^{-1} mol^{-1}

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

have the largest activation enthalpy if solvational factors were dominant. That the reverse trend occurs suggests that solvational factors are approximately constant for each member of the series and indeed if solvational factors could be allowed for, a bigger difference in the activation enthalpies between successive members of the series would possibly be observed.

The lowest spin-allowed ligand-field band can be used as a measure of the σ-electron donation from nitrogen to rhodium and this occurs at approximately the same position for all three alkylamine complexes which is consistent with the nearly identical value of pK_b for the amines.[21] However, the position of this band for the penta-ammine complex is shifted slightly by *ca.* 9 nm to higher energy indicating a bigger σ-electron donation from NH_3 than from NH_2R even though NH_2R is a stronger base than NH_3. Electronic effects may therefore be of some significance in explaining differences in the rates of reactions between the complexes with R = H and with R = alkyl. It is, however, difficult to assess these effects; thus the influence on the equilibrium reaction (1) can only be measured indirectly by assuming the same trend for nitrogen and oxygen acidities, and, comparing the pK_a of the corresponding aqua complexes where it has been found [11] that $[Rh(NH_2Me)_5(H_2O)]^{3+}$ is more acidic than the penta-ammine complex. This is in keeping with the smaller σ-electron donation of NH_2Me in the chloro-complex. A crystal structure determination of the complexes $[Co(NH_2Me)_5Cl][NO_3]_2$[22a] and $[Rh(NH_3)_5Et]Br_2$[22b] has revealed that there is distortion of the bond angles N–Co–N and C–Rh–N from 90°, due to non-bonded interactions, and this may be responsible for the reduced σ-electron donation from NH_2Me to rhodium in this complex. Thus although there is the possibility that the equilibrium reaction (1) may increase on going from R = H to R = Me, in opposition to this will be the effect on the rate of the dissociative step; a reduced electron donation from the ligand to the metal will result in a smaller electron density on the rhodium and hence a reduced rate of dissociation of the negatively charged Cl^-. Consequently, it may be assumed that electronic effects are unimportant in this series of complexes with the possible exception that they may have an influence on the difference in rates between the complex with R = H and the remainder of the series but this influence is likely to be small because of the opposing trends in the equilibrium reaction (1) and the following dissociative reaction (2). However, the spectroscopic data do indicate that the complexes with R = alkyl are more sterically strained than the penta-ammine complex. Also, ground state distortion has been invoked [23] to account for the increase in $\varepsilon_{max.}$ of the first spin-allowed ligand-field band of Rh^{III} complexes containing bulky or sterically rigid ligands. Such an increase in $\varepsilon_{max.}$ along the series R = H to R = Pr^n is observed for the complex ions $[Rh(NH_2R)_5Cl]^{2+}$ studied here.[1]

Table 5. Kinetic data for the reactions of $[Rh(NH_2R)_5Cl]^{2+}$ with hydroxide

R	10^5k_2/ dm^3 mol^{-1} s^{-1} [a]	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
H [b]	10.8	27.5	15.6
Me	159	26.3 ± 0.3	16.9 ± 1.4
Et	353	25.5 ± 0.9	15.8 ± 3.0
Pr^n	737	24.2 ± 0.6	12.9 ± 2.0

[a] At 25 °C. [b] Ref. 12.

Hence, in summary, for the base hydrolysis of this series of complexes $[Rh(NH_2R)_5Cl]^{2+}$, steric factors are more important than solvational or electronic effects so that a predicted decrease in the activation enthalpy along the series R = H to R = Pr^n is observed, consistent with the dissociative character of the mechanism.

The rate parameters for the base hydrolysis of the corresponding complexes $[M(NH_2R)_5Cl]^{2+}$ with M = Co^{III} [7] and Cr^{III} [8] have been reported. In both cases the rate constants increased along the series R = H to R = Pr^n. The activation enthalpy decreased on going from R = H to R = Me, the decrease in the case of Co^{III} was *ca.* 10 kcal mol^{-1} whereas for Cr^{III} it was *ca.* 1.3 kcal mol^{-1}. However, for the later members of the Cr^{III} series the activation enthalpy remained virtually constant and the further increase in rate was due to the increasingly positive value of the activation entropy. A similar trend was observed for the series with Co^{III}, although here there was a further small decrease (0.8 kcal mol^{-1}) in the activation enthalpy on going from R = Et to R = Pr^n. The large decrease in the activation enthalpy for Co^{III} on going from R = H to R = Me probably arises because of the small size of the ion compared with the other ions thus making the Co^{III} more sensitive to steric strain; the ionic radii of the ions are 52.5, 61.5, and 67 pm for Co^{III}, Cr^{III}, and Rh^{III} respectively.[24] Although the behaviours of the Co^{III} and Cr^{III} series of compounds have also been interpreted in terms of the S_N1(c.b.) mechanism, it is only in the case of the Rh^{III} series that a gradual decrease in the activation enthalpies with increasing steric strain was observed. One possible reason for this is that solvational effects may be more important for the two first-row transition metal ions, thus disguising the expected trend in the enthalpy of activation due to relief of steric strain. The increasingly positive values of the entropies of activation for the Cr^{III} series are consistent with this interpretation as solvation of the complexes and hence electrostriction [25] is expected to become less along the series. For the rhodium(III) complexes, the values of the entropies of activation vary very little and are in agreement with the values predicted for a S_N1(c.b.) mechanism.[4,26] The near constancy in the values of the entropies of activation can be explained if it is assumed that a major contribution to the entropy of activation for the base hydrolysis of this series of complexes is from electrostriction and, as argued previously, solvational differences between successive members of the series are thought to be relatively small.

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Received 31*st January* 1983; *Paper* 3/138