$\phi_A^{(1)}$ being the excited eigenstate coupling with $\phi_A^{(0)}$ through $\hat{L}_x$ and Δ_1 the energy gap between the two states. λ is the local spin–orbit parameter. A_y and A_z are obtained by circular permutation $x \rightarrow y \rightarrow z$ and $1 \rightarrow 2 \rightarrow 3$. All the terms A_u, $u = x$, y, z, are positive since $j^{(ioio)}$ is much larger than $j^{(iioo)}$ for any i. It has been suggested[13,27] that the integral $j^{(x^2-y^2,xy,x^2-y^2,xy)}$, which involves the overlap density $\rho^{(x^2-y^2,xy)}$ between orthogonal magnetic orbitals localized in the plane of the bridging network, is the largest among the $j^{(ioio)}$ integrals. It follows that we can approximate D_{zz}^{ex} by

$$D_{zz}^{\text{ex}} \simeq -\frac{2}{3}\frac{\lambda^2}{\Delta_z^2}L_z^{(x^2-y^2,0)}L_z^{(0,x^2-y^2)}j^{(x^2-y^2,0,x^2-y^2,0)}$$

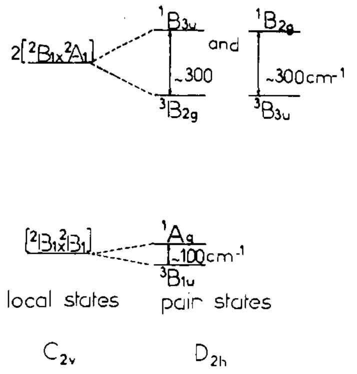
which can be rewritten as

$$D_{zz}^{\text{ex}} \simeq -\frac{1}{24}\Delta g_z^2 k^2 j^{(x^2-y^2,0,x^2-y^2,0)} \qquad (5)$$

where $\Delta g_z = 2 - g_{A_z}$ refers to the doublet local state. k is a covalent factor defined as

$$L_z^{(x^2-y^2,0)} = -2ik$$

With $\Delta g_z = 0.2414$ and $k \sim 0.9$, we obtain for $j^{(x^2-y^2,0,x^2-y^2,0)}$ a value of the order of 150 cm^{-1}. Of course, this value should only be considered as a rough approximation. In particular, the equations (3) and (4) are valid only when all the integrals $S^{(oi)} = \langle\phi_A^{(0)}|\phi_B^{(i)}\rangle$ are zero. Otherwise, the A_u's contain additional terms in $\beta^{(oi)}S^{(oi)}$ where $\beta^{(oi)}$ is a one-electron-transfer integral involving the ground state of an ion and an excited state of the other. In the present case, the orientation of **g** suggests that the local ground states are not pure xy states so that some $S^{(oi)}$ may be not rigorously vanishing. Nevertheless, this EPR study completes the magnetic investigation by giving an order of magnitude of $2j^{(x^2-y^2,0,x^2-y^2,0)} \sim 300$ cm^{-1} for the $^3B_{2g}$–$^1B_{3u}$ and $^3B_{3u}$–$^1B_{2g}$ splittings within the states arising from the interaction between the $^2B_1$ (xy) ground state of an ion and the $^2A_1$ ($x^2 - y^2$) excited state of the other in $[Cu_2(t\text{-Bupy})_4(N_3)_2](ClO_4)_2$, as schematized in **3**, where we refer to idealized C_{2v} site symmetries and D_{2h} molecular symmetry.



3

Finally, we can notice that, although the nature of the bridges is different, the title compound closely follows the correlation between D_{zz} and the Cu···Cu separation recently proposed.[16]

Acknowledgment. This work is supported by NATO Research Grant No. 0271/83. We are most grateful to D. Vivien, who kindly put to our disposal his program of EPR simulation.

Registry No. $[Cu_2(t\text{-Bupy})_4(N_3)_2](ClO_4)_2$, 93966-35-9.

