Articles

An ^{17}O-NMR Study of the Exchange of Water on AlOH(H$_2$O)$_5$$^{2+}$(aq)

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The pH-dependence of the rate of water exchange between hydrated aluminum complexes and bulk aqueous solution is reported from variable-temperature dynamic ^{17}O-NMR measurements. Over the temperature range 298−348 K, the pseudo-first-order rate coefficient for exchange at any given temperature, $k_{ex,obs}^T$, is described by $k_{ex,obs}^T = k_1^T + k_2^T[\text{H}^+]^{-1}$, where k_1^T is the rate coefficient for exchange of inner-sphere water molecules with bulk solution for the Al(H$_2$O)$_6$$^{3+}$(aq) complex at that temperature, and $k_2^T[\text{H}^+]^{-1}$ is the pH-dependent contribution to $k_{ex,obs}^T$ from the first hydrolysis product: AlOH(H$_2$O)$_5$$^{2+}$(aq). The rate parameters are $k_1^{298} = 1.3$ s^{-1}, $\Delta H_1^{\ddagger} = 84.7$ kJ·mol^{-1}, $\Delta S_1^{\ddagger} = 41.6$ J·mol^{-1}·K^{-1} (from 6); and $k_2^{298} = 7.2 \times 10^{-2}$ M·s^{-1}, $\Delta H_2^{\ddagger} = 90.4$ kJ·mol^{-1}, $\Delta S_2^{\ddagger} = 36.6$ J·mol^{-1}·K^{-1} (this work). From this result we obtained the activation parameters for water exchange on the AlOH(H$_2$O)$_5$$^{2+}$(aq) complex: $k_{ex,AlOH(H_2O)_5^{2+}}^{298} = 3.1 \times 10^4$ s^{-1}, $\Delta H^{\ddagger} = 36.4$ kJ·mol^{-1}, $\Delta S^{\ddagger} = -36.4$ J·mol^{-1}·K^{-1}. Thus, deprotonation of an inner-sphere water in Al(H$_2$O)$_6$$^{3+}$(aq) enhances by a factor of $\approx$10^4 the lability of other inner-sphere oxygens. This labilizing effect of hydroxyl is much larger than for other geochemically important ligands, including fluoride.

Introduction

The rates of exchange of solvent molecules from simple metal complexes have proven useful for understanding complicated reactions, even those at mineral surfaces.[1,2] For this reason we have studied the effect of several geochemically important ligands on the rate of solvent exchange for Al(III)[3−5] and found the lability of inner-sphere water molecules to be very sensitive to the type and number of other bound ligands. Although aluminum is among the most common elements in the Earth's crust, the rates of solvent exchange for its hydrolyzed complexes have not been reported. In this paper we extend earlier work on Al(H$_2$O)$_6$$^{3+}$(aq)[3,6] to report the rate of exchange of water molecules from bulk solvent to the inner-coordination sphere of AlOH(H$_2$O)$_5$$^{2+}$(aq). Our results indicate that hydroxyl has a large labilizing effect on other inner-sphere hydration waters also in the complex.

Experimental Section

Solutions were prepared from dried chloride salts to be 51.7 mM or 100.0 mM in dissolved aluminum and 0.25 M in dissolved manganese. The stoichiometries were checked by analysis for chloride. Sodium chloride was added to fix the apparent ionic strength at 2.0 M in all solutions. The solvent water was enriched to 12% in ^{17}O (Isotec Inc.). Solution pH at 298 K ranged from 3.65 to ∼0.97 and was adjusted with 1 M HCl and 1 M NaOH. The pH was measured using a combination electrode (ORION-Ross) which was calibrated at 25, 50, and 75 °C (±0.5 °C) by titrating acidified aluminium−manganous solutions. The calibrating solutions were virtually identical to the ^{17}O-enriched samples used in the NMR experiments, but contained isotopically normal, filtered water with an initial resistance greater than 17 MΩ. The electrode exhibited a linear relation between E_0 and temperature, and the reported pH-values at all temperatures refer to proton concentration rather than to proton activity. All samples were purged with argon.

