Water–Ammonia Exchange at Amminerhodium(III) Complexes in Aqueous Ammoniacal Solution

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The kinetics of water–ammonia exchange at *trans*-$[Rh(NH_3)_4(OH)_2]^+$ and $[Rh(NH_3)_5(OH)]^{2+}$ have been studied in aqueous ammoniacal solution. The reaction of *trans*-$[Rh(NH_3)_4(OH)_2]^+$ with ammonia to form $[Rh(NH_3)_5(OH)]^{2+}$ has been studied in the temperature range 68—90 °C. The pH dependence of the observed rate constant indicates H_2O to be the leaving group. The kinetics could be interpreted in terms of the usual Eigen–Wilkins interchange mechanism, with a more associative character than cobalt(III). The reaction of $[Rh(NH_3)_5(OH)]^{2+}$ with ammonia has been studied in the temperature range 112—142 °C, where the reaction results in an equilibrium mixture of $[Rh(NH_3)_5(OH)]^{2+}$ and $[Rh(NH_3)_6]^{3+}$. The equilibrium constant has been determined spectrophotometrically and kinetically. The forward reaction is pH-independent. The reverse reaction, which gives a small contribution to the overall rate, is base-catalysed. These results can be explained by a direct interchange of OH^- and NH_3 or by the conjugate-base mechanism.

A SUBSTANTIAL amount of information has been gathered about substitution reactions of octahedral rhodium(III) complexes in aqueous solution.[1-6] Most of these studies have been centred on formation and breaking of the Rh–X bond in complexes of formula $[Rh(NH_3)_5X]^{2+}$ or $[Rh(en)_2X_2]^+$ (en = ethylenediamine) and with X an ionic ligand such as Cl^-, Br^-, I^-, NCS^- *etc.* All these studies involve aquation, base hydrolysis, or anation, in which the rhodium(III)-amine skeleton is inert. The mechanistic picture emerging from these studies is that substitution at rhodium(III) tends to be more associative in character than at cobalt(III). Although this seems to be the prevalent picture of rhodium(III) reactions, for a number of substitutions a dissociative (*D*) mechanism is indicated.[7-9]

Most of the information known about cobalt(III) amine substitution reactions deals with a stable cobalt-amine skeleton, in which ligands other than amines are reactive. Consequently, not much is known about the kinetics and mechanism of the Co^{III}–NH_3 bond. To fill this gap, some years ago investigations were started at our laboratories of water–ammonia exchange reactions of some ammineaquocobalt(III) complexes.[10-14] The complex *cis*-$[Co(NH_3)_4(OH_2)_2]^{3+}$ has been the starting product for most of these studies. In aqueous ammoniacal solution this complex splits off the aquo-protons in two consecutive rapid acid–base equilibria,[11] the three resulting tetra-ammines undergo *cis–trans* rearrangement.[10] These equilibria are followed by a slower uptake of ammonia to form $[Co(NH_3)_5(OH)]^{2+}$.[11]

The medium dependence of the uptake of ammonia indicates that both the dihydroxo-complex and the aquohydroxo-complex are reactive species. The reaction with ammonia could be described by a dissociative-interchange (I_d) mechanism.[15] In the absence of ammonia the tetra-amminecobalt(III) complexes undergo tetramerisation.[16,17] In order to study the breaking of the Co–NH_3 bond, the reaction of $[Co(NH_3)_5(OH)]^{2+}$ to form $[Co(NH_3)_4(OH)_2]^+$ has been studied.[14] This reaction proceeds *via* outer-sphere complexes of $[Co(NH_3)_5(OH)]^{2+}$ or its conjugate base with water or hydroxyl ions.

The studies of water–ammonia exchange reactions were extended to some rhodium(III) complexes in order to study the kinetics of formation and breaking of the Rh–NH_3 bond for the reasons given above.

RESULTS AND DISCUSSION

Alkaline aqueous solutions of the $[Co(NH_3)_4(OH)_2]^+$ ion show tetramerisation[16,17] and *cis–trans* isomerisation[10] complicating the study of ammonia uptake.[11-13] The presence of these and similar reactions was checked for *trans*-$[Rh(NH_3)_4(OH)_2]^+$ by following pH and the u.v.–visible absorption spectrum of alkaline solutions (pH = 7—10.5) of this complex as a function of time. Even after 50 h at 50 °C in a closed vessel no change of pH or spectrum was observed and no release of ammonia could be detected by an ammonia electrode. Consequently, neither a tetramerisation or other polymerisation, nor a *trans–cis* isomerisation have to be reckoned with under the circumstances used for the ammonia uptake reactions.

