

# Slow Proton Exchange Kinetics in Aqueous Solutions of Hexaaquarhodium(III): Influence of the Second Hydration Sphere

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Received February 11, 1994<sup>⊗</sup>

The exchange processes between water protons in the first hydration sphere of the rhodium(III) ion and water protons in the bulk solvent have been studied using <sup>1</sup>H NMR spectroscopy. The pseudo-first-order rate constants for proton exchange between bulk water and the first hydration sphere of rhodium(III) have been determined as a function of pH at 293 K from <sup>1</sup>H NMR line-broadening experiments on aqueous solutions of rhodium(III), at magnetic field strengths of 5.87 T (250 MHz) and 9.40 T (400 MHz). A minimum in the rate of proton exchange is observed at pH ≈ 3 where the average lifetime of a specific proton in the first hydration sphere is  $\tau_{\text{H}}^{\text{Rh}} = 7$  ms in an 0.1 M solution of Rh(III). The rate of proton exchange increases with increasing pH when pH > 3 indicating a reaction path involving exchange between  $[\text{Rh}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  and bulk water protons. When pH < 3, the rate of proton exchange increases asymptotically with decreasing pH. The pH dependence in this acidic region is explained by a mechanism for which the rate-determining step is the exchange of a proton from a hydronium ion in the second hydration sphere of rhodium(III) with one in the bulk. At very low pH (< 1) the proton exchange rate approaches a constant value where a rate-determining step involving transfer of a proton from  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  to the second sphere of hydrogen-bonded water molecules is proposed. The rate constant for this process is  $k_1 = 6.0 (\pm 0.2) \times 10^4 \text{ s}^{-1}$ . The direct exchange between first sphere water protons in  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  and bulk water protons is too slow to be detected. The acid dissociation constants for  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ ,  $\text{p}K_{\text{a}1} = 3.6 \pm 0.1(2\sigma)$ , and  $[\text{Rh}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ ,  $\text{p}K_{\text{a}2} = 4.7 \pm 0.2(2\sigma)$ , have been determined by potentiometry in the ionic medium used in the kinetic experiments  $\{[\text{ClO}_4^-] = 3 \text{ M}; 3[\text{Rh}^{3+}] + [\text{Li}^+] + [\text{H}^+] = 3 \text{ M}\}$ .

## Introduction

The hexahydrated metal ions rhodium(III), chromium(III) and aluminum(III) have recently been shown to be essentially isostructural with respect to their hydration structures in aqueous solution, all three having well-defined first and second hydration spheres.<sup>1,2</sup> The structural ordering of these ions beyond the first hydration sphere has been attributed to the formation of strong hydrogen bonds between water molecules in the first and second hydration spheres.<sup>2</sup>

In aqueous solution these metal ions perform their translational and rotational motion accompanied by an average of about 18 water molecules (6 in the first sphere and about 12 in the second).<sup>1–3</sup> The average lifetime of a water-oxygen atom in the first hydration sphere of these ions is  $\tau_{\text{O}}^{\text{Al}} \approx 0.8 \text{ s}$ ,  $\tau_{\text{O}}^{\text{Cr}} \approx 4 \times 10^5 \text{ s}$ , and  $\tau_{\text{O}}^{\text{Rh}} \approx 5 \times 10^8 \text{ s}$ .<sup>4–6</sup> Exchange of water molecules between the second hydration sphere and the surrounding bulk solvent is, however, much faster.<sup>3</sup> Therefore, the rate-determining step in the exchange of water molecules between  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  and the bulk water must involve transfer of a water oxygen from the first to the second hydration sphere.

Similarly, hindrance posed by the second hydration sphere can be expected to affect the rate and mechanism of proton

exchange between  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  and bulk water. The kinetics of proton exchange between water molecules in the first hydration sphere of trivalent metal ions and water molecules in the bulk solvent have previously been studied for aqueous solutions of hexahydrated aluminum(III)<sup>7</sup> and various chromium(III) species.<sup>8–11</sup> For these metal ions, description of the proton exchange reactions between coordinated water molecules and the bulk water is simplified by the negligibly slow rate of the corresponding oxygen atom exchange.<sup>12</sup> In spite of this simplification, a diversity of mechanistic interpretations have been proposed in order to explain the variation in the observed rate of proton exchange as a function of pH for hexahydrated chromium(III)<sup>8,9</sup> and aluminum(III).<sup>7</sup>

Generally, proton exchange between hydrated metal ions and water proceeds via three parallel pathways.<sup>10</sup> In the case of chromium(III), all three paths were found and discussed: (1) Around pH = 0 an increase in the rate of proton transfer was observed which was attributed to the protonation of hexaaquachromium(III) ions in the rate-determining step.<sup>8</sup> The explanation of this acid-dependent path was later modified<sup>9</sup> whereby coordinated water in the second hydration sphere was believed to function as a bridge for the transfer of protons to the bulk water. (2) The inverse acid dependence of the rate of proton transfer at pH > 2 was attributed to the formation of hydroxo complexes. (3) On the other hand, the acid independent region

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<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, March 15, 1995.

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at  $\text{pH} \approx 1 - 2$  was explained by the simple transfer of a proton from the hexaquaaluminum(III) ion to an adjacent bulk water molecule.

Grünwald introduced a new concept for the case of hexaquaaluminum(III) ions in which the contribution of several solvent molecules was discussed.<sup>7,13</sup> For aluminum(III), an acid-dependent increase in the rate of proton transfer was not observed although studies were conducted down to  $\text{pH} = 0.5$ .<sup>7</sup> At low pH, the proton transfer was believed to occur by donation of a proton from the first hydration sphere of the hexaquaaluminum(III) ion to a water molecule in the second hydration sphere.<sup>7</sup> At higher pH the rate of proton exchange was found to be proportional to the square of the total aluminum ion concentration, but with an inverse acid dependence. This observation was explained by a mechanism involving proton exchange between the pentaquaammonohydroxoaluminum(III) ion and the bulk water, in which the hexaquaaluminum(III) ion also participated. A more recent study of the aluminum(III) system claims first-order acid dependence at very low pH.<sup>14</sup>

