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FULL PAPER

Variable-pressure kinetic study of bromide complexation on aquarhodium(III) †

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A variable-pressure kinetic study of the complexation of bromide with $Rh^{3+}(aq)$ ($I = 2.03$ mol dm^{-3} ($NaClO_4^-$), range 0.1–206.8 MPa) as a function of $[H^+]$ (0.06–1.00 mol dm^{-3}) at 70 °C is reported. The final product is *trans*-$[Rh(OH_2)_4Br_2]^+$ with formation of the bromopentaaqua ion rate determining. The decrease in the extent of rate saturation with $[Br^-]$ observed on lowering $[H^+]$ below 0.20 mol dm^{-3} is consistent with greater participation from the more labile pentaaquahydroxo ion in a parallel ion-pair interchange processes with the hexaaqua ion but with K_{os} ($RhOH^{2+}$–Br^-) < K_{os} (Rh^{3+}–Br^-). Complexation on the hexaaqua ion is associatively activated ($\Delta V^{\ddagger}_{I} = -3.3 \pm 1.0$ cm^3 mol^{-1}) but dissociatively activated on the pentaaquahydroxo species ($\Delta V^{\ddagger}{}_{I}{}^{OH} = +7.7 \pm 1.0$ cm^3 mol^{-1}). These findings support the recent *ab-initio* calculations by Rotzinger *et al.* and variable-pressure kinetic study of the water exchange process by Merbach *et al.* which indicate a favourable I_a pathway for low-spin $[Rh(OH_2)_6]^{3+}$ despite its $t_{2g}{}^6$ configuration. Earlier proposals of a D process for both ions on the basis of the observed rate saturation can now be discounted and the present findings lend further compelling support for the use of the activation volume as a powerful mechanistic probe. Reasons for the greater penetration by the entering donor within replacement reactions on 4d and 5d M^{3+} complexes are considered.

Introduction

The mechanism of water ligand exchange and replacement (interchange) on the 2nd row aqua ion $[Rh(OH_2)_6]^{3+}$ has been the subject of much debate.[1,2] Its low spin $t_{2g}{}^6$ configuration suggests it should prefer a dissociatively-activated process since bond formation with any entering ligand should be highly restricted. This was initially supported by the work of Harris and coworkers in the 1970s[3–5] who found virtually identical rate constants and similar activation enthalpies for substitution on $[Rh(OH_2)_6]^{3+}$ by Cl^- and Br^- ions and by H_2O ($k \sim 2$–3×10^{-9} s^{-1}, $\Delta H^{\ddagger}$ 120–131 kJ mol^{-1}). Furthermore they assigned an extreme D mechanism to the process as a result of downward curvature detected in k_{obs} *vs.* $[X^-]$ plots in H^+ range 0.5–2.0 mol dm^{-3} according to eqns. (1)–(3)

$$[Rh(OH_2)_6]^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Rh(OH_2)_5]^{3+} + H_2O \qquad (1)$$

$$[Rh(OH_2)_5]^{3+} + L \xrightarrow{k_2} [Rh(OH_2)_5L]^{3+} \qquad (2)$$

$$\text{Rate} = \frac{k_1k_2[Rh(OH_2)_6{}^{3+}][L]}{k_{-1} + k_2[L]} \qquad (3)$$

below for the condition where $k_2[L] \approx k_{-1}$ with eventual saturation occurring at high [L] when $k_2[L] \gg k_{-1}$. The presence of the D mechanism on $[Rh(OH_2)_6]^{3+}$ was also previously envoked to explain the formation of the final product *trans*-$[Rh(OH_2)_4X_2]^+$ (X = Cl^- or Br^-) *via* a rapid second halide substitution on the initially formed $[Rh(OH_2)_5X]^{2+}$ *via trans*-labilisation from X in a further D process. Subsequent variable-pressure ^{17}O NMR kinetic studies however are in conflict with this mechanism with negative $\Delta V^{\ddagger}$ values for water exchange obtained for $[Rh(OH_2)_6]^{3+}$ (–4.2 cm^3 mol^{-1})[6] and for its heavier group partner $[Ir(OH_2)_6]^{3+}$ (−5.7 cm^3 mol^{-1})[7] not consistent with operation of eqns. (1) and (2) but rather suggestive of associative interchange (I_a) processes.