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Contribution from the Departments of Chemistry and Physics,
The University of Calgary, Calgary, Alberta, Canada T2N 1N4

Conjugate Base Pathway for Water Exchange on Aqueous Chromium(III): Variable-Pressure and -Temperature Kinetic Study

FAN-CHOU XU,[1a] H. ROY KROUSE,[1b] and THOMAS W. SWADDLE*[1a]

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Oxygen-18 tracer studies at ionic strength 0.7 mol kg^{-1} with $[H^+]$ ranging from 0.0031 to 0.12 mol kg^{-1}, temperature from 25 to 55 °C, and pressure from 0.1 to 400 MPa gave the following kinetic parameters for water exchange on aqueous $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5OH^{2+}$, respectively: k(298.15 K, 0.1 MPa) = 2.4×10^{-6} and 1.8×10^{-4} s^{-1}; $\Delta H^* = 108.6 \pm 2.7$ and 111.0 ± 2.5 kJ mol^{-1}; $\Delta S^* = +11.6 \pm 8.6$ and $+55.6 \pm 8.1$ J K^{-1} mol^{-1}; $\Delta V^* = -9.6 \pm 0.1$ and $+2.7 \pm 0.5$ cm^3 mol^{-1}. For $Cr(H_2O)_6^{3+}$, ln k is accurately a linear function of pressure to 400 MPa at least, implying no solvational change in the activation process. The mechanistic significance of these results is discussed.

Introduction

Hunt, Plane, and Taube, in their pioneering studies[2-5] of the primary hydration of aqueous metal ions, studied the rate of exchange of $H_2{}^{18}O$ between $Cr(H_2O)_6^{3+}$ and solvent water while varying the reaction conditions including the hydrogen ion concentration. They found no significant dependence of the observed first-order rate coefficient k_{obsd} upon $[H^+]$ down to pH ~2. On the other hand, Plumb and Harris[6] found a two-term rate equation of the type

$$k_{\text{obsd}} = k_0 + k_{-1}[H^+]^{-1} \qquad (1)$$

to apply in the exchange of $H_2{}^{18}O$ with Rh^{3+}(aq). More recently it has been shown[7,8] that a similar equation in which the term $k_{-1}[H^+]^{-1}$ is often dominant governs the rate of water exchange on monomeric Fe^{3+}(aq) as given by ^{17}O NMR line broadening with $0.008 \leqslant [H^+] \leqslant 6$ mol kg^{-1}.

The reported absence of an exchange pathway for Cr^{3+}(aq) corresponding to the $k_{-1}[H^+]^{-1}$ term, i.e., to exchange on the conjugate base $Cr(H_2O)_5OH^{2+}$

$$Cr(H_2O)_6^{3+} \overset{K_a}{\rightleftharpoons} Cr(H_2O)_5OH^{2+} + H^+ \qquad (2)$$

calls for reinvestigation, since pK_a values for $M(H_2O)_6^{3+}$ (M = Fe, Rh, Cr) do not vary very widely (2.9,[8] 3.3,[6] and 4.1,[9] respectively at 25 °C and ionic strength I = 0.5–1.0 mol L^{-1}). Indeed, preliminary studies by Eagle in our laboratories suggested that $Cr(H_2O)_5OH^{2+}$ is some 60 times more reactive in water exchange than is $Cr(H_2O)_6^{3+}$ at 45 °C, the corresponding ratios for Rh^{3+}(aq) and Fe^{3+}(aq) being ~690 at 64 °C[10] and 750 at

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25 °C,[7] respectively. Thus, given the improved techniques and mass spectrometers now available, we have been able to work with chromium(III) concentrations 10–50 times lower, and hence with much lower $[H^+]$ (see below), than was possible in the 1950s and so have obtained meaningful activation parameters for water exchange on $Cr(H_2O)_5OH^{2+}$ from 25 to 55 °C and 0.1–400 MPa.