Reaction of trans-$[Rh(NH_3)_4(OH)_2]^+$ *with Ammonia.*—The kinetics of the reaction of *trans*-$[Rh(NH_3)_4(OH)_2]^+$ with ammonia were studied in ammonia buffers at a constant ionic medium of 1.00 mol dm^{-3}. The u.v.–visible spectrum of the reaction product was identical to that of $[Rh(NH_3)_5(OH)]^{2+}$.[18] At constant ammonia concentration, the observed rate constant was proportional to the ammonium ion concentration, and at constant $[NH_4^+]$ the observed rate constant varied linearly with $[NH_3]$, with a non-zero intercept. The reaction can thus be described by the rate equation (1).

$$k_{obs.} = a_0 + a_1[NH_4^+] + a_2[NH_3][NH_4^+] \quad (1)$$

A least-squares fit of equation (1) to the observed rate constants resulted in the parameter values of a_1 and a_2, given in Table 1.† The mean deviation between the observed and calculated rate constants is generally less

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† Additional material available on request.

than 3%. The parameter a_0 is zero within experimental error. The activation parameters of a_1 and a_2 are in Table 2. The activation plots did not show curvature.

TABLE 1

Kinetic parameters for the reaction of *trans*-$[\mathrm{Rh(NH_3)_4(OH)_2}]^+$ with ammonia in aqueous ammoniacal solutions

θ_c/°C	$10^4\ a_1$/dm^3 mol^{-1} s^{-1}	$10^4\ a_2$/dm^6 mol^{-2} s^{-1}
68.6	0.58 ± 0.03	0.19 ± 0.03
76.3	1.78 ± 0.05	0.54 ± 0.03
81.4	3.52 ± 0.16	0.88 ± 0.08
88.5	8.35 ± 0.33	2.23 ± 0.25
90.4	11.0 ± 0.3	2.67 ± 0.18

The published pK values for the diaquo-complex [19] and the measured u.v.–visible spectra indicate that at the pH values of the solutions used the complex will be present almost entirely in the dihydroxo-form. Equation (1) may be rewritten as (1′).

$$k_{\mathrm{obs.}} = a_0 + (a_1'[\mathrm{NH_3}] + a_2'[\mathrm{NH_3}]^2)[\mathrm{H^+}] \qquad (1')$$

Equation (1′) governs the ammonia uptake [13] by *cis*- and *trans*-$[\mathrm{Co(NH_3)_4(OH)_2}]^+$, with a_0 as a complicated function of $[\mathrm{NH_3}]$. Therefore the mechanism will be similar in both cases, so that the reaction of *trans*-$[\mathrm{Rh(NH_3)_4(OH)_2}]^+$ with ammonia can be described by the Eigen–Wilkins interchange mechanism,[20] postulated for $[\mathrm{Co(NH_3)_4(OH)_2}]^+$,[13] equations (2)—(4), where $K_a{}^4$

$$[\mathrm{Rh(NH_3)_4(OH_2)(OH)}]^{2+} \xrightleftharpoons{K_a{}^4} [\mathrm{Rh(NH_3)_4(OH)_2}]^+ + \mathrm{H^+} \qquad (2)$$

$$[\mathrm{Rh(NH_3)_4(OH_2)(OH)}]^{2+} + \mathrm{NH_3} \xrightleftharpoons{\beta^4} [\mathrm{Rh(NH_3)_4(OH_2)(OH)}]^{2+}\cdots\mathrm{NH_3} \qquad (3)$$

$$[\mathrm{Rh(NH_3)_4(OH_2)(OH)}]^{2+}\cdots\mathrm{NH_3} \xrightarrow{k_{\mathrm{ex.}}{}^4} [\mathrm{Rh(NH_3)_5(OH)}]^{2+} + \mathrm{H_2O} \qquad (4)$$

represents a rapid acid–base equilibrium, β^4 the formation constant of the outer-sphere complex with ammonia, and $k_{\mathrm{ex.}}{}^4$ the rate-determining exchange of $\mathrm{NH_3}$ and $\mathrm{H_2O}$ between the inner and outer co-ordination sphere. The superscript 4 on the parameters denotes that a tetra-ammine complex is represented.