The pre-association of reactants (the Eigen–Wilkins mechanism) is generally accepted as a relevant process central to the majority of ligand substitution (anation) processes in aqueous solution.[8] The Eigen–Wilkins interchange mechanism is shown in eqns. (4) and (5).

$$[Rh(OH_2)_6]^{3+} + L \overset{K_{os}}{\rightleftharpoons} [Rh(OH_2)_6]^{3+}, L \qquad (4)$$

$$[Rh(OH_2)_6]^{3+}, L \xrightarrow{k_1} [Rh(OH_2)_5L]^{n+} + H_2O \qquad (5)$$

Here detectable downward curvature (saturation) in plots of k_{obs} *vs.* [L] arises from either a significantly large value for the reactant-pair association constant K_{os} (frequently the case when oppositely charged reactants are involved as is the case here) or from a high value of [L] or a combination of both, *i.e.* when $K_{os}[L] \gg 1$ in eqn. (6).

$$\text{Rate} = \frac{k_1K_{os}[Rh(OH_2)_6{}^{3+}][L]}{(1 + K_{os}[L])} \qquad (6)$$

In an attempt to resolve this apparent conflict Rotzinger and Merbach[9] recently modelled the energetics of water replacement on $[Rh(OH_2)_6]^{3+}$ using an *ab-initio* quantum mechanical treatment. The aim was to characterise the transition states involved for the I_a and D processes on $[Rh(OH_2)_6]^{3+}$ and to calculate their respective activation energies. The D process was found to operate with a value for the activation enthalpy (136.6 kJ mol^{-1}) significantly higher by 21.8 kJ mol^{-1} than for the associative I_a pathway (114.8 kJ mol^{-1}) which itself is close to the values observed experimentally for water replacement

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† Electronic supplementary information (ESI) available: further kinetic data and plots (Fig. 1S, Table 1S and 2S). See http://www.rsc.org/suppdata/dt/b2/b207017k/

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reactions.[5,6] Furthermore the calculated Rh–OH_2 bond length for the leaving water ligand within the lowest energy pathway was far below that predicted by the D process, the latter requiring the leaving water in the TS to reside in the secondary hydration shell. The facilitation of the I_a process was explained in terms of intrinsically strong Rh–OH_2 bonds which disfavour the alternative D (or I_d) pathway. This calls into question the mechanistics (eqns. (1) and (2)) proposed previously by Harris.

Herein we report a reinvestigation of the kinetics of the Br^- anation process on Rh^{3+}(aq) at 70 °C under conditions of variable [Br^-], [H^+] and pressure. The present results provide compelling evidence for a classical Eigen—Wilkins ion-pair interchange I_a mechanism operating for Br^- anation on $[Rh(OH_2)_6]^{3+}$ thereby supporting the conclusions of the more recent theoretical modelling and water exchange studies. Corresponding Br^- anation on $[Rh(OH_2)_5OH]^{2+}$ occurs *via* a parallel I_d process.

Experimental

Materials

Solutions of Rh^{3+}(aq) in dilute perchloric acid were prepared by refluxing $RhCl_3{\cdot}3H_2O$ (Johnson-Matthey) in fuming 70% aqueous perchloric acid followed by Dowex® 50WX2 cation-exchange chromatographic purification as described previously.[10] Stock solutions of Rh^{3+}(aq) were standardised at the peak maxima at 311 nm (ε = 67.4 $dm^3\ mol^{-1}\ cm^{-1}$) and 396 nm (62 $dm^3\ mol^{-1}\ cm^{-1}$). Sodium bromide, sodium perchlorate and perchloric acid (all Aldrich AR grade) were used as supplied. Stock solutions of sodium bromide and perchlorate and the H^+ concentration of Rh^{3+}(aq) solutions were determined by exchange onto a column of Dowex® 50WX8 cation-exchange resin (H^+ form, 50–100 µm mesh) and titration of the liberated H^+ with standard aqueous NaOH.

Kinetic studies

The progress of the Br^- anation reaction was carried out at 70.0 ± 0.1 °C by monitoring the appearance of the product *trans*-$[Rh(OH_2)_4Br_2]^+$ at 483 nm under pseudo first order conditions with [Br^-] in large excess (0.10–1.00 mol dm^{-3}) over $[Rh^{3+}]_T$ (1–2 × 10^{-3} mol dm^{-3}). The [H^+] was varied from 0.06–1.00 mol dm^{-3} and the ionic strength (2.03 mol dm^{-3}) was maintained with sodium perchlorate. Doubly distilled water was used throughout.