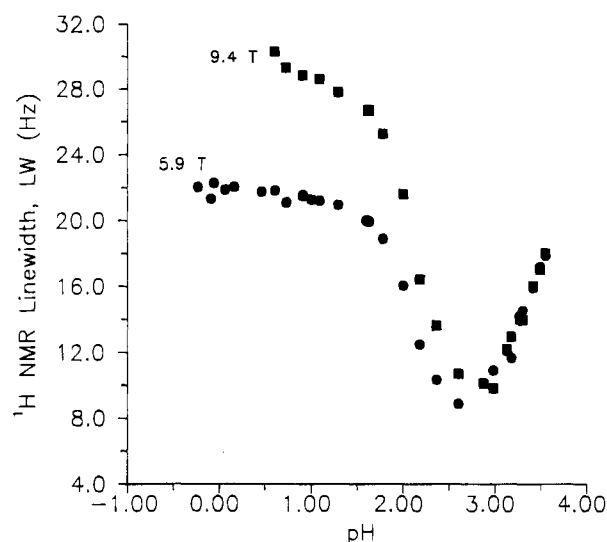
In the present study we have investigated proton exchange phenomena of hexahydrated rhodium(III) ions in aqueous solution to allow comparison with the previously studied aluminum(III) and chromium(III) systems and to provide a mechanistic interpretation in the light of the detailed structural information now available.<sup>1,2</sup>

NMR spectroscopy has been the method of choice in this study since the rate of proton exchange is such that the kinetics may be conveniently followed by the  $^1\text{H}$  NMR line-broadening technique. As a preliminary to the data treatment, the acid dissociation constants for the hexaquaaluminum(III) and pentaquaammonohydroxorhodium(III) ions were determined in the ionic medium used in the kinetic experiments  $\{[\text{ClO}_4^-] = 3 \text{ M}; 3[\text{Rh}^{3+}] + [\text{Li}^+] + [\text{H}^+] = 3 \text{ M}\}$ .

## Experimental Section

The acid dissociation constants for the hexaquaaluminum(III) ion,  $\text{p}K_{\text{a}1}$ , and the pentaquaammonohydroxorhodium(III) ion,  $\text{p}K_{\text{a}2}$ , were determined by glass electrode (Radelkis) potentiometry using established methods.<sup>15</sup> Solutions of 0.010 and 0.0064 M  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  were prepared in an ionic medium containing  $[\text{ClO}_4^-] = 3 \text{ M}$  and  $3[\text{Rh}^{3+}] + [\text{Li}^+] + [\text{H}^+] = 3 \text{ M}$ . The total concentration of perchloric acid was 0.010 M. The samples were titrated with 0.2 M NaOH until the first trace of precipitation. The values of  $\text{p}K_{\text{a}1}$  and  $\text{p}K_{\text{a}2}$  were determined from a nonlinear least-squares fit of the titration data.

$^1\text{H}$  NMR spectra were recorded in locked mode on Bruker AC250 and AM400 spectrometers, i.e. at magnetic field strengths of 5.87 and 9.40 T, respectively, on an 0.106 M aqueous solution of  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  in the chosen ionic medium with 7%  $\text{D}_2\text{O}$ . The pH of the solution was measured using a glass electrode (for  $\text{pH} > 1$ ), and varied by the addition of concentrated solutions of NaOH or  $\text{HClO}_4$  over the range  $\text{pH} = -0.2$  to  $+3.7$ . Although the maximum pH represented the limit at which homogeneous samples could be obtained, the concentration of oligomeric hydroxo bridged Rh(III) species is expected to be negligible in freshly prepared solutions at moderate pH.<sup>17</sup> The spectra were recorded at 293 K for samples in 5 mm NMR tubes. The  $^1\text{H}$  NMR line-broadening was also measured at 9.4 T at three different temperatures (273, 293, and 310 K), and as a function of the total rhodium(III) concentration over the range 0.05–0.19 M, at constant pH. Solution densities were measured with a digital densitometer



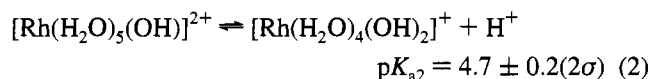
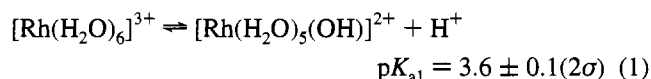
**Figure 1.** Variation of the exchange-broadened  $^1\text{H}$  NMR line width of a 0.106 M solution of hexaquaaluminum(III) as function of pH at 293 K. Spectra were recorded at two magnetic field strengths; 5.87 T (250 MHz) (●) and 9.40 T (400 MHz) (■).

(Anton Paar DMA 35), and the concentration of the hexaquaaluminum(III) ion was determined spectrophotometrically (Cary 3) at 395 nm.<sup>18</sup>

The line widths of the  $^1\text{H}$  NMR signals were determined by fitting single Lorentzians to each observed spectrum using the Bruker DISNMR software. The line-broadening due to chemical exchange was determined as the difference between the line width of each rhodium-containing solution and a solution of the pure ionic medium, at each pH and magnetic field.

## Results

**Potentiometric Titrations.** The acid dissociation constants were determined for the following reactions in an ionic medium of  $[\text{ClO}_4^-] = 3 \text{ M}$  and  $3[\text{Rh}^{3+}] + [\text{Li}^+] + [\text{H}^+] = 3 \text{ M}$  at 298 K.



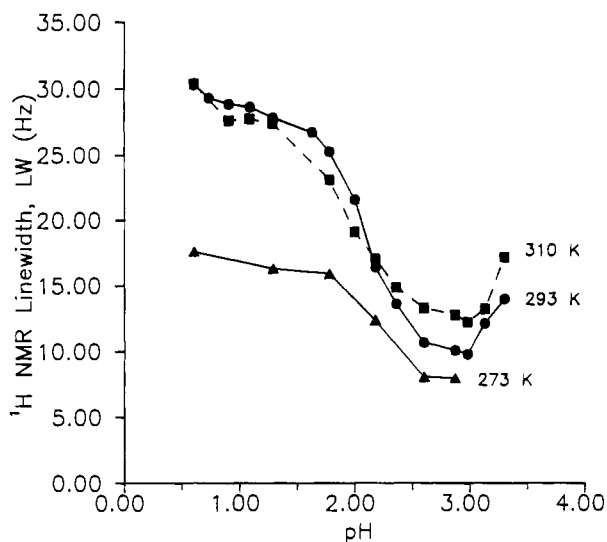
Two deprotonation steps were required to obtain a satisfactory non-linear least-squares fit of the titration data (see **Discussion**).