By the same token, the presently accepted[11] kinetic parameters for water exchange on $Cr(H_2O)_6^{3+}$ itself (k_0, ΔH_0^*, ΔS_0^*, ΔV_0^*) need to be revised to eliminate small contributions from the conjugate base pathway. In particular, the improved precision of our current results and the availability of pressure equipment rated to 400 MPa provide an opportunity to check the validity of the usual assumption that the volume of activation ΔV_0^* for simple solvent exchange on solvated metal ions is truly constant over the pressure ranges normally used by high-pressure solution kineticists. This assertion, apart from its empirical value, implies (if it is correct) that the solvent-exchange process is properly described as an *interchange* mechanism,[12] i.e., one in which the solvation sheath does not have time to reequilibrate with bulk solvent during the lifetime of any intermediate of increased or reduced primary coordination number. The results of our first high-pressure study of the $Cr^{3+}(aq)$ water exchange, which had a pressure ceiling of 240 MPa and employed a commercial general purpose mass spectrometer, indicated a solvational change during activation of less than 1 molecule of water *but* with an uncertainty of at least ±1 molecule;[13] our present results reduce this uncertainty sufficiently to vindicate the original claim[11] that the mechanism is indeed of the interchange type.

Experimental Section

Certified analytical grade reagents were used throughout. Procedures were generally similar to those described previously,[11] with the following changes. Solid $[Cr(H_2O)_6](ClO_4)_3{\cdot}nH_2O$ ($n \sim 3$) was made by reduction of CrO_3 with H_2O_2 in aqueous $HClO_4$, recrystallized from either 0.1 or 1.0 mol L^{-1} $HClO_4$, sucked as dry as possible on a sintered-glass filter, and stored over silica gel. Some preparations were labeled with ~1.5% $H_2{}^{18}O$ solvent (Biorad) containing ~1 mol L^{-1} $HClO_4$ at 60 °C for 2 h and were recrystallized at 0 °C after concentration of the solution at 60 °C in a rotary evaporator. All these products were checked spectrophotometrically for freedom from hydrolytic Cr(III) oligomers (absorbances at the minimum at 238 nm were typically ~30% of that at the 260-nm maximum) and analyzed for Cr content spectrophotometrically as $CrO_4{}^{2-}$.

These products contained small amounts of occluded $HClO_4$, which had been present to suppress hydrolytic oligomerization in the recrystallization step. Rough estimates of the $HClO_4$ content were made by dissolving the weighed solid in water and flushing the solution through a column of Dowex 50W-X8 H^+ form ion-exchange resin, titrating the eluted H^+, and subtracting the H^+ equivalent of the absorbed Cr^{3+}. These values corroborated the more precise determinations of the occluded acid content $[H^+]_{occ}$ of solutions of $[Cr(H_2O)_6](ClO_4)_3{\cdot}nH_2O$ (either alone or with added $NaClO_4$ to adjust the ionic strength to 0.7 mol kg^{-1} as required for kinetics) made by measuring their pH with an Orion Research 801A meter and Beckman 38502 combination electrode and correcting the reading for hydrogen ion contributed by hydrolysis of the $Cr(H_2O)_6^{3+}$ ion, $[H^+]_{hyd}$

$$\begin{aligned}[H^+]_{occ} &= [H^+]_{meter} - [H^+]_{hyd} \\ &= [H^+]_{meter} - K_a[Cr^{3+}]/[H^+]_{meter} \qquad (3)\end{aligned}$$

where K_a(eq 2) = 5.86×10^{-5} at room temperature (21 °C) and $I \sim 0.7$ mol kg^{-1}.[9] For this purpose, the pH meter was standardized in the usual way against potassium hydrogen phthalate buffer, but correction factors (typically +0.150 pH unit) were evaluated for the anticipated range of $[H^+]_{meter}$ at the selected ionic strength by measurements on appropriate $HClO_4/NaClO_4$ solutions. Allowance for a slight persistent drift in the readings was made by taking readings at a fixed interval (10 min) after immersion of the electrodes.

Solutions for the kinetic measurements were made with $I = 0.7$ mol L^{-1} in one of three ways. (a) For high-pressure studies at 45 °C and $[H^+] \sim 0.1$ mol L^{-1} only, solid samples of chromium(III) perchlorate *n*-hydrate (not isotopically labeled) were weighed into 100-mL graduated flasks, 10 mL of 1.0 mol L^{-1} $HClO_4$ was added, and the solution was made to the mark with 1.5% $H_2{}^{18}O$. (b) For most other experirments, $H_2{}^{18}O$-labeled chromium(III) perchlorate *n*-hydrate was weighed into 50-mL graduated flasks with the requisite amounts of $HClO_4$ and $NaClO_4{\cdot}H_2O$ and made to the mark with pure water. (c) For some runs at 45 °C and 100 or 325 MPa, runs at 25 °C and low $[H^+]$, and all runs at 55 °C, the reaction mixture was prepared by dilution of an aliquot of a stock solution containing appropriate amounts of $HClO_4$, $NaClO_4$, and labeled $[Cr(H_2O)_6](ClO_4)_3$, which was kept frozen until required.