For the high pressure studies (up to >200 MPa) the reaction solutions were loaded into a pressure transmitting cylindrical pill-box type quartz cuvette immersed within an atmosphere of *n*-hexane (Aldrich HPLC grade) inside a 1 cm thick stainless steel cylindrical autoclave fitted with optically-transmitting sapphire windows which was located within the beam of the spectrophotometer. Use of such a cell has been described previously.[11]

The pressure was applied manually *via* a hydraulic syringe pump. Rate constants (k_{obs}) for each condition of [Br^-], [H^+] and pressure were obtained over at least 2–3 half lives in most cases by an iterative fit of the absorbance rise at 483 nm *vs*. time using a standard exponential function provided by the GRAFIT® software program.[12]

Results and discussion

As in the earlier studies of Buchacek and Harris[5] the product of the reaction under these conditions is *trans*-$[Rh(OH_2)_4Br_2]^+$ (λ_{max} = 483 nm) with formation of $[Rh(OH_2)_5Br]^{2+}$ rate determining. Fig. 1 shows k_{obs} values (h^{-1}) plotted *vs.* [Br^-] at each value of [H^+] employed. Rate constants (k_{obs}, s^{-1}) determined at 0.1 MPa are tabulated as a function of [Br^-] and [H^+] in the supplementary material (ESI, Table S1 †). As previously observed[5] the k_{obs} *vs.* [Br^-] plots in the [H^+] range 0.50–1.00 mol dm^{-3} show distinct downward curvature and eventual saturation for [Br^-] values >1.00 mol dm^{-3}. This is illustrated in Fig. 1S of the ESI for the [H^+] range 0.22–1.00 mol dm^{-3}. In the present study however, we extended the [H^+] range to much lower values (0.06 mol dm^{-3}) but still expected to see detectable downward curvature throughout if the extreme D process (1) and (2) proposed by Harris and coworkers was relevant since $[Rh(OH_2)_5OH]^{2+}$ should also participate. Instead for [H^+] values <0.22 mol dm^{-3} we obtained linear plots of k_{obs} *vs.* [Br^-], Fig. 1, over the range of [Br^-] employed. This clearly demonstrates that an extreme D process cannot be relevant for this system. Instead these results point clearly to operation of Eigen–Wilkins ion-pair pre-association interchange process with plots of k_{obs} *vs.* [Br^-] becoming linear at the lower acidities due to increased involvement from $[Rh(OH_2)_5OH]^{2+}$ with $K_{os}^{OH}[Br^-] \leqslant 1$ due to a smaller value of K_{os}^{OH} in the overall scheme shown below (eqns. (7)–(14)).

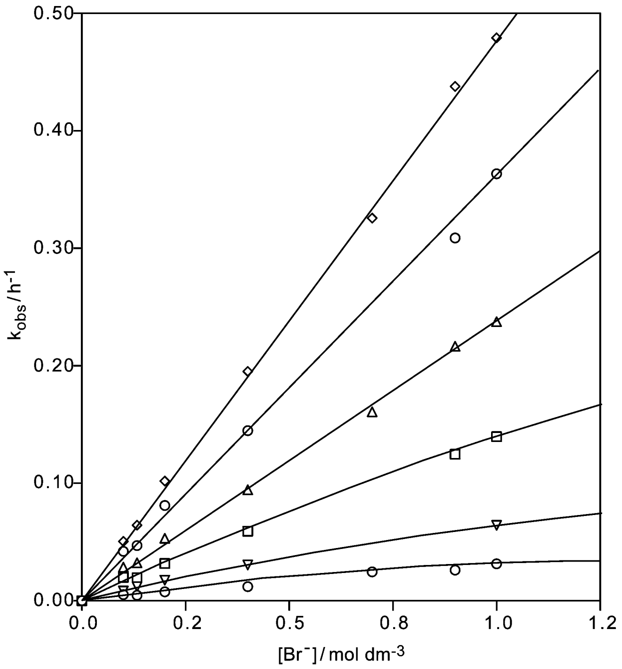

Fig. 1 Plots of k_{obs} values (h^{-1}) *vs.* [Br^-] (0.10–1.00 mol dm^{-3}) for [H^+] values; 0.06 (◇), 0.09 (○) 0.13 (△), 0.22 (□), 0.50 (▽) and 1.00 mol dm^{-3} (○), T = 70 °C, I = 2.03 mol dm^{-3} ($NaClO_4$).