**$^1\text{H}$  NMR Line-Broadening Experiments.** At both magnetic fields and all pH values a single  $^1\text{H}$  NMR signal was observed at 293 K. The variation in the exchange-broadened  $^1\text{H}$  NMR line width of this signal for an 0.106 M solution of rhodium(III) as a function of pH for measurements at 5.87 T (250 MHz) and 9.40 T (400 MHz), is shown in Figure 1. The exchange-broadened line width is independent of the field strength for  $\text{pH} > 3$ , i.e. independent of the chemical shift difference (in Hz) between the proton exchange sites. This behavior is diagnostic of "slow" proton exchange on the time scale of the NMR experiment in this pH region. For  $\text{pH} < 3$  the exchange-broadened line widths differ for the measurements at 5.87 and 9.40 T at each pH. This implies that the line widths are dependent on the chemical shift difference (in Hz) between the exchange sites, indicating that the system is in "intermediate" or "fast" exchange on the actual NMR time scale.

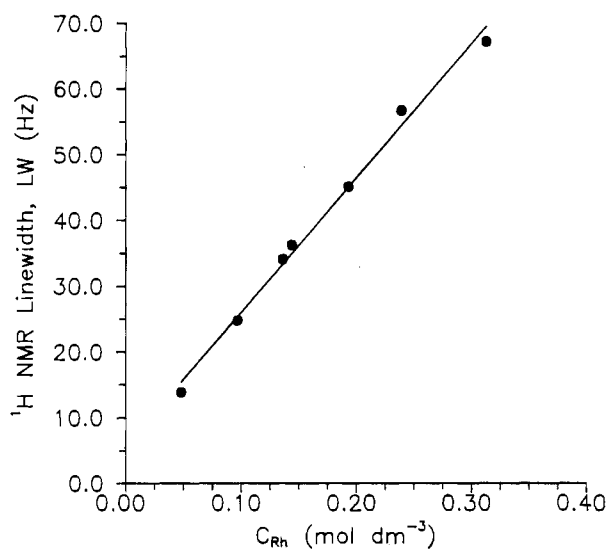
The variation of the  $^1\text{H}$  NMR line width as a function of pH at three different temperatures; 273 K, 293 K and 310 K is shown in Figure 2. For  $\text{pH} > 2.5$  the  $^1\text{H}$  NMR line width was

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**Figure 2.** Variation of the exchange-broadened  $^1\text{H}$  NMR line width measured at 9.40 T (400 MHz) for an 0.106 M solution of hexaaquarhodium(III) as function of pH; 273 K ( $\blacktriangle$ ), 293 K ( $\bullet$ ), and 310 K ( $\blacksquare$ ). The lines connect the experimental points.



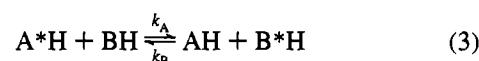
**Figure 3.** Variation of the exchange-broadened  $^1\text{H}$  NMR line width of aqueous solutions of hexaaquarhodium(III) as a function of the total rhodium concentration,  $C_{\text{Rh}}$ , at 293 K for  $[\text{H}^+] = 2.1 \text{ M}$ .

found to increase monotonously on increasing the temperature from 273 to 310 K confirming the "slow" exchange in this pH region. At lower pH, however, the line widths at 293 and 310 K were found to be approximately equal indicating a proton exchange rate between the "slow" and "fast" limits.

In order to determine the kinetic order of the hexaaquarhodium(III) ion in the rate equation at low pH, the variation in the  $^1\text{H}$  NMR line width was measured as a function of the total rhodium concentration,  $C_{\text{Rh}}$ , see Figure 3. The linear dependence of the  $^1\text{H}$  NMR line width indicates that the rate of proton exchange is first-order with respect to the concentration of the hexaaquarhodium(III) ion, as will be shown later.

**Data Treatment.** In the following treatment a two-site model will be assumed for the proton exchange. Water protons present in the first hydration sphere of the rhodium(III) species,  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  or  $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ , will be denoted as site A and those in the bulk water as site B. In the case of one dominating exchange site, possible exchange between the less populated sites can be neglected,<sup>19</sup> therefore, the proton transfer may be

expressed using the following general exchange reaction.



The populations of protons, expressed as their mole fractions, at the sites A and B may be represented by  $p_{\text{Rh}}$  and  $p_{\text{bulk}}$ , respectively. The populations of first sphere protons was  $p_{\text{Rh}} = 0.018$ , except for the case when the total rhodium concentration dependence was studied. The water proton population,  $p_{\text{bulk}} = 1 - p_{\text{Rh}}$ , was calculated from the known total rhodium concentration and the solution density. The exchange system may be described as strongly biased since  $p_{\text{Rh}} \ll p_{\text{bulk}}$ .<sup>20</sup> The relative populations of the exchange sites explain why only a single  $^1\text{H}$  NMR signal was observed in both the "slow" and "fast" exchange regions. In "fast" exchange only a single population-averaged signal is expected and observed. However, in the "slow" exchange region where at least two signals are expected only the bulk water signal was observed; the signal from coordinated water is weak due to the low population and broad due to the chemical exchange. For strongly biased two-site systems, the following equation has been derived relating the lifetime ( $\tau_{\text{A}}$ ) of the NMR active nucleus at the less populated site to the observed line width ( $\text{LW}_i$ ) at the dominating site;<sup>21</sup>

$$\text{LW}_i = \frac{4\pi p_{\text{A}} \tau_{\text{A}} (\Delta\nu_i)^2}{1 + 4\pi^2 \tau_{\text{A}}^2 (\Delta\nu_i)^2} \quad (4)$$

where  $\Delta\nu_i$  is the chemical shift difference in Hz between the two exchange sites A and B at specific magnetic field strength,  $i$ .

From the acid dissociation constants  $\text{p}K_{\text{a}1}$  and  $\text{p}K_{\text{a}2}$  determined above, it is clear that when  $\text{pH} < 2$  the  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  ion will dominate. However, for higher pH values two rhodium species may be present as sites for proton exchange, namely the  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  ion and the first hydrolysis complex  $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ . If we define the pseudo-first-order rate constant for exchange from a site A (in this case the first hydration sphere of the rhodium(III) ion), as  $k_{\text{obs}}^{\text{Rh}} = 1/\tau_{\text{H}}^{\text{Rh}}$ , then for parallel exchange reactions from two sites A' and A'', the overall rate is given by  $k_{\text{obs}}^{\text{Rh}} = k_{\text{obs}}^{\text{A}'} + k_{\text{obs}}^{\text{A}''}$ , the sum of the observed rate constants from the two sites. Hence,  $k_{\text{obs}}^{\text{Rh}}$ , the pseudo-first-order rate constant for proton exchange from the hydration sphere of rhodium(III) is the sum of the observed proton exchange rate constants from  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  for  $\text{pH} > 2$ .