TABLE 2

Activation parameters for water–ammonia exchange

Complex	Parameter	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	I/mol dm^{-3}	Ref.
trans-$[\mathrm{Rh(NH_3)_4(OH)_2}]^+$	a_1	135 ± 2	68 ± 5	1.00	*a*
	a_2	122 ± 3	21 ± 9	1.00	*a*
	a_1' [b]	79	101	1.00	*a*
$[\mathrm{Co(NH_3)_4(OH)_2}]^+$ [c]	a_1'	97	181	0.20	11
$[\mathrm{Rh(NH_3)_5(OH)}]^{2+}$	$k_1{}^5$	133 ± 6	0 ± 16	0.10	*a*
	$k_{-1}{}^6$	210 ± 6	154 ± 15	0.10	*a*
	$k_{-1}{}^6\ (K^{\mathrm{NH_3}})^{-1}$	210	234	0.10	*a*

[a] This work. [b] $a_1' = k_{\mathrm{ex.}}{}^4\beta^4/K_a{}^4$ (see text). [c] a_1' is the same for the *cis* and *trans* complexes (ref. 12).

This scheme explains equation (1′) with $a_1' = k_{\mathrm{ex.}}{}^4\beta^4/K_a{}^4$. In the case of $[\mathrm{Co(NH_3)_4(OH)_2}]^+$ the a_2' term of equation (1′) has been proved to arise from a lowering of the dielectric constant of the medium, caused by adding ammonia.[13] The difference with the cobalt(III) case is the absence of a pH-independent term in the rate expression (1′) for the rhodium(III) complex ($a_0 = 0$). The a_0 term in equation (1′) denotes the contribution of $[\mathrm{Co(NH_3)_4(OH)_2}]^+$ to the rate constant, thus implying direct loss of $\mathrm{OH^-}$.[13] Evidently this reaction route is not favourable in the analogous rhodium(III) complex.