$$[Rh(OH_2)_6]^{3+} + Br^- \xrightleftharpoons{K_{os}} [Rh(OH_2)_6]^{3+}, Br^- \tag{7}$$

$$[Rh(OH_2)_6]^{3+} \xrightleftharpoons{K_{aRh}} [Rh(OH_2)_5OH]^{2+} + H^+ \tag{8}$$

$$[Rh(OH_2)_5OH]^{2+} + Br^- \xrightleftharpoons{K_{os}^{OH}} [Rh(OH_2)_5OH]^{2+}, Br^- \tag{9}$$

$$\begin{tikzcd}
{[Rh(OH_2)_6]^{3+}, Br^-} \arrow[dr, "k_1"] & \\
& {[Rh(OH_2)_5Br]^{2+}} \\
{[Rh(OH_2)_5OH]^{2+}, Br^-} \arrow[ur, "k_1^{OH}"'] &
\end{tikzcd} \tag{10}$$

$$[Rh(OH_2)_5Br]^{2+} \xrightarrow[Br^-]{fast} trans\text{-}[Rh(OH_2)_4Br_2]^+ \quad \lambda_{max} = 483\,nm \tag{11}$$

$$Rate = \frac{k_1K_{os}[Rh(OH_2)_6{}^{3+}][Br^-]}{(1 + K_{os}[Br^-])} + \frac{k_1{}^{OH}K_{os}{}^{OH}[Rh(OH_2)_5OH^{2+}][Br^-]}{(1 + K_{os}{}^{OH}[Br^-])} \tag{12}$$

Table 1 Values of k_IK_{os} (Rh^{3+}) and $k_I^{OH}K_{os}^{OH}K_{aRh}$ ($RhOH^{2+}$) *vs.* P/MPa, T = 70 °C, I = 2.03 mol dm^{-3} ($NaClO_4$)

Pressure/MPa	$10^6k_IK_{os}$/dm^3 mol^{-1} s^{-1}	$10^6k_I^{OH}K_{os}^{OH}K_{aRh}$/s^{-1}
0.1	3.26 ± 2.24	8.30 ± 0.24
68.9	3.35 ± 2.06	6.02 ± 0.22
137.8	3.57 ± 1.27	4.99 ± 0.13
206.8	3.53 ± 1.53	4.04 ± 0.16

$$\text{Rate} = k_{obs}[Rh^{3+}]_T \tag{13}$$

$$k_{obs} = \left(\frac{k_IK_{os}[H^+]}{(K_{aRh}+[H^+])(1+K_{os}[Br^-])} + \frac{k_I^{OH}K_{os}^{OH}K_{aRh}}{(K_{aRh}+[H^+])(1+K_{os}^{OH}[Br^-])}\right)[Br^-] \tag{14}$$

It is clear that in the earlier work by Buchacek and Harris[5] the kinetic study had not been extended to low enough acidities in order to fully resolve the contribution from $[Rh(OH_2)_5OH]^{2+}$, the second term in eqns. (12) and (14). The linearity of k_{obs} *vs.* $[Br^-]$ plots for $[H^+]$ values <0.22 mol dm^{-3} indicates that the second term in eqn. (14) dominates under these conditions with $k_I^{OH} \gg k_I$ despite the smaller value of K_{os}^{OH} such that $K_{os}^{OH}[Br^-] \ll 1$. Since under the conditions of the study $K_{aRh} \ll [H^+]$ (eqn. (14)) can be reduced to eqn. (15) for the linear plots of k_{obs} *vs.* $[Br^-]$ at the lower acidities.

$$\frac{k_{obs}}{[Br^-]} = k_IK_{os} + \frac{k_I^{OH}K_{os}^{OH}K_{aRh}}{[H^+]} \tag{15}$$

For the curved k_{obs} *vs.* $[Br^-]$ plots at the higher acidities $k_{obs}/[Br^-]$ was taken as the initial slope of the dependence of k_{obs} on $[Br^-]$ as $[Br^-] \longrightarrow 0$ wherein $K_{os}[Br^-] \ll 1$. These values are available as ESI (Table 2S) and consistent with this linear plots of $k_{obs}/[Br^-]$ *vs.* $[H^+]^{-1}$ (eqn. (15)) (Fig. 2) were obtained from which values of k_IK_{os} (dm^3 mol^{-1} s^{-1}) and $k_I^{OH}K_{os}^{OH}K_{aRh}$ (s^{-1}), representing the individual contributions from $[Rh(OH_2)_6]^{3+}$ and $[Rh(OH_2)_5OH]^{2+}$, can be evaluated from the intercept and slope respectively.