The main difficulty in applying eq 4 is that we only observe a single  $^1\text{H}$  NMR signal in our spectra, even in the "slow" exchange regime. Hence, the chemical shift difference ( $\Delta\nu$ ) between the exchange sites cannot be determined directly. This is not critical if the exchange is "slow" (i.e.  $\tau_{\text{A}}$  is large) and  $(\tau_{\text{A}}\Delta\nu)^2 \gg (2\pi)^{-2}$ , since in this case  $1 \ll 4\pi^2\tau_{\text{A}}^2(\Delta\nu_i)^2$  and eq 4 therefore reduces to  $\text{LW}_i = p_{\text{A}}/(\pi\tau_{\text{A}})$ . Furthermore, since the system is in dynamic equilibrium such that  $p_{\text{A}}/\tau_{\text{A}} = p_{\text{B}}/\tau_{\text{B}}$ , and strongly biased with  $p_{\text{B}} \approx 1$ , it follows that

$$\text{LW}_i = 1/(\pi\tau_{\text{bulk}}) = k_{\text{obs}}^{\text{bulk}}/\pi \quad (5)$$

where  $k_{\text{obs}}^{\text{bulk}}$  is the pseudo-first-order rate constant for proton exchange from bulk water to the hydration sphere of rhodium(III). A consequence of eq 5 is that in the "slow" exchange regime the line width should be independent of the magnetic field strength. It can be seen from Figure 1 that for  $\text{pH} > 3$  no difference is observed between the line widths measured at 5.87

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**Table 1.** Calculated<sup>a</sup> Chemical Shift Difference ( $\Delta\delta$ , in ppm) between the <sup>1</sup>H NMR Signal of the Hydration Sphere of Rhodium(III) and That of Bulk Water, as a Function of pH

pH	$\Delta\delta$	pH	$\Delta\delta$
0.61	4.86	1.78	4.26
0.73	4.69	2.00	3.60
0.91	4.84	2.18	2.83
1.09	4.76	2.36	2.35
1.29	4.74	2.60	2.19
1.63	4.49		

<sup>a</sup> According to eq 4; see text.

and 9.40 T, indicating that in this region the exchange is in fact "slow" on the <sup>1</sup>H NMR time scale. Therefore, the values of  $k_{\text{obs}}^{\text{bulk}}$  were calculated directly from the line width data at each pH.

When the proton exchange is "fast", eq 4 may be used rigorously to calculate the proton lifetime ( $\tau_{\text{H}}^{\text{Rh}}$ ) in the first hydration sphere of rhodium(III) and the chemical shift difference ( $\Delta\nu$ ) from the different line widths measured at two magnetic field strengths (see Table 1). To the best of our knowledge, this approach has not been reported previously in the literature. The basis of the calculation is the fact that the lifetime  $\tau_{\text{A}}$  and the mole fraction  $p_{\text{A}}$  do not depend on the magnetic field. Obviously, different  $\Delta\nu_i$  values lead to different linewidths  $LW_i$  at the two fields. Furthermore, the two chemical shift differences (in Hz) are related by the spectrometer frequency (SF in MHz), since  $\Delta\nu_1/\text{SF}_1 = \Delta\nu_2/\text{SF}_2$ . From the resulting two equations the unknown quantities  $\Delta\nu_1$  and  $\tau_{\text{A}}$  are easily calculated. By using the values in Table 1 and making the approximation that  $p_{\text{bulk}} \approx 1$ , the pseudo-first-order rate constants,  $k_{\text{obs}}^{\text{bulk}}$ , for proton exchange from the bulk water to the first hydration sphere of rhodium(III) could be calculated for each pH in the "fast" exchange region. The calculated chemical shift difference ( $\Delta\delta = \Delta\nu/\text{SF}$  in ppm) is constant as expected for pH < 1.5, but varies at higher pH (see Table 1); this variation will be explained later in the section titled **Mechanistic Interpretation**.

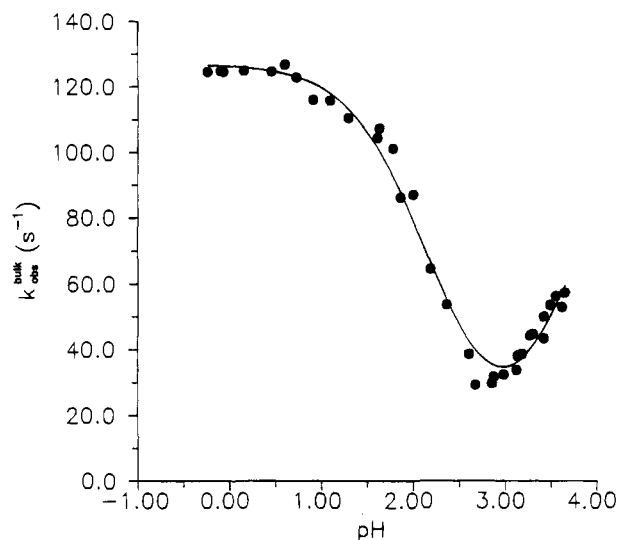
All experimentally determined  $k_{\text{obs}}^{\text{bulk}}$  values are shown in Figure 4 and are discussed below.

## Discussion

The following qualitative observations can be made from the results in Figure 4: (1) the proton exchange rate is quite slow in the studied pH range and passes through a minimum at pH  $\approx$  3; (2) the rate of proton exchange increases asymptotically with decreasing pH when pH < 3, and approaches a constant value at low pH; (3) the rate of proton exchange increases with pH when pH > 3.