Thermodynamic Calculations. The thermodynamic data for aluminum hydrolysis given by Palmer and Wesolowski[7] and Wesolowski and Palmer[8] was used in calculations of the exchange rate and activation parameters for the AlOH(OH$_2$)$_5$$^{2+}$(aq) complex. It has been shown[7] that the hydrolysis chemistry of aluminum is very similar (within our experimental error) at ionic strengths of 2.0 and 5.0 M, and we therefore use data reported for $I = 5.0$ M ($I = 2.0$ in this study). Chloride ion has been shown to have very little effect on the speciation of aluminum[3] in the solutions in this study. We used constants from Busey and Mesmer[9] for the ionization of water, and pH was measured at temperature.

NMR Spectroscopy. The rate coefficients were measured by the dynamic ^{17}O-NMR line-broadening technique, details of which are discussed elsewhere.[3,4,6] The ^{17}O-NMR experiments were performed with a GE Omega 500 spectrometer based on an 11.7 T magnet ($\nu_o = 67.8$ MHz for ^{17}O) fitted with a variable-temperature 10-mm broadband

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probe. The ^{17}O-NMR spectra were taken at temperatures ranging from −7 to 115 °C with single-pulse excitation using 20 μs pulses ($\pi = 46$ μs), recycle delay of 10 ms, and 8000−64000 acquisitions. The temperature controller was found to be accurate to ±1 °C using a thermocouple placed within the sample volume, and errors associated with temperature are within our estimated uncertainties. The signal from bulk water is broadened beyond detection by the addition of Mn(II), which sets up the condition T_2(bulk water) ≪ T_2(bound water).[10] B_o homogeneity was checked with the ^{27}Al resonance of an identically shaped sample containing the same manganese concentration.

The ^{17}O-T_2 values for the bound water are obtained from the NMR linewidths: $T_2 = 1/(\text{FWHM}\cdot\pi)$, where FWHM is the full-width at half-maximum of the peak height. The pH and temperature dependence of T_2 for components of the ^{17}O-NMR spectra is modeled by eq 1, which incorporates the contributions from both chemical exchange and quadrupolar relaxation:

$$\frac{1}{T_2} = k^T_{\text{ex,obs}} + W_{\text{q,298}}\, e^{\frac{E_\text{q}}{R}\left[\frac{1}{T}-\frac{1}{298}\right]} \qquad (1)$$

where $W_{\text{q,298}}$ is the quadrupolar relaxation rate [$1/T_2(q)$] at 298 K, $k^T_{\text{ex,obs}}$ is the apparent pseudo-first-order rate constant for solvent exchange, and an Arrhenius-like relation is used to approximate the temperature dependence of the quadrupolar relaxation rate: $1/T_2(q) \propto$ $e^{-E_\text{q}/RT}$. The parameters T and R are temperature in Kelvin and the gas constant, respectively. An Arrhenius-like temperature dependence was also assumed for $k^T_{\text{ex,obs}}$ in order to obtain best-fit values for the quadrupolar relaxation term.

The $k^T_{\text{ex,obs}}$ values have contributions from exchange of waters from all hydrated complexes because the lifetimes of hydrolyzed complexes are short compared to the water exchange rate due to rapid proton exchange with solvent waters. For example, the complexes Al(H₂O)₆³⁺(aq) and AlOH(H₂O)₅²⁺(aq) interconvert via proton exchange with bulk waters at a rate that is rapid relative to rates of water exchange from the hydration spheres.[11] For solutions containing only these complexes, a single ^{17}O-NMR resonance is observed at approximately +22 ppm (in the absence of Mn(II)) corresponding to the hydration waters. [The sample geometry used in this study results in an additional temperature-dependent shift due to susceptibility effects; no attempt was made to measure chemical shifts.] The linewidth of this single ^{17}O-NMR resonance is proportional to the concentration of each species [Al(H₂O)₆³⁺(aq) and AlOH(H₂O)₅²⁺(aq)], weighted by the corresponding rate of water exchange (see refs 12,13).