The activation parameters for water–ammonia exchange at *trans*-$[\mathrm{Rh(NH_3)_4(OH)_2}]^+$ are given in Table 2, together with the available data on cobalt(III). Rates of reaction with ammonia of *cis*- and *trans*-$[\mathrm{Co(NH_3)_4(OH)_2}]^+$ are the same within experimental error.[12] In order to make a straightforward comparison, the activation parameters for *trans*-$[\mathrm{Rh(NH_3)_4(OH)_2}]^+$ were converted to the formulation of equation (1′), with the aid of the hydrolysis constant $K^{\mathrm{NH_3}}$ of ammonia ($\Delta H = 0$, $\Delta S = -80$ J K^{-1} mol^{-1}) [21] and with $\Delta H^{\ominus} = 56$ kJ mol^{-1}, $\Delta S^{\ominus} = -113$ J K^{-1} mol^{-1} for K_w,[22] using the formula $a_1' = a_1 K^{\mathrm{NH_3}} K_w{}^{-1}$. A comparison of the activation parameters for a_1' of $[\mathrm{Co(NH_3)_4(OH)_2}]^+$ and *trans*-$[\mathrm{Rh(NH_3)_4(OH)_2}]^+$ shows that both $\Delta H^‡$ and $\Delta S^‡$ are lower for the rhodium(III) complex. This may be an indication of a less dissociative activation mode for the rhodium(III) complex. It should be noted that $a_1' = k_{\mathrm{ex.}}{}^4\beta^4/K_a{}^4$, so the activation parameters also contain the thermodynamic parameters for β^4 and $K_a{}^4$. The value of ΔH for β^4 will be close to zero.[23] ΔH Values for the acid dissociation constant of $[\mathrm{Co(NH_3)_5(OH_2)}]^{3+}$ and $[\mathrm{Rh(NH_3)_5(OH_2)}]^{3+}$ are 33 and 25 kJ mol^{-1} respectively.[24] If it is assumed that the difference in ΔH for $K_a{}^4$ between the tetra-ammines of rhodium(III) and cobalt(III) is the same as for the analogous penta-ammines, the activation enthalpies for $k_{\mathrm{ex.}}{}^4$ at cobalt(III) and rhodium(III) will differ by as much as 26 kJ mol^{-1}. The entropy changes for the acid dissociation constants of $[\mathrm{Co(NH_3)_5(OH_2)}]^{3+}$ and $[\mathrm{Rh(NH_3)_5(OH_2)}]^{3+}$ are: -5 J K^{-1} mol^{-1} and -38 J K^{-1} mol^{-1}, respectively.[24] Using this difference for the change in ΔS for $K_a{}^4$ on going from cobalt(III) to rhodium(III) and assuming the change in β^4 to be small, the activation entropy for $k_{\mathrm{ex.}}{}^4$ will decrease by 113 J K^{-1} mol^{-1} on going from cobalt(III) to rhodium(III). Summarizing, after corrections for the thermodynamic parameters for $K_a{}^4$ and β^4 are applied, $k_{\mathrm{ex.}}{}^4$ for *trans*-$[\mathrm{Rh(NH_3)_4(OH)_2}]^+$ will be characterized by an even more pronounced lowering of both $\Delta H^‡$ (by 26 kJ mol^{-1}) and $\Delta S^‡$ (by 113 J K^{-1} mol^{-1}) compared to $[\mathrm{Co(NH_3)_4(OH)_2}]^+$. As suggested above this may indicate a change of mechanism from I_d to I_a on going from cobalt(III) to rhodium(III), which is quite common. By means of measuring the volume of activation, water exchange at $[Rh(NH_3)_5(OH_2)]^{3+}$ has been proven to be associative in character.[6] Also, anation reactions of $[Rh(NH_3)_5(OH_2)]^{3+}$ by chloride and bromide have been ascribed to a possible nucleophilic assistance of the incoming group upon activation.[5] Bott *et al.*[5] have concluded that *trans*-$[Rh(en)_2(OH_2)_2]^{3+}$ behaves similarly to $[Rh(NH_3)_5(OH_2)]^{3+}$.

Reaction of $[Rh(NH_3)_5(OH)]^{2+}$ *with Ammonia.*—The study of the kinetics of the reaction between pentaamminehydroxorhodium(III) and ammonia was started at a constant ionic medium of 1.00 mol dm^{-3}. However at this electrolyte concentration a precipitate is formed upon cooling the samples, so the reactions were studied at the lower value of 0.10 mol dm^{-3}. The published pK values [24] and the u.v.–visible spectra [18] indicate that at the pH values of the solutions used the complex will be present entirely in the hydroxo-form. The observed rate constant as a function of $[NH_3]$ and $[NH_4^+]$ could be described by the rate equation (5).

$$k_{\text{obs.}} = b_0 + b_1[NH_3] + b_2[NH_3][NH_4^+]^{-1} \tag{5}$$

Equation (5) was fitted to the observed rate constants at varying $[NH_3]$ and $[NH_4^+]$; the resulting values of b_1 and b_2 are given in Table 3.* The intercept b_0 was zero within experimental error at all temperatures. Because of the sampling system used to study these reactions, the accuracy was rather low: the mean deviation between the observed and calculated rate constants generally was only better than 5%. The absorbance of the reacting solutions on completion of the reaction (after more than five half lives) was found to be dependent on the ammonium ion concentration, moving closer towards the value for pure $[Rh(NH_3)_6]^{3+}$ as more ammonium perchlorate was added. So the reaction product appears to be an equilibrium mixture of $[Rh(NH_3)_5(OH)]^{2+}$ and $[Rh(NH_3)_6]^{3+}$, equation (6).