The value of the acid dissociation constant for the hexaaquarhodium(III) ion ( $\text{p}K_{\text{a}1} = 3.6 \pm 0.1$  in 3 M LiClO<sub>4</sub>) is in reasonable agreement with other determinations, e.g.  $\text{p}K_{\text{a}1} = 3.4 \pm 0.1$  in 2 M perchlorate<sup>18,22</sup> and  $\text{p}K_{\text{a}1} = 3.45$  in 5 M NaClO<sub>4</sub>.<sup>5</sup>

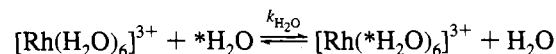
The acid dissociation constant for the pentaquamonohydroxorhodium(III) ion,  $\text{p}K_{\text{a}2} = 4.7 \pm 0.2$ , has not been determined previously. Hydroxo-bridged polymeric rhodium(III) species<sup>17,22,23</sup> could influence our titration data at high pH. However, our titrations were performed at low rhodium concentrations ranging from 0.006 to 0.010 M. There was no significant variation in the dissociation constants obtained from different titrations; thus, errors due to polymeric species on  $\text{p}K_{\text{a}2}$  can be excluded.<sup>24</sup>



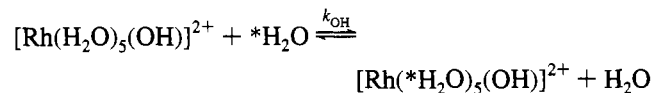
**Figure 4.** Variation of the pseudo-first-order rate constant ( $k_{\text{obs}}^{\text{bulk}}$ ) for proton exchange from bulk water to the first hydration sphere of Rhodium(III) as a function of pH, the values of  $k_{\text{obs}}^{\text{bulk}}$  are calculated from the <sup>1</sup>H NMR line width data shown in Figure 1. The full curve gives the fitted data on the basis of the proposed rate equation; see eq 12.

**Identification of the Reaction Pathways.** The  $\text{p}K_{\text{a}}$  values indicate that  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Rh}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  are the only important rhodium species present over the pH range investigated in our experiments. The second hydrolysis complex,  $[\text{Rh}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ , may contribute to the proton exchange at the highest pH values studied. However, the concentration of  $[\text{Rh}(\text{H}_2\text{O})_4(\text{OH})_2]^+$  constitutes less than 5% of the total rhodium content even at pH = 3.7 and falls off rapidly with decreasing pH. Thus on the basis of the species known to be present we have considered the following symmetrical proton exchange pathways:

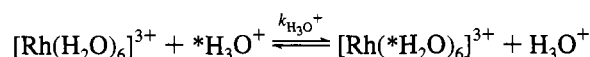
Path 1: Direct exchange between first sphere water protons in hexaaquarhodium(III) and bulk water protons



Path 2: Exchange between first sphere protons in pentaquamonohydroxorhodium(III) and bulk water protons



Path 3: Exchange between first sphere water protons in hexaaquarhodium(III) and hydronium ions in the bulk



It should be noted at this stage that no detailed mechanistic interpretation is made regarding the elementary reactions and rate-determining steps of each path. For example, path 1 may well proceed via an elementary reaction involving deprotonation of the hexaaquarhodium(III) ion to give  $[\text{Rh}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ , as has been suggested for the proton exchange reactions involving hydrated chromium(III) species.<sup>9-11</sup>

The overall rate law is given by the sum of the terms from the three parallel exchange pathways, each having a different hydronium ion dependence: i.e. path 3 giving first-order hydronium ion dependence, path 1 zero-order, and path 2 inverse

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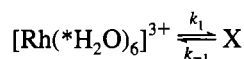
first-order dependence. Rate laws with the above pH dependence have been used to describe the proton exchange kinetics of hexaaquachromium(III)<sup>9,10</sup> and some organochromium(III) complexes.<sup>10,11</sup> Indeed, such a rate law can be successfully fitted to our proton exchange data over a limited range of hydronium ion concentrations (pH  $\approx$  2–3.7). However, the model fails at lower pH when the rate of exchange becomes independent of the hydronium ion concentration; see Figure 4.

At very low pH, the dominating rhodium species is  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ . The remaining concentration of the  $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  ion is very low; e.g. at pH = 0.6, it constitutes only 0.1% of the total rhodium concentration. Considering the species present in this region, path 3 could be expected to dominate, and the rate should therefore increase with decreasing pH, contrary to our observations. Evidently, another explanation of the proton exchange process is required at low pH. It should be noted that there is no indication from our potentiometric titration data that protonation of  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  occurs at low pH. The formation of a protonated species could otherwise be invoked to explain the observed variation of  $k_{\text{obs}}$ .

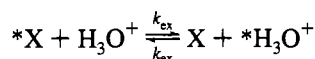
An additional reaction pathway could be considered involving bimolecular proton exchange between hexaaquarhodium(III) and the hydroxide ion. However, the second-order rate constant estimated from  $k_{\text{obs}}^{\text{bulk}}$  at pH = 3 for this path would be  $\approx 10^{14} \text{ M}^{-1} \text{ s}^{-1}$  which is significantly faster than for a diffusion controlled reaction.

Previously, the influence of the second sphere of tightly hydrogen-bonded water molecules has been used to explain the observed proton exchange behavior of the hexaaquaaluminum(III) ion at low pH.<sup>7</sup> The proposed mechanism involved transfer of a first sphere water proton to a second sphere water molecule, followed by exchange between the hydronium ion thus formed and an  $\text{H}_3\text{O}^+$  ion from the bulk of the solution. In order to explain the present observations we have assumed that the mechanism for proton transfer in path 3, from the first coordination sphere of the hexaaquarhodium(III) ion to the bulk water, can be described with three consecutive steps: (1) formation of an intermediate X, involving the second hydration sphere of hexaaquarhodium(III) (see **Mechanistic Interpretation** below), followed by (2) proton exchange with a bulk hydronium ion, and finally (3) rapid proton exchange between the hydronium ion and bulk water, as illustrated in the following reaction scheme.

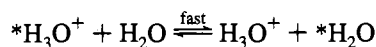
path 3, step 1



path 3, step 2



path 3, step 3



**Derivation of the Rate Equation.** Considering the contribution of each reaction path to the overall proton exchange rate, it follows from path 1 that

$$\text{rate} = R_{\text{H}_2\text{O}} = k_{\text{H}_2\text{O}}[\text{Rh}(\text{H}_2\text{O})_6]^{3+}C_{\text{H}_2\text{O}} \quad (6)$$

where  $C_{\text{H}_2\text{O}}$  is the water concentration. If the pseudo-first-order rate constant for proton exchange from bulk water to the first hydration sphere of the rhodium(III) ion is introduced, such that  $R_{\text{H}_2\text{O}} = k_{\text{obs}}^{\text{bulk}}C_{\text{H}_2\text{O}}$ , it follows that

$$k_{\text{obs}}^{\text{bulk}} = k_{\text{H}_2\text{O}}[\text{Rh}(\text{H}_2\text{O})_6]^{3+} = \frac{k_{\text{H}_2\text{O}}C_{\text{Rh}}K_{\text{p}}[\text{H}_3\text{O}^+]}{1 + K_{\text{p}}[\text{H}_3\text{O}^+]} \quad (7)$$

where the  $C_{\text{Rh}}$  is the total rhodium(III) concentration and  $K_{\text{p}} = 1/K_{\text{a1}}$ . Similarly for path 2

$$R_{\text{OH}} = k_{\text{OH}}[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})^{2+}]C_{\text{H}_2\text{O}} \quad (8)$$

hence

$$k_{\text{obs}}^{\text{bulk}} = \frac{k_{\text{OH}}C_{\text{Rh}}}{1 + K_{\text{p}}[\text{H}_3\text{O}^+]} \quad (9)$$