If only the Al(H₂O)₆³⁺(aq) and AlOH(H₂O)₅²⁺(aq) complexes contribute to the linewidth, the apparent rate coefficient varies linearly with [H⁺]⁻¹ (or AlOH(H₂O)₅²⁺(aq) concentration):

$$k^T_{\text{ex,obs}} = k^T_1 + k^T_2[\text{H}^+]^{-1} \qquad (2)$$

The temperature dependence of the rate coefficient for exchange of water molecules from the inner-coordination sphere to the bulk solution takes the form:

$$k^T_n = \frac{k_\text{b}T}{h}\, e^{\frac{\Delta S_n^\ddagger}{R}}\, e^{\frac{-\Delta H_n^\ddagger}{RT}}, \quad n = 1 \text{ or } 2, \qquad (3)$$

where k_b and h are Boltzmann's and Planck's constants, respectively. The parameter k^T_1 is the rate coefficient for exchange of inner-sphere water molecules with bulk solution for the hexaqua complex ($k^T_{\text{ex,Al(H₂O)₆³⁺}}$) in this case the exponential terms include the activation entropy [$\Delta S^\ddagger$] and activation enthalpy [$\Delta H^\ddagger$] for chemical exchange. The other parameter k^T_2 relates to the elementary reaction rate coefficient for the AlOH(H₂O)₅²⁺(aq) complex as $k^T_2 = k^T_{\text{ex,AlOH(H₂O)₅²⁺}}K^T_{\text{a1}}$, where K^T_{a1} is the conditional equilibrium constant for the reaction shown in eq 4:

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$$\text{Al(H}_2\text{O)}_6^{3+} \leftrightarrow \text{AlOH(H}_2\text{O)}_5^{2+} + \text{H}^+ \qquad (4)$$
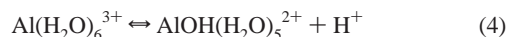
The activation parameters are similarly adjusted for the standard entropy and enthalpy of eq 4 at temperature (see below).

Results

Apparent rate coefficients [$k^T_{\text{ex,obs}}$] are calculated by fitting the measured ^{17}O-NMR T_2 values to eq 1, and a few of these results are shown in Figure 1a. Terms that account for quadrupolar relaxation, W_q and E_q, derived from these fits are consistent with previous studies[3,6] for the Al(H₂O)₆³⁺(aq) (22 kJ·mol⁻¹ and 2410 s⁻¹, respectively).

We find that the $k^T_{\text{ex,obs}}$ values for the series of samples at a given temperature vary linearly with [H⁺]⁻¹ (Figure 1b), indicating that the second term in eq 2 is important, and that for the more-hydrolyzed complexes, such as the dihydroxy complex, Al(OH)₂(H₂O)₄⁺(aq), the product of the relative concentration and the rate coefficient is too small to measurably affect the observed exchange rate of water. Although thermodynamic data[14−18] show that products from polymerization or precipitation might form above pH = 3.0, our results indicate that any contributions to the linewidths from these products are insignificant (i.e. the linearity of Figure 1b over the entire pH range). In addition, the ^{17}O-NMR resonances from any products resulting from polymerization or precipitation will occur as discrete species, because their rates of water exchange will be much greater than the rates of chemical exchange with the monomers. Hence, any signal from these species will appear as a separate peak, and will not contribute significantly to the temperature variation in the linewidth of the monomer peak in the ^{17}O-NMR spectra.

Rate constants and activation parameters for the Al(H₂O)₆³⁺(aq) complex have been previously reported[3,6] and are listed in Table 2. To obtain values for the contribution from the hydrolysis product AlOH(H₂O)₅²⁺(aq) we fit the data in Table 1 to eq 3 (Figure 1c), which yields $k^{298}_2 = 7.2 \times 10^{-2}$ M·s⁻¹, $\Delta H_2^\ddagger = 90.4$ kJ·mol⁻¹, and $\Delta S_2^\ddagger = 36.6$ J·mol⁻¹·K⁻¹. Using data from refs 7 and 8, the enthalpy and entropy of acid dissociation for Al(H₂O)₆³⁺(aq) ($\Delta H_\text{a}^\circ = 54$ kJ·mol⁻¹, $\Delta S_\text{a}^\circ = 73$. J·mol⁻¹·K⁻¹ and p$K^{298}_\text{a1} = 5.64$ ($I = 2.0$ M)) were used to obtain the following values for the exchange of water molecules on the AlOH(H₂O)₅²⁺(aq) complex: $k^{298}_{\text{ex,AlOH(H₂O)₅²⁺}} = 3.1 \times 10^4$ s⁻¹, $\Delta H^\ddagger = 36.4$ kJ·mol⁻¹, and $\Delta S^\ddagger = -36.4$ J·mol⁻¹·K⁻¹ (Table 2).