TABLE 3

Parameters describing the equilibrium between $[Rh(NH_3)_5(OH)]^{2+}$ and $[Rh(NH_3)_6]^{3+}$

θ_c/°C	$10^5\ b_1$/dm^3 mol^{-1} s^{-1}	$10^7\ b_2$/s^{-1}	$K^{5,6\ a}$/ dm^3 mol^{-1}	$K^{5,6\ b}$/ dm^3 mol^{-1}
111.5	0.588 ± 0.035	0.241 ± 0.011	244	230
125.0	2.64 ± 0.02	2.43 ± 0.07	109	84
135.0	6.1 ± 0.5	13 ± 1	47	63
142.0	14.6 ± 0.8	31 ± 3	47	43

[a] Calculated from the kinetic parameters: $K^{5,6} = b_1/b_2$.
[b] Mean values of spectrophotometric determinations.

$$[Rh(NH_3)_5(OH)]^{2+} + NH_4^+ \underset{k_{-1}^6}{\overset{k_1^5}{\rightleftharpoons}} [Rh(NH_3)_6]^{3+} + H_2O \tag{6}$$

From the absorbance of the equilibrium mixture at 342 nm (the wavelength at which the change in absorbance is largest) and the known absorption coefficients of $[Rh(NH_3)_5(OH)]^{2+}$ and $[Rh(NH_3)_6]^{3+}$ at this wavelength, the ratio $[Rh(NH_3)_6{}^{3+}]/[Rh(NH_3)_5(OH)^{2+}]$ could be calculated as a function of $[NH_3]$ and $[NH_4^+]$. This ratio appeared to be independent of $[NH_3]$ and proportional to $[NH_4^+]$, which proves the formulation of the equilibrium constant $K^{5,6}$ according to equation (7).

$$K^{5,6} = [Rh(NH_3)_6{}^{3+}]/[Rh(NH_3)_5(OH)^{2+}][NH_4^+] = k_1^5/k_{-1}^6 \tag{7}$$

This means that in equation (5) the two terms refer to the forward (b_1) and the reverse (b_2) reaction of equilibrium (6), so that $b_1 = k_1^5$ and $b_2 = k_{-1}^6$. To check this interpretation the mean values of $K^{5,6}$, calculated from the absorbance measurements, and those calculated from the kinetic parameters are compared in Table 3. As can be seen from the values of $K^{5,6}$ and k_{-1}^6 the contribution of k_{-1}^6 to the overall reaction is generally small. Consequently, the accuracy of the photometrically determined $K^{5,6}$ is rather low, but both sets of $K^{5,6}$ values appear to follow each other closely, which reinforces the interpretation of equation (5). The activation parameters of k_1^5 and k_{-1}^6 are presented in Table 2. No curvature was found in the activation plots.

The medium dependence of the forward and the reverse reaction may now be used to work out a mechanism. The uptake of ammonia (k_1^5) appears to be independent of pH, so it may be concluded that OH^- is the leaving group and the reaction is not proceeding *via* the conjugate aquo-complex $[Rh(NH_3)_5(OH_2)]^{3+}$, as found for *trans*-$[Rh(NH_3)_4(OH)_2]^+$. Assuming again an interchange mechanism, k_1^5 will be equal to $k_{\text{ex.}}^5\beta^5$ (definitions as in the preceding reaction). The enthalpy of activation for the composite parameter k_1^5 is 133 kJ mol^{-1}, which is 30 kJ mol^{-1} higher than for the water exchange of $[Rh(NH_3)_5(OH_2)]^{3+}$; [6] as ΔH for β^5 may be expected to be close to zero [23] this difference reflects the difference in ease of leaving between OH^- and H_2O. This characteristic of the hydroxo-group of being a poor leaving group is also evident from the slow water exchange of $[Rh(NH_3)_5(OH)]^{2+}$ in basic aqueous solution.[25] The entropy of activation for both ammonia uptake and water exchange [6] is close to zero and because ΔS for β^5 will be rather small, the reaction of $[Rh(NH_3)_5(OH)]^{2+}$ with ammonia will proceed *via* an associative interchange (I_a) mechanism, like water exchange.[6]

The rate of the reverse reaction (k_{-1}^6) appears to be proportional to the ratio $[NH_3]/[NH_4^+]$, *i.e.* to the concentration of hydroxide ions in solution. The mechanism, which must be the microscopic reverse of the forward reaction (k_1^5), will then also be of the Eigen–Wilkins interchange type. Consequently the rate-determining step is the interchange between inner-sphere NH_3 and outer-sphere OH^-, analogous to reactions (3) and (4). One may even assume that the entering group assists the leaving group in loosening the Rh–O bond. Because both the reactions share the same transition state, a similar effect will appear in the forward reaction, and the transition state of reaction (6) will be as shown below.†

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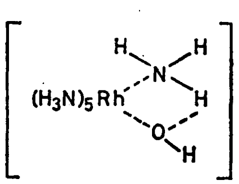
* Additional material available on request.