Values of k_IK_{os} and $k_I^{OH}K_{os}^{OH}K_{aRh}$ at four reaction pressures are listed in Table 1. At 1 atm (0.1 MPa) the value of $k_I^{OH}K_{os}^{OH}$ at 70 °C is 8.3 × 10^{-3} dm^3 mol^{-1} s^{-1} assuming K_{aRh} (70 °C) = 1.0 × 10^{-3} mol dm^{-3}.[3] If one assumes values of K_{os} and K_{os}^{OH} as ~1.4 and ~0.2 dm^3 mol^{-1}, respectively (perfectly reasonable within experimental error with those obtained empirically[13] and by experiment[1] at ionic strength ~2.0 mol dm^{-3}), the resulting values of k_I (Table 1) and k_I^{OH} at 0.1 MPa and T = 70 °C are then identical to those obtained for water exchange respectively on $[Rh(OH_2)_6]^{3+}$ and $[Rh(OH_2)_5OH]^{2+}$ under the same conditions (2.3 × 10^{-6} s^{-1} and 4.2 × 10^{-2} s^{-1}).[6] The rate constants reported by Buchacek and Harris[5] for eqns. (1) and (2) are for the composite term k_1k_2/k_{-1} and can therefore not be compared with those evaluated here.

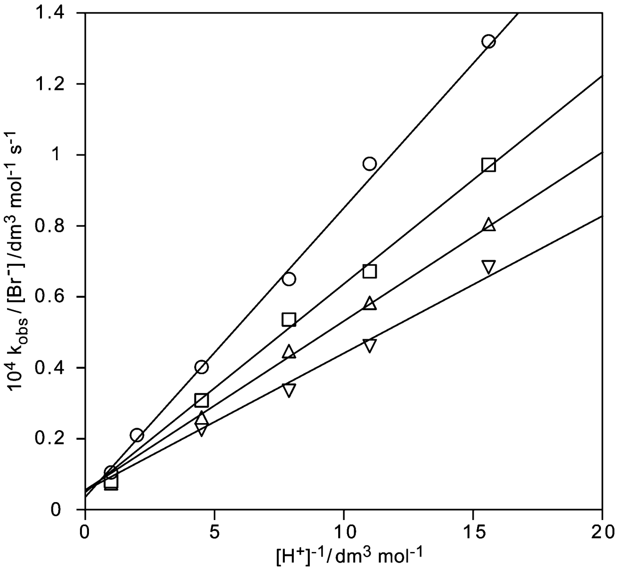

Fig. 2 Plots of $k_{obs}/[Br^-]$ *vs.* $[H^+]^{-1}$ as a function of pressure (MPa), 0.1 (○), 68.9 (□), 137.8 (Δ) 206.8 (∇). For the curved plots of k_{obs} *vs.* $[Br^-]$ for $[H^+]$ values >0.13 mol dm^{-3} the value of $k_{obs}/[Br^-]$ was taken as the initial slope as $[Br^-] \longrightarrow 0$.