Discussion

Deprotonation of a single water molecule on Al(H₂O)₆³⁺(aq) to form the AlOH(H₂O)₅²⁺(aq) complex increases the lability of the other water ligands in the inner-coordination sphere by a factor of ≈10⁴ (Table 2). This enhancement is much larger than for the isoelectronic AlF(H₂O)₅²⁺(aq) complex (Table 2) and is among the largest measured for trivalent metals (Table 3). Of the trivalent metals, only Rh(III) exhibits as large a rate enhancement upon hydroxylation (Table 3, reference 19). Such a large difference in solvent exchange rates in aluminum

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a)

b)

c)
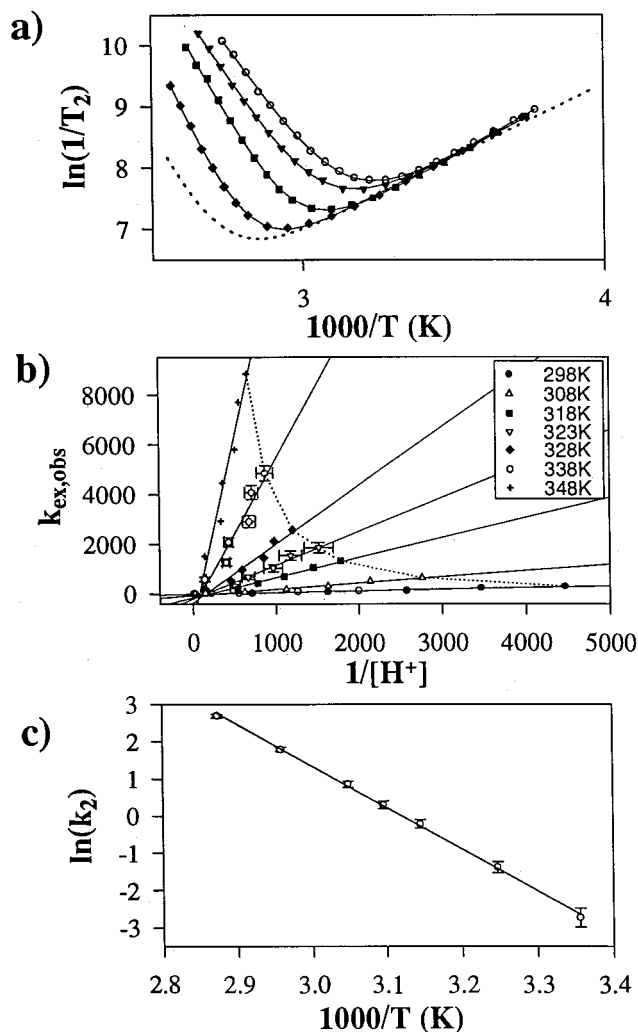
Figure 1. (a) Temperature dependence of $1/T_2$ values for AlCl$_3$–MnCl$_2$–H$_2$^{17}O solutions. Results for the Al(H$_2$O)$_6$$^{3+}$(aq) complex in the complete absence of hydrolysis products are indicated by the dotted line.[3] Only data for solutions at pH values (298 K) of 3.65 (○), 3.30 (▼), 2.35 (■), and 0.97 (♦) are shown; open symbols for ΣAl = 0.05 M, filled symbols for ΣAl = 0.10 M. The solid lines are fits to the data using eqs 1 and 3, where $k_n^T = k_{ex,obs}^T$. (b) Apparent rate coefficients for the exchange of a hydration water from the inner-coordination sphere of the complex and bulk solution. The different symbols for the data at 298 K correspond to ΣAl = 0.10 M (●) and ΣAl = 0.050 M (○); all other data is for ΣAl = 0.050 M. The slope of each line obtained from unconstrained linear regression is equal to k_2^T for that temperature (Table 1). The dotted line illustrates the temperature dependence of pH for one of the samples (sample shown as (○) in (a)). Error bars associated with the values of $k_{ex,obs}$ correspond to the estimated standard deviation of the mean of $k_{ex,obs}$, obtained by propagating a conservative 10% uncertainty in raw linewidths. The errors in [H$^+$]$^{-1}$ were estimated to be ±0.05 pH units. Error bars are only shown for data at 323 and 338 K to simplify the figure. (c) Temperature dependence of k_2^T. Error bars associated with the values of ln(k_2^T) correspond to the estimated standard deviation of the mean of k_2^T, obtained with the same values used to calculate the estimated standard deviation of $k_{ex,obs}$. The solid line is the fit to the data using eq 3.