For path 3 we apply the steady-state approximation to the intermediate X in order to obtain the contribution of this path to the overall rate law, hence

$$\frac{d[\text{X}]}{dt} = k_1[\text{Rh}(\text{H}_2\text{O})_6]^{3+} - k_{-1}[\text{X}] - k_{\text{ex}}[\text{X}][\text{H}_3\text{O}^+] = 0 \quad (10)$$

Assuming that step 2 is rate-determining,  $R_{\text{ex}} = k_{\text{ex}}[\text{X}][\text{H}_3\text{O}^+]$ , it follows that

$$k_{\text{obs}}^{\text{bulk}} = \frac{k_1k_{\text{ex}}C_{\text{Rh}}K_{\text{p}}[\text{H}_3\text{O}^+]^2}{(k_{-1} + k_{\text{ex}}[\text{H}_3\text{O}^+])(1 + K_{\text{p}}[\text{H}_3\text{O}^+])C_{\text{H}_2\text{O}}} \quad (11)$$

By combining the contributions for each of the three reaction pathways, we obtain an expression for the overall pseudo-first-order rate constant for proton exchange from the bulk water to the first hydration sphere of the rhodium(III) ion.

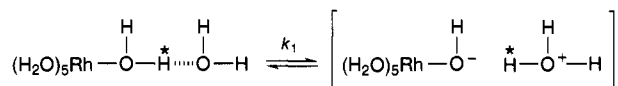
$$k_{\text{obs}}^{\text{bulk}} = \frac{k_{\text{H}_2\text{O}}C_{\text{Rh}}K_{\text{p}}[\text{H}_3\text{O}^+]}{1 + K_{\text{p}}[\text{H}_3\text{O}^+]} + \frac{k_{\text{OH}}C_{\text{Rh}}}{1 + K_{\text{p}}[\text{H}_3\text{O}^+]} + \frac{k_1k_{\text{ex}}C_{\text{Rh}}K_{\text{p}}[\text{H}_3\text{O}^+]^2}{(k_{-1} + k_{\text{ex}}[\text{H}_3\text{O}^+])(1 + K_{\text{p}}[\text{H}_3\text{O}^+])C_{\text{H}_2\text{O}}} \quad (12)$$

The above expression was fitted to the experimental pseudo-first-order rate constants,  $k_{\text{obs}}^{\text{bulk}}$ , over the pH range  $-0.2$  to  $+3.7$  using a nonlinear Gauss–Newton–Marquardt algorithm. The fit to the experimental data is shown in Figure 4. The following rate constants were obtained:  $k_{\text{H}_2\text{O}} = 0 \text{ M}^{-2} \text{ s}^{-1}$ ,  $k_{\text{OH}} = 1000 \pm 100 \text{ M}^{-2} \text{ s}^{-1}$ ,  $k_{\text{ex}}/k_{-1} = 160 \pm 30 \text{ M}^{-1}$  and  $k_1 = 6.0 (\pm 0.2) \times 10^4 \text{ s}^{-1}$ , where the error limits represent the 95% confidence interval for the fitted parameters. It should be noted that the rate constants in the above derivation refer to *arbitrary* or *nonspecific* protons in the first hydration sphere of the rhodium(III) ion or in the bulk water. Furthermore, no inference is made at this stage concerning the number of exchanging protons in, for example, the  $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  ion, such factors being included in the rate constant  $k_{\text{OH}}$  as defined in eq 8.

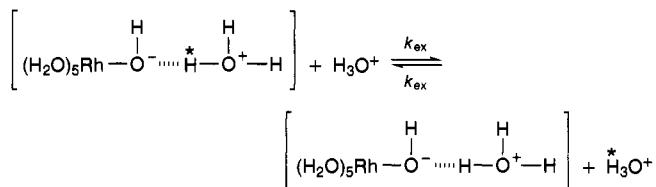
**Mechanistic Interpretation.** The extremely long lifetime of a specific water–oxygen atom in the first hydration sphere of  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ ,  $\tau_{\text{O}} \approx 5 \times 10^8 \text{ s}$ ,<sup>6</sup> and the somewhat shorter water–oxygen lifetime in  $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ ,  $\tau_{\text{O}} \approx 2 \times 10^4 \text{ s}$ ,<sup>6</sup> are both considerably longer than the proton lifetime observed in our experiments. In this respect, rhodium(III) is even more inert than the chromium(III) and aluminum(III) ions. The mechanistic interpretation of proton exchange processes can therefore be made simply in terms of proton and not water molecule exchange.

In the acidic part of the investigated pH-region, path 3 dominates the proton exchange. The reaction leading to the formation of the intermediate X in step 1 of path 3 is believed

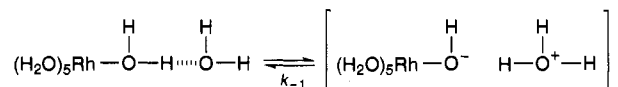
to be breaking of an O—H bond in a first sphere water molecule giving rise to a labeled hydronium ion in the second hydration sphere. This reaction having the rate constant  $k_1$  is illustrated schematically below for a single first-sphere water molecule hydrogen-bonded to a single second-sphere water molecule:



Subsequently, exchange occurs between the labeled hydronium ion in the second sphere and a bulk hydronium ion, i.e. step 2 of path 3:



After rapid proton exchange between the bulk hydronium ion and a bulk water molecule, see step 3 of path 3, the labeled proton is finally observed in the bulk water. To fulfil the condition of microscopic reversibility, the reaction cycle is completed by the transfer of a proton from the hydronium ion in the second hydration sphere to the first hydration sphere, with the rate constant  $k_{-1}$ :

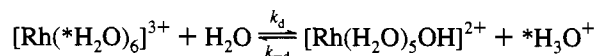


We can now attempt to explain the observed pH dependence of the proton exchange rate. First, for  $\text{pH} > 3$ , the rate of proton exchange increases with pH in direct proportion to the concentration of the pentaquaammonohydroxorhodium(III) species, according to eq 8.