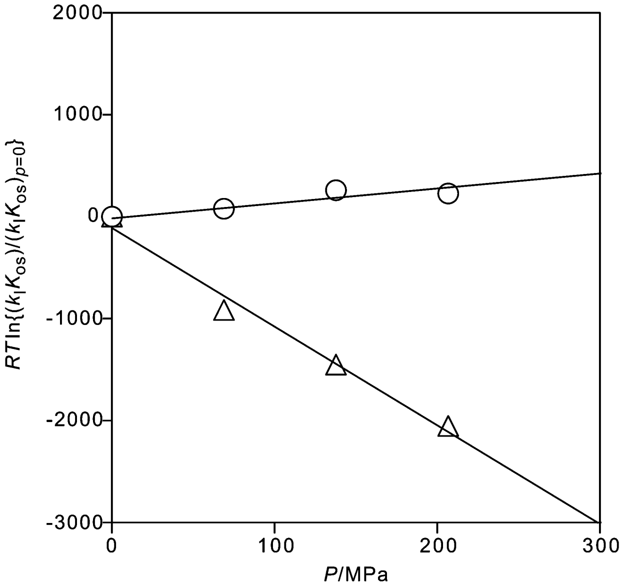

Fig. 3 Plots of $RT\ln\{(k_IK_{os})/(k_IK_{os})_{P=0}\}$ (○) and $RT\ln\{(k_I^{OH}K_{os}^{OH}K_{aRh})/(k_I^{OH}K_{os}^{OH}K_{aRh})_{P=0}\}$ (Δ) *vs.* P (MPa), T = 70 °C, I = 2.03 mol dm^{-3} ($NaClO_4$).

Plots of the natural logarithm respectively of k_IK_{os} and $k_I^{OH}K_{os}^{OH}K_{aRh}$ *vs.* pressure (MPa) are shown in Fig. 3 and these allow a determination of the activation volume, $\Delta V^\ddagger_{obs}$ for each process from the slopes respectively (× RT).[14] From the pressure dependance of k_IK_{os} (Br^- anation on $[Rh(OH_2)_6]^{3+}$), $\Delta V^\ddagger_{obs} = \Delta V^\ddagger_I + \Delta V^\circ_{os} = -1.3 \pm 1.0$ cm^3 mol^{-1} From the pressure dependance of $k_I^{OH}K_{os}^{OH}K_{aRh}$ (Br^- anation on $[Rh(OH_2)_5OH]^{2+}$) $\Delta V^\ddagger_{obs} = \Delta V^{\ddagger OH}_I + \Delta V^{\circ OH}_{os} + \Delta V^\circ_{KaRh} = +9.7 \pm 0.5$ cm^3 mol^{-1}. Values of ΔV°_{os} (3+/1− pair) and $\Delta V^{\circ OH}_{os}$ (2+/1− pair) can be estimated from electrostatic models.[15] Values of ~ +2 ± 1 cm^3 mol^{-1} are relevant for either pair at ionic strengths ≥ 1.0 mol dm^{-3}.[16] Taking the value for ΔV°_{KaRh} as −0.2 cm^3 mol^{-1}[6] allows values of $\Delta V^\ddagger_I$ ($[Rh(OH_2)_6]^{3+}$) and $\Delta V^{\ddagger OH}_I$ ($[Rh(OH_2)_5OH]^{2+}$) for the interchange (substitution) step to be calculated as −3.3 ± 1.0 cm^3 mol^{-1} and +7.7 ± 1.0 cm^3 mol^{-1}, respectively, which may be compared with the values obtained for water exchange respectively on the two ions of −4.2 cm^3 mol^{-1} and +1.5 cm^3 mol^{-1}.[6] Thus the rate constants and activation volumes obtained here for Br^- anation on Rh^{3+}(aq) are consistent with operation of an Eigen–Wilkins ion-pair interchange mechanism which is associatively-activated (I_a) on $[Rh(OH_2)_6]^{3+}$ but dissociatively-activated (I_d) on the lower charged monohydroxo ion $[Rh(OH_2)_5OH]^{2+}$. These findings corroborate the conclusions reached from the water exchange study and the recent *ab-initio* modelling of the energetics along the reaction coordinate and provide further support for the use of activation volumes as powerful mechanistic indicators of substitution reactions. The similar values of rate constants obtained for water exchange and Br^- and Cl^- anation on $[Rh(OH_2)_6]^{3+}$ are thus not an indication of the operation of a limiting dissociative process but merely evidence of a lack of a discrimination for these ligands by $[Rh(OH_2)_6]^{3+}$ within the I_a mechanism. The significantly more positive value of $\Delta V^\ddagger_I$ seen here for the $[Rh(OH_2)_5OH]^{2+}$,Br^- ion–pair ($+7.7$ cm^3 mol^{-1}) than that obtained for the symmetric water exchange process reflects a weaker interaction with the departing water molecule at the transition state (longer Rh–OH_2 bond) as a consequence of charge neutralisation and desolvation.