complexes has long been suspected from studies of ligand exchange reactions (e.g., refs 20–23) in cases where the rate-controlling step is removal of an inner-sphere water molecule. Garrison and Crumbliss,[20] for example, report that acetohydroxamate enters the inner-coordination sphere of AlOH(H$_2$O)$_5$$^{2+}$(aq) at a rate 10^4 faster than for Al(H$_2$O)$_6$$^{3+}$(aq).

Table 1. Temperature Dependence of k_2^T for the AlOH(H$_2$O)$_5$$^{2+}$(aq) Complex

T (K)	k_2^T (M·s^{-1})
298	0.0654
308	0.251
318	0.807
323	1.36
328	2.35
338	6.01
348	14.8

Both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are reduced when a water molecule in the inner-coordination sphere of Al(H$_2$O)$_6$$^{3+}$(aq) is replaced with a hydroxyl ion (Table 2). The results of Hugi-Cleary et al.[6] for Al(H$_2$O)$_6$$^{3+}$(aq) are probably most accurate because they complemented ^{17}O-NMR line-broadening measurements with an injection-experiment to directly measure k_{ex} at low temperatures. The $\Delta H^{\ddagger}$ value they report for Al(H$_2$O)$_6$$^{3+}$(aq) ($\Delta H^{\ddagger} = 81-85$ kJ·mol^{-1}) is much larger than $\Delta H^{\ddagger} = 36.4$ kJ·mol^{-1} for AlOH(H$_2$O)$_5$$^{2+}$(aq). Both the absolute values of $\Delta H^{\ddagger}$ for Al(H$_2$O)$_6$$^{3+}$(aq) and AlOH(H$_2$O)$_5$$^{2+}$(aq), and the relative changes, compare well with values reported for Fe(H$_2$O)$_6$$^{3+}$(aq) and FeOH(H$_2$O)$_5$$^{2+}$(aq). Swaddle and Merbach[12] report $\Delta H^{\ddagger}$ values of 64.0(±2.5) and 42.4(±1.5) kJ·mol^{-1} for the Fe(H$_2$O)$_6$$^{3+}$(aq) and FeOH(H$_2$O)$_5$$^{2+}$(aq) complexes, respectively. The similarity in activation energies for the aluminum and ferric complexes is reasonable considering that Al(III) and Fe(III) are both hard Lewis acids.

Hugi-Cleary et al.[6] report an I$_d$ mechanism of solvent exchange around Al(H$_2$O)$_6$$^{3+}$(aq), and we expect hydroxylation of Al(H$_2$O)$_6$$^{3+}$(aq) to cause the reaction to become more dissociative due to the combination of reduced charge and coordinative saturation of the smaller Al(III) cation. Therefore positive $\Delta V^{\ddagger}$ values are predicted for the AlOH(H$_2$O)$_5$$^{2+}$(aq) complex, in spite of the measured $\Delta S^{\ddagger} < 0$, which is usually associated with an exchange reaction with considerable associative character.