† This formulation of the transition state was suggested by one of the referees.

The proposed mechanism is very close to the Chan outer-sphere mechanism [26] for the base-catalyzed reactions of amine complexes. However, Bohte and Balt [14] have argued on the basis of a much more extensive set of data for the series of ammineaquocobalt(III) complexes, that the OH^{-}–NH_3 exchange can better be explained by the familiar conjugate-base (CB) mechanism.[27]



For the present case, because forward and reverse reactions must obey the principle of microscopic reversibility, the reaction sequence will be (A = NH_3) given by (8)—(11). In this scheme the hydroxo-compound attains a more reactive form by an intramolecular proton jump

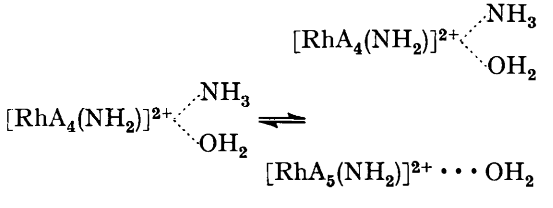
$$[RhA_5(OH)]^{2+} \overset{P}{\rightleftharpoons} [RhA_4(NH_2)(OH_2)]^{2+} \quad (8)$$

$$[RhA_4(NH_2)(OH_2)]^{2+} + NH_3 \overset{\beta^5}{\rightleftharpoons} [RhA_4(NH_2)(OH_2)]^{2+} \cdots NH_3 \quad (9)$$

$$[RhA_4(NH_2)(OH_2)]^{2+} \cdots NH_3 \underset{k_{CB}^6}{\overset{k_{CB}^5}{\rightleftharpoons}} [RhA_5(NH_2)]^{2+} \cdots OH_2 \quad (10)$$

$$[RhA_5(NH_2)]^{2+} + NH_4^{+} \overset{(K_{CB}^6)^{-1}}{\rightleftharpoons} [RhA_6]^{3+} + NH_3 \quad (11)$$

in a fast pre-equilibrium (P = equilibrium constant) (8). In this way the complex gains the easier leaving group H_2O and the labilizing group NH_2^{-}.[14] This cation forms an outer-sphere complex with ammonia (9). The rate-determining step for the forward and reverse reaction is the interchange of NH_3 and H_2O between inner and outer co-ordination sphere of the conjugate base (10). Although this concept of NH_3–H_2O interchange at the conjugate base is introduced here primarily for reason of simplicity of presentation, there are serious indications for the operation of similar processes in the base-catalyzed reactions of amine complexes, the S_N2CB [28] and the $S_N1(CB)IP$ mechanisms (IP = ion pair).[29] In addition, the base-catalyzed ammoniation of penta-amminerhodium(III) complexes in liquid ammonia exhibits activation parameters indicative of solvent assistance in the rate-determining step.[30] However, for the present case a two-step process for reaction (10) cannot be excluded, equations (10a) and (10b). Now a five-coordinate intermediate, presumably formed in a D process, is postulated. The mechanism may be progressively complicated by assuming a outer-sphere equilibrium of this intermediate with ammonia.



$$[RhA_4(NH_2)(OH_2)]^{2+} \cdots NH_3 \rightleftharpoons [RhA_4(NH_2)]^{2+}\begin{smallmatrix}\cdot\cdot\cdot NH_3\\ \cdot\cdot\cdot OH_2\end{smallmatrix} \quad (10a)$$

$$[RhA_4(NH_2)]^{2+}\begin{smallmatrix}\cdot\cdot\cdot NH_3\\ \cdot\cdot\cdot OH_2\end{smallmatrix} \rightleftharpoons [RhA_5(NH_2)]^{2+} \cdots OH_2 \quad (10b)$$