A similar I_a mechanism would appear to operate for 1:1 substitution reactions on t_{2g}^6 $[Ir(OH_2)_6]^{3+}$ ($\Delta V^{\ddagger}_{H_2O} = -5.7$ cm^3 mol^{-1})[7] leaving $t_{2g}^6e_g^4$ ion $[Ga(OH_2)_6]^{3+}$ ($\Delta V^{\ddagger}_{H_2O} = +5.0$ cm^3 mol^{-1})[1,2] as the only 4d hexaaqua trivalent ion favouring a dissociatively-activated pathway. It has been commonly assumed that associative mechanisms can only operate on metal centres with partly filled t_{2g} orbitals. While size (available space between resident ligands) will play a role in the defining the extent of penetration into the primary coordination sphere by any entering ligand (the radius of Ga^{3+} (62 pm) being somewhat smaller than that for Rh^{3+} (67 pm)[17]) it appears that this cannot be the only factor explaining the apparent accommodation of an extra (seventh) ligand, at least partially, within transition states arising from reactions at ground state t_{2g}^6 octahedral centres. *Ab-initio* calculations have revealed that the negative activation volume for water exchange on $[Rh(OH_2)_6]^{3+}$ (-4.2 cm^3 mol^{-1}) is due to the decrease in volume resulting from the loss of part of the molar volume of the incoming water molecule as it penetrates the primary coordination sphere in forming the I_a transition state. Attempted imposition of the alternative D process results in a significantly higher activation energy by ~22 kJ mol^{-1} due to the intrinsic strength of the resident Rh–OH_2 bonds.[9] Thus the I_a pathway is able to compete successfully with the D process and is the mechanistic path of choice for $[Rh(OH_2)_6]^{3+}$. Since similar calculations on the isoelectronic t_{2g}^6 ion $[Ru(OH_2)_6]^{2+}$ indicate a D (or I_d process)[9] it appears that the greater charge on the trivalent $[Rh(OH_2)_6]^{3+}$ is a dominant factor promoting the greater penetration by the entering ligand in forming the transition state in the latter case.

In regard to the mechanism of formation of *trans*-$[Rh(OH_2)_4Br_2]^+$ and of further bromo–aqua products it is noted that significantly positive activation volumes (~$+15$ cm^3 mol^{-1}) have been obtained from kinetic studies of both aquation and Cl^- substitution on $[RhCl_4(OH_2)_2]^-$, $[RhCl_5(OH_2)]^{2-}$ and $[RhCl_6]^{3-}$.[18] Thus it is highly likely that following the rate-determining entry of the first Br^- ligand into the Rh^{3+} coordination sphere subsequent Br^- substitutions occur by dissociatively-activated pathways promoted by steric/electronic/charge neutralising effects from the resident Br^- ligand(s).

We can thus conclude in general terms that the preferred ligand substitution mechanism is governed by an interplay between the following; (i) the available space between the resident ligands (sterics), (ii) the strength of the bond to the resident ligand being replaced, (iii) the presence of strong σ-donation from certain resident ligands *e.g.* Cl^-, Br^- or OH^- and (iv) the electrostatic attraction for the entering ligand (defined by the size of the cationic charge on the complex). For hexaaqua ions (iii) can be largely neglected. However for $[Rh(OH_2)_6]^{3+}$ (ii) is very high and with (iv) also high this allows the I_a process to compete successfully. In the case of $[Ru(OH_2)_6]^{2+}$ however (ii) and (iv) are both lower and this allows the D (I_d) process to become energetically favourable. For $[Ga(OH_2)_6]^{3+}$ both (i) and (ii) are low which compensates for (iv) being high so the D (I_d) process is again the preferred process. On the other hand substitution processes on $[Rh(OH_2)_5OH]^{2+}$ and on other hydroxopentaaqua trivalent ions (*e.g.* M = Cr, Fe, Ru, Ir, Ga)[1,2] are dissociative (I_d) in character throughout governed by the presence of (iii) (from OH^-) causing both (ii) and (iv) to decrease, the latter due to the partial negative charge induced over all resident ligands and the resulting lower overall cationic charge on the complex. Finally in the case of the chloro–aqua complexes of Rh^{III} (iii) is also a significant factor and with (i), (ii) and (iv) all lower, as a result of the resident Cl^- ligands, the dissociative pathway becomes favoured. Indeed the values of $\Delta V^{\ddagger}$ (~ $+15$ cm^3 mol^{-1}) for both Cl^- anation and aquation reactions on $[RhCl_4(OH_2)_2]^-$ and $[RhCl_5(OH_2)]^{2-}$[18] indicate these to be more realistic candidates for the extreme D process.[2,19]

Acknowledgements

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