The reaction rate parameters for AlOH(H$_2$O)$_5$$^{2+}$(aq) are surprisingly dissimilar to those for the isoelectronic AlF(H$_2$O)$_5$$^{2+}$(aq) complex. At 298 K the rates of exchange of water molecules from the inner-coordination sphere of AlF(H$_2$O)$_5$$^{2+}$(aq) to the bulk solution are only ~10^2 times more rapid than in Al(H$_2$O)$_6$$^{3+}$(aq). Furthermore, this increased rate for AlF(H$_2$O)$_5$$^{2+}$(aq) is largely attributed to an increase in the $\Delta S^{\ddagger}$ value upon fluoridation of Al(H$_2$O)$_6$$^{3+}$(aq). There is a relatively small difference in the activation enthalpies for solvent exchange between the inner-coordination sphere and bulk solution in Al(H$_2$O)$_6$$^{3+}$(aq) and AlF(H$_2$O)$_5$$^{2+}$(aq) complexes (Table 2). Charge-donation from hydroxyl to the aluminum is much greater than for the more electronegative fluoride, as one expects from the greater covalency of the aluminum–oxygen bond relative to the aluminum–fluorine bond.

Thermodynamic data for aluminum complexes are particularly precise because of this metal's geochemical importance. When comparing the activation parameters for the M(H$_2$O)$_5$(OH)$^{2+}$ complexes in Table 3, it is important to note that dramatically different values would have been calculated for Al(H$_2$O)$_5$(OH)$^{2+}$ if we had fit the reported p$K_{a1}(T)$ values using eq 5:

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Table 2. Rate Coefficients for Exchange of Water Molecules for the Inner-Coordination Sphere to the Bulk Solution

species	k_{ex}^{298} (s^{-1})	$\Delta H^{\ddagger}$ (kJ·mol^{-1})	$\Delta S^{\ddagger}$ (J·K^{-1}·mol^{-1})	ref
Al(H$_2$O)$_6^{3+}$	1.3	84.7	41.6	6
Al(H$_2$O)$_6^{3+}$	2.0	73 ($\pm$4)	6.0 ($\pm$11)	3
Al(H$_2$O)$_5$(OH)$^{2+}$	(3.1 $\pm$ 0.8) $\times10^4$ ^{a}	36.4 ($\pm$5)	−36.4 ($\pm$15)	this paper
Al(H$_2$O)$_5$F^{2+}	(1.1 $\pm$ 0.16) $\times10^2$ ^{a}	79 ($\pm$5)	60 ($\pm$8)	3

^{a} The single estimated standard deviations are estimated by propagating a 10% uncertainty in the linewidths through the equations.

Table 3. Rate Coefficients for Exchange of Water Molecules from the Inner-Coordination Sphere of Hexacoordinated Complexes of Some Trivalent Metals and Their First Hydrolysis Products. Uncertainties Are as Reported in the Original Work or in Later Compilations by the Original Authors