Without loss of generality the discussion here can be limited to the interchange CB mechanism. We have then equations (12) and (13). Coming back to k_{-1}^6, in order to make a more general comparison, the activation parameters for k_{-1}^6 were converted to the hydroxide scale by using the hydrolysis constant K^{NH_3} for ammonia.[21] A comparison of the activation parameters (Table 2) with literature data on $[Rh(NH_3)_5X]^{2+}$ complexes (X = Cl^- or Br^-)[2,3] indicates that both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for $k_{-1}^6 (K^{NH_3})^{-1}$ are extremely high. The activation parameters for base hydrolysis of $[Co(NH_3)_6]^{3+}$ are: $\Delta H^{\ddagger} = 146$ kJ mol^{-1} and $\Delta S^{\ddagger} = 130$ J K^{-1} mol^{-1},[31] so also compared to this complex the activation parameters for the base hydrolysis of the hexa-amminerhodium(III) ion are very high. These high values of both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are a further strong indication [27] that a CB mechanism is in operation.

$$k_1^5 = P\beta^5 k_{CB}^5 \quad (12)$$

$$k_{-1}^6 = K_{CB}^6 k_{CB}^6 \quad (13)$$

EXPERIMENTAL

Materials.—The compound $[Rh(NH_3)_5Cl]Cl_2$ was prepared according to a standard method.[32] It was converted to $[Rh(NH_3)_5(OH_2)][ClO_4]_3$ by boiling in aqueous sodium hydroxide, followed by filtration and precipitation with concentrated perchloric acid.[3] The complex was recrystallized from dilute perchloric acid. The u.v.–visible spectrum agreed with the previously published one [18] {Found: Rh, 20.3. Calc. for $[Rh(NH_3)_5(OH_2)][ClO_4]_3$: Rh, 20.4%}.

The compound $[Rh(NH_3)_6][NO_3]_3$ was prepared according to Thomas and Crosby,[33] freed from $[Rh(NH_3)_5(OH_2)][NO_3]_3$ as described,[34] and converted to the perchlorate salt by dissolving it in water, followed by precipitation with concentrated perchloric acid. Finally, the complex was recrystallized from dilute perchloric acid. The u.v.–visible spectrum agreed with literature data [18,35] {Found: Rh, 20.5. Calc. for $[Rh(NH_3)_6][ClO_4]_3$: Rh, 20.45%}.

trans-$[Rh(NH_3)_4(OH_2)_2][ClO_4]_3$. The compound $[Rh(NH_3)_5Cl]^{2+}$ was converted to *trans*-$[Rh(NH_3)_4(OH_2)H]^{2+}$ by a published procedure.[36] The latter complex was converted to the *trans*-diaquo-complex by adding H_2O_2 and boiling with $HClO_4$. Upon cooling and addition of concentrated $HClO_4$, the complex precipitated. The complex was recrystallized from dilute $HClO_4$. The u.v.–visible spectrum recorded in 0.10 mol dm^{-3} $HClO_4$ showed maxima at 353 and 273 nm, with absorption coefficients of 52 and 96 dm^3 mol^{-1} cm^{-1} respectively, which is in good agreement with published data [19] {Found: Rh, 20.5. Calc. for $[Rh(NH_3)_4(OH_2)_2][ClO_4]_3$: Rh, 20.35%}.

cis-$[Rh(NH_3)_4(OH_2)_2][ClO_4]_3$. The compound $[Rh(NH_3)_5Cl]^{2+}$ was converted to tetra-ammineoxalatorhodium(III), and the latter to *cis*-$[Rh(NH_3)_4Cl_2]^{+}$ by the method of Hancock.[37] The compound *cis*-$[Rh(NH_3)_4Cl_2]^{+}$ was boiled in 1 mol dm^{-3} aqueous Na[OH] for 30 min; after filtering the still hot solution *cis*-$[Rh(NH_3)_4(OH_2)_2][ClO_4]_3$ was precipitated by adding concentrated $HClO_4$. The complex was recrystallized from dilute $HClO_4$. The u.v.–visible spectrum showed maxima at 325 and 268 nm, with absorption coefficients of 106 and 90 dm^3 mol^{-1} cm^{-1}, respectively. This is in good agreement with the spectrum described by Hancock,[38] $\lambda = 326$ nm ($\varepsilon = 107$ dm^3 mol^{-1} cm^{-1}) and $\lambda = 268$ nm ($\varepsilon = 91$ dm^3 mol^{-1} cm^{-1}) {Found: Cl, 20.7; N, 11.0; O, 44.15. Calc. for $[Rh(NH_3)_4(OH_2)_2][ClO_4]_3$: Cl, 21.05; N, 11.1; O, 44.3%}. An attempt was made to prepare the *cis*-diaquo-complex by direct hydrolysis of tetra-ammineoxalatorhodium(III) in 1 mol dm^{-3} $HClO_4$. However, upon addition of concentrated $HClO_4$ and cooling, a white precipitate of varying properties formed. It is not clear yet what happens in this synthesis.