At relatively low pH (below  $\text{pH} \approx 3$ ) the rate-determining step is believed to be step 2 of path 3, and therefore the proton exchange rate is given by  $R = k_{\text{ex}}[\text{X}][\text{H}_3\text{O}^+]$ . Consequently, the rate increases with the hydronium concentration (decreasing pH). However, at very low pH, where the high proton concentration causes step 2 to proceed at a much higher rate, the rate-determining step becomes step 1 of path 3, and since there is no hydronium ion dependence for this step the rate of proton exchange approaches a constant value. In analogy with step 2 of path 3, the exchange of a proton from a hydronium ion in the second hydration sphere with a hydronium ion in the bulk has been proposed as a mechanistic path during the proton exchange between water molecules in the first hydration sphere of the aluminum(III) ion and bulk water molecules.<sup>7</sup>

The rate constants obtained by fitting eq 12 to the experimental data in Figure 4 indicate that proton exchange takes place only between (1) the pentaquaammonohydroxorhodium(III) ion and bulk water *via* path 2 as the pH approaches  $\text{p}K_{\text{a}1} = 3.6$  and (2) between the hexaaquarhodium(III) ion and the hydronium ion *via* path 3 at lower pH values.

The fitted value of  $k_{\text{H}_2\text{O}} = 0 \text{ M}^{-2} \text{ s}^{-1}$  implies that direct exchange of protons between the first hydration sphere of the hexaaquarhodium(III) ion and the bulk water does not contribute significantly to the overall rate of proton exchange. This finding is rather surprising as one would intuitively expect the following elementary reaction to be responsible for some of the proton exchange in path 1:



The hexaaquarhodium(III) ion is demonstrably acidic ( $\text{p}K_{\text{a}1} = 3.6$ ) *via* the forward reaction designated  $k_d$  above. Thus if  $k_d$  is slow, microscopic reversibility requires that the protonation reaction  $k_{-d}$  is even slower. This is in contradiction with results for other metal ions where  $k_{-d}$  has been shown to be essentially diffusion-controlled.<sup>10,11,25</sup> However, if the transfer of a proton from the first to the second hydration sphere of rhodium(III) (path 3, step 1) is identified as the reaction responsible for the production of the  $[\text{Rh}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  ion, and this step is rate determining (i.e.  $k_d = k_1$ ), then  $k_{-d} = k_1/K_{\text{a}1}$ . Using our values of  $k_1$  and  $K_{\text{a}1}$ , it follows that  $k_{-d} = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , in fair agreement with the values obtained by electric field dissociation relaxation methods for aluminum(III) and chromium(III) ions where  $k_{-d} = 4.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $7.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.<sup>25</sup> Even though these trivalent ions have structurally similar hydration shells, differences in the electrostatic potential gradient due to their different sizes and degree of bond polarization may well be the reason for the variation in their  $k_{-d}$  values.

**Chemical Shift Differences.** The proposed mechanism can also explain the variation of the chemical shift difference ( $\Delta\delta$  in ppm) for the exchange between the hydration sphere of rhodium and the bulk water for  $\text{pH} < 2.6$ , see Table 1. For convenience, we use  $\Delta\delta$  calculated from eq 4.

The calculated chemical shift difference is approximately constant ( $\Delta\delta \approx 4.8$  ppm) for  $\text{pH} < 1.5$  (see Table 1). This is consistent with step 1 of path 3 in which the only exchange sites are  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{H}_2\text{O}$  (with X as a steady-state intermediate), i.e. a two-site system. For higher pH values,  $\Delta\delta$  decreases in a continuous manner with increasing pH. This decrease cannot be a result of an increasing concentration of the hydrolysed species,  $[\text{Rh}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ , since this would imply an unrealistically large chemical shift difference,  $\Delta\delta > 20$  ppm.

However, for the range  $1.5 < \text{pH} < 2.6$ , step 2 of path 3 gradually becomes the rate-determining step, so that the rate of exchange between X and the bulk water is comparable to the rate of step 1 of path 3. Thus, this is no longer the two-site exchange system for which eq 4 was originally deduced. This is a truncated system containing a steady-state intermediate which gives no signal, but which affects the chemical shift difference calculated by eq 4. Nevertheless, eq 4 gives the correct rate constant. This was confirmed by comparison with spectra simulated from a complete line-shape analysis<sup>26</sup> of the three-site exchange system containing bulk water,  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ , and the intermediate X at a very low concentration, e.g.  $p_x = 0.0005$ .

The chemical shift difference in Table 1 is in reasonable agreement (considering the different medium) with an experimental observation of the  $^1\text{H}$  NMR chemical shift difference between bulk water protons and protons in the first hydration sphere of rhodium(III),  $\Delta\delta = 3.7$  ppm, when measured in mixed acetone/water solutions at low temperature.<sup>17</sup> We have also measured  $^1\text{H}$  NMR spectra for a concentrated (2 M) solution of  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  in water as a function of temperature. In the temperature range 243–298 K only one broad signal was observed, but at 233 K and below this signal was partially resolved into two peaks: one for the protons in the hydration sphere of rhodium and one for the bulk water protons. It is difficult to estimate the pH in this very concentrated solution because of the unknown activity coefficients, but the resulting shift difference ( $\Delta\delta \approx 3$  ppm) is in qualitative agreement with the calculated values (Table 1).

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Our calculated value for  $\Delta\delta$  is also close to the 4.6 ppm measured for a 1.6 M aqueous solution of aluminum, for which the bulk water peak could be resolved from the peak of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  at 267 K.<sup>27</sup>

The chemical shift difference may also be estimated as follows.<sup>21</sup> It can be shown on the basis of equation 4 that with increasing temperature the experimental NMR line width first increases, then goes through a maximum, and finally decreases. The maximum line width is given by  $\text{LW}_{\text{max}} = p_A \Delta\nu$ . From Figure 2 it can be seen that at low pH approximately equal line widths were observed at 293 and 310 K;  $\text{LW} \approx 28$  Hz. If we then assume that 28 Hz is the maximum line width ( $\text{LW}_{\text{max}}$ ) it follows that the chemical shift difference at this field strength (9.4 T) is  $\Delta\delta = 3.9$  ppm, again in reasonable agreement with the experimental value<sup>17</sup> and our previous estimate from the field dependence.