complex	k_{ex}^{298} (s^{-1})	$\Delta H^{\ddagger}$ (kJ·mol^{-1})	$\Delta S^{\ddagger}$ (J·mol^{-1}·K^{-1})	$\Delta V_o^{\ddagger}$ (cm^3·mol^{-1})	mechanism	ref
Ga(H$_2$O)$_6^{3+}$(aq)	4.0 $\times$ 10^2	67.1 ($\pm$2.5)	30.1 ($\pm$7.7)	+5.0 ($\pm$0.5)	I$_d$	24
GaOH(H$_2$O)$_5^{2+}$(aq)	1.1 $\times$ 10^5	58.9	−	+6.2	I$_d$	24
Ti(H$_2$O)$_6^{3+}$(aq)	1.8 $\times$ 10^5	43.4 ($\pm$0.7)	1.2 ($\pm$2.2)	−12.1 ($\pm$0.4)	I$_a$	25
Fe(H$_2$O)$_6^{3+}$(aq)	1.6 $\times$ 10^2	64.0 ($\pm$2.5)	12.1 ($\pm$6.7)	−5.4 ($\pm$0.4)	I$_a$	12,13
FeOH(H$_2$O)$_5^{2+}$(aq)	1.2 $\times$ 10^5	42.4 ($\pm$1.5)	5.3 ($\pm$4)	+7.0 ($\pm$0.5)	I$_d$	12,13
Al(H$_2$O)$_6^{3+}$(aq)	1.3	84.7 ($\pm$0.3)	41.6 ($\pm$0.9)	+5.7 ($\pm$0.2)	I$_d$	6
AlOH(H$_2$O)$_5^{2+}$(aq)	3.1 $\times$ 10^4	36.4 ($\pm$5)	−36.4 ($\pm$15)			this paper
Cr(H$_2$O)$_6^{3+}$(aq)	2.4 $\times$ 10^{-6}	108.6 ($\pm$2.7)	11.6 ($\pm$8.6)	−9.6 ($\pm$0.1)	I$_a$	26
CrOH(H$_2$O)$_5^{2+}$(aq)	1.8 $\times$ 10^{-4}	111 ($\pm$2.5)	55.6 ($\pm$8.1)	+2.7 ($\pm$0.5)	I	26
Ru(H$_2$O)$_6^{3+}$(aq)	3.5 $\times$ 10^{-6}	89.8 ($\pm$4)	−48.3 ($\pm$14)	−8.3 ($\pm$2.1)	I$_a$	27
RuOH(H$_2$O)$_5^{2+}$(aq)	5.9 $\times$ 10^{-4}	95.8	14.9	+0.9	I	27
Rh(H$_2$O)$_6^{3+}$(aq)	2.2 $\times$ 10^{-9}	131.2 ($\pm$23)	29.3 ($\pm$26)	−4.1 ($\pm$0.6)	I$_a$	19
RhOH(H$_2$O)$_5^{2+}$(aq)	4.2 $\times$ 10^{-5}	103	−	+1.5	I	19
Ir(H$_2$O)$_6^{3+}$(aq)	1.1 $\times$ 10^{-10}	130.5 ($\pm$0.6)	2.1 ($\pm$2.1)	−5.7 ($\pm$0.5)	I$_a$	28
IrOH(H$_2$O)$_5^{2+}$(aq)	5.6 $\times$ 10^{-7}	−	−	+1.5	I	28
V(H$_2$O)$_6^{3+}$(aq)	5.0 $\times$ 10^2	49.4 ($\pm$0.8)	−27.8 ($\pm$2)	−8.9 ($\pm$0.4)	I$_a$	29

$$pK_{a1}(T) = \frac{1}{2.303R}\left(\frac{\Delta H_a^{\circ}}{T} - \Delta S_a^{\circ}\right) \qquad (5)$$

rather than using the values of ΔH_a° and ΔS_a° for eq 4 reported in references (7) and (8). The activation parameters in this case would have been $\Delta H_a^{\circ} = 46$ kJ·mol^{-1} and $\Delta S_a^{\circ} = 47$ J·mol^{-1}·K^{-1}, as opposed to the reported values of $\Delta H_a^{\circ} = 54$ kJ·mol^{-1} and $\Delta S_a^{\circ} = 73$ J·mol^{-1}·K^{-1}. The resulting activation parameters for the Al(H$_2$O)$_5$(OH)$^{2+}$ complex would have been $\Delta H^{\ddagger} = 44$ kJ·mol^{-1} and $\Delta S^{\ddagger} = -11$ J·mol^{-1}·K^{-1} (where $\Delta H^{\ddagger} = \Delta H_2^{\ddagger} - \Delta H_a^{\circ}$ and $\Delta S^{\ddagger} = \Delta S_2^{\ddagger} - \Delta S_a^{\circ}$), as opposed to $\Delta H^{\ddagger} = 36$ kJ·mol^{-1} and $\Delta S^{\ddagger} = -36$ J·mol^{-1}·K^{-1}. Suprisingly, both sets of ΔH_a° and ΔS_a° values give the correct value of K_{a1} using eq 5, and both sets of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values give the same value of $k_{ex,AlOH(H_2O)_5^{2+}}^{298}$ using eq 3 (within experimental error). Comparisons are made in Table 3 between complexes for which ΔH_a° is well known, such as Al(H$_2$O)$_5$(OH)$^{2+}$, with those for which the ΔH_a° values are uncertain. In many cases these are calculated using eq 5 and the temperature dependencies of pK_{a1} values, which themselves can be poorly known. Hugi-Cleary

et al.[24] emphasize a similar point when they discuss the very large range in pK_{a1} values for Ga(III) hydrolysis (see Table IV in reference 24).

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