Kinetics.—The experimental set-up and procedure was the same as described previously.[21] The water–ammonia exchange of *trans*-$[Rh(NH_3)_4(OH)_2]^+$ was studied at five different temperatures between 68 and 90 °C at a constant ionic medium of 1.00 mol dm^{-3}, which was adjusted by adding a calculated amount of sodium perchlorate. The ammonia concentration was varied between 0.33 and 2.60 mol dm^{-3}, the ammonium perchlorate concentration between 0.04 and 0.40 mol dm^{-3}. The complex concentration was *ca.* 4×10^{-3} mol dm^{-3}. Isosbestic points were found at 342, 300, and 247 nm. The spectrum of the final product was identical to that of $[Rh(NH_3)_5(OH)]^{2+}$.[18] Reactions were followed at 272 and 330 nm; as no wavelength dependence of the observed rate constant was found, most of the reactions were followed only at 272 nm. At 81.4 and 88.5 °C, reactions were followed at five different NH_3 concentrations and five different NH_4^+ concentrations. At the other temperatures, four different NH_3 concentrations and five different NH_4^+ concentrations were selected.

The u.v.–visible spectrum of *cis*-$[Rh(NH_3)_4(OH)_2]^+$ at 76 °C and $[NH_3] = 1.33$ mol dm^{-3}, $[NH_4^+] = 0.20$ mol dm^{-3} showed a clear change in absorbance towards the spectrum of $[Rh(NH_3)_5(OH)]^{2+}$. Isosbestic points were found at 330, 290, 280, and 245 nm. However, upon varying the medium and temperature, no reproducible pattern emerged.

The slower reaction of $[Rh(NH_3)_5(OH)]^{2+}$ with ammonia needed much higher temperatures, so these reactions could not be studied in a conventional spectrophotometric cell.[21] Therefore, stainless steel vessels with Teflon coatings were used to contain the reaction mixtures. The vessels were kept in a thermostatted oil bath (temperature constancy ± 0.1 °C) and at appropriate time intervals a vessel was withdrawn, cooled, and the absorbance of a sample of the solution recorded at 342 nm on a Zeiss PMQ II spectrophotometer. Rate constants were calculated from 20 readings at 135 °C and 10 readings at the other temperatures (111.5, 125.0, 142.0 °C). The ionic medium was adjusted to 0.10 mol dm^{-3} by adding a calculated amount of $Na[ClO_4]$. The ammonia concentration was varied between 0.65 and 2.60 mol dm^{-3}, the ammonium perchlorate concentration between 0.02 and 0.08 mol dm^{-3}. The complex concentration was *ca.* 3×10^{-3} mol dm^{-3}. Isosbestic points were found at 310, 293, and 260 nm. During the reaction the absorption maxima of the solution moved towards those reported for $[Rh(NH_3)_6]^{3+}$.[18,35] At 111.5 and 125.0 °C reactions were followed at four different NH_3 concentrations and five, and four respectively, different NH_4^+ concentrations. At 135.0 and 142.0 °C, five NH_3 concentrations and four NH_4^+ concentrations were selected.

All reactions studied kinetically obeyed a first-order rate law; the fitting error was always within 1%. Varying the complex concentration over one order of magnitude did not influence the observed rate constant within the fitting error. First-order rate constants were obtained by a computerized least-squares method.[39] Activation parameters were calculated by means of a least-squares method on the basis of the Eyring formula.[39] The pH was measured with a Mettler DK10/DK11 pH-meter, using an Electrofact 7 G 411 glass electrode and a sodium sulphate reference electrode, calibrated with NBS buffers. Ammonia concentrations were measured with an EIL 8002-2 ammonia selective electrode.

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