**Comparison with Aluminum(III) and Chromium(III).** The lifetime of a proton in the first hydration shell of rhodium(III) was calculated from the relationship,  $k_{\text{obs}}^{\text{bulk}} p_{\text{bulk}} = k_{\text{obs}}^{\text{Rh}} p_{\text{Rh}}$ . Since there are 12 exchanging protons in the hydration sphere of the rhodium(III) ion, then the lifetime of a *specific* proton is given by  $\tau_{\text{H}}^{\text{Rh}} = 12/k_{\text{obs}}^{\text{Rh}}$ . From our results the *specific* proton lifetime in the first hydration sphere of rhodium(III) varies from  $\tau_{\text{H}}^{\text{Rh}} = 2$  ms at pH = 0 to 7 ms at pH = 3. For comparison, the *specific* proton lifetime in the hexaaquachromium(III) and hexaaquaaluminum(III) ions has been estimated from other work<sup>7,9</sup> to  $\tau_{\text{H}} = 0.1$ – $0.2$  ms in the pH range 0–2. For divalent metal ions such as nickel(II) the proton lifetime is several orders of magnitude shorter,  $\tau_{\text{H}}^{\text{Ni}} = 1 \mu\text{s}$ .<sup>9</sup>

In the light of our results, a discussion of proton exchange mechanisms for these structurally similar ions must address two questions: (1) Why is the pH-independent region not observed for hydrated chromium(III) and aluminum(III) ions? (2) Why is the proton exchange slower for rhodium(III) over the pH-range investigated?

On the basis of the mechanism proposed above, the region of pH-independent proton exchange at low pH is critically dependent on the ratio  $k_1/k_{\text{ex}}$ . For example, if the rate of proton transfer from the first to the second hydration sphere ( $k_1$ ) is fast, compared with the proton exchange of an hydronium ion in the second sphere with one in the bulk ( $k_{\text{ex}}$ ), then the former process does not become rate determining until very low pH and thus the pH-independent region may not be observed experimentally. This seems to be the case for the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Cr}(\text{H}_2\text{O})_5\text{CH}_2\text{CN}]^{2+}$  ions.<sup>9,10</sup> However, an early study of the water proton exchange of the  $[\text{Cr}(\text{H}_2\text{O})_5\text{N}_3]^{2+}$  ion in aqueous solution does show a levelling off of the line broadening at high acidity.<sup>11</sup>

For the hydrated ions  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Rh}^{3+}$  the constant O-H(D) stretching frequency for the first sphere water molecules indicates a similar hydrogen-bond length between the first and second sphere water molecules.<sup>2</sup> Furthermore, the hexaaquarhodium(III) and hexaaquachromium(III) ions have been shown to be isostructural in aqueous solution by a large-angle X-ray scattering study, both ions being surrounded by a second sphere of water molecules at a mean distance  $\text{M}-\text{O}_{\text{II}} = 4.02 \text{ \AA}$  in aqueous solution.<sup>1</sup> However, there are indications of subtle differences in the nature of the bonding which may influence proton exchange. A theoretical calculation of isolated hexaaquarhodium(III) and -chromium(III) complexes showed a somewhat higher degree of charge transfer to the rhodium ion although

its ionic radius is slightly larger, and a Mulliken population analysis gave the effective charges as +2.10 (Rh) and +2.21 (Cr), respectively.<sup>28</sup> The resulting larger electrostatic repulsion from the chromium ion on the protons of the first-sphere water molecules probably leads to a lower activation energy for proton transfer from the first to the second hydration sphere,<sup>29</sup> and thus a faster reaction with a larger  $k_1$  than for the rhodium ion.

The proton exchange between the hydrated rhodium(III) ion and bulk water is slower than for chromium(III) and aluminum(III), irrespective of effects associated to changes in the hydronium ion concentration. This may be due to the lack of observable *direct* exchange between first sphere water protons and bulk water ( $k_{\text{H}_2\text{O}} = 0 \text{ M}^{-2} \text{ s}^{-1}$ ) molecules *via* path 1 for rhodium(III).

The activation parameters for reaction paths 2 and 3 were estimated from Arrhenius plots of the temperature dependence data in Figure 2. For path 2,  $\Delta H_{\text{OH}}^\ddagger = 36 \text{ kJ mol}^{-1}$ , and  $\Delta S_{\text{OH}}^\ddagger = -180 \text{ J mol}^{-1} \text{ K}^{-1}$ ; for step 1 of path 3,  $\Delta H_{k_1}^\ddagger = 7 \text{ kJ mol}^{-1}$  and  $\Delta S_{k_1}^\ddagger = 10 \text{ J mol}^{-1} \text{ K}^{-1}$ . Although these values are uncertain, the highly negative  $\Delta S_{\text{OH}}^\ddagger$  indicates an ordered transition state for path 2. The small value of  $\Delta S_{k_1}^\ddagger$  is in agreement with the suggested mechanism (step 1 of path 3), in which the hydration sphere of rhodium is basically unchanged, and hence, no significant entropy change is expected. Comparison of these parameters with corresponding data for aluminum(III) and chromium(III) could provide useful mechanistic information.

### Concluding Remarks

The specific lifetimes of first sphere water protons around the hydrated trivalent cations rhodium(III), chromium(III) and aluminum(III) are generally several orders of magnitude longer than for divalent metal ions such as nickel(II). These trivalent hexahydrated ions are structurally very similar in aqueous solution, each having a well-defined second hydration sphere<sup>1,2</sup> through which proton exchange must occur. Despite these similarities it appears that subtle differences in the bonding lead to noticeable differences between rhodium(III) on the one hand and chromium(III) and aluminum(III) on the other. For example, only in the case of rhodium(III) is the transfer of a proton from the first to the second hydration sphere sufficiently slow to be rate determining, resulting in a region of constant rate at low pH. Furthermore, direct proton exchange between the first hydration sphere and bulk water molecules appears to be too slow to be detected.

**Acknowledgment.** We acknowledge the Swedish Natural Science Research Council (NFR) for continuing financial support and a research studentship (M.C.R.), the National Scientific Research Foundation (OTKA 1724, Hungary, I.B.), Trade Bank Co. Universitas Foundation (Debrecen, Hungary, I.B.), the Swedish Institute for a fellowship to I.B. and a travel stipendium to M.C.R., and OKs Miljöstiftelse for a supporting grant. Dr. Imre Tóth is thanked for many stimulating discussions. We are also grateful to one of the reviewers for valuable comments on our mechanistic interpretation.

IC940142S

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