For runs at atmospheric pressure, the solutions were kept in closed, darkened[5] flasks in a thermostated bath (±0.01 K) and samples were pipetted out as required. Runs at high pressure were conducted in the apparatus described previously[14] except that the tantalum sampling capillary was replaced with one of Teflon. In all cases, 10–12 samples were collected over at least 3 half-lives of the exchange reaction and quenched to 0 °C, the $Cr(H_2O)_6^{3+}$ was precipitated as the phosphate, and the recovered coordinated water was converted CO_2 with 99.99% guanidinium chloride (Chemical Dynamics Corp.) as previously described.[11] The abundance of $^{12}C^{16}O^{18}O$ relative to $^{12}C^{16}O_2$ was measured on a mass spectrometer constructed around Micromass 903 components. Triple collection of ion currents of singly charged masses 44, 45, and 46 permitted corrections for any minor variations in ^{13}C and ^{17}O abundances. Ultraviolet spectra of selected solution samples after 10 half-lives of the exchange reaction showed oligomerization during runs to be negligible.

Results

The kinetic results are summarized in Table I, in which the total H^+ concentration $[H^+]_{tot}$ is the sum of the occluded, added ($[H^+]_{add}$), and hydrolytic hydrogen ion contributions. This last, $[H^+]_{hyd}$, had to be calculated from the temperature and pressure dependences of K_a for reaction 2

$$\ln K_a{}^{P,T} = \Delta S/R - (\Delta H + P\Delta V)/RT \qquad (4)$$

where ΔS = 51.4 J K^{-1} mol^{-1}, ΔH = 38.9 kJ mol^{-1},and ΔV = −3.8 cm^3 mol^{-1} (recalculated from Swaddle and Kong;[9] these parameters actually refer to I = 0.5 mol kg^{-1}, but the difference at I = 0.7 will be negligible). Concentrations were converted from a working scale of mol L^{-1} at 21 °C and 0.1 MPa to mol kg^{-1} by factors (1.0295 for 0.02 mol L^{-1} $Cr(ClO_4)_3/HClO_4/NaClO_4$, 1.0174 for 0.10 mol L^{-1} $Cr(ClO_4)_3/HClO_4$) derived from the measured densities of the solutions. Throughout this paper, the uncertainty limits cited are standard deviations given by linear least-squares regression. The rate constants k_{obsd} refer to the observed first-order rate coefficients for water exchange and, hence, to the exchange of a particular coordinated water molecule;[15–17] in some earlier papers,[11,18] k_{obsd} was erroneously divided by a statistical factor, and the resulting rate coefficients and entropies of activation should therefore be disregarded.

The total hydrogen ion content of each solution specified in Table I was the sum of the contributions of occluded $HClO_4$, added $HClO_4$, and hydrolysis of $Cr(H_2O)_6^{3+}$ as per eq 2.

$$[H^+]_{total} = [H^+]_{occ} + [H^+]_{added} + [H^+]_{hyd} \qquad (5)$$

The hydrolytic contribution was given by

$$[H^+]_{hyd} = K_a[Cr^3]/[H^+]_{total} \qquad (6)$$

where K_a was calculated from eq 4 for the appropriate temperature and pressure, and combination of (5) and (6) gave a quadratic equation solvable for $[H^+]_{total}$.

It was found that k_{obsd} values were reproducible to about ±2%, except at low $[H^+]_{total}$ at 25 and 55 °C (not reported in Table I), and were accurately described by eq 1. Values of the parameters k_0 and k_{-1} that represent the data at atmospheric pressure are listed in Table II; k_0 represents water exchange on $Cr(H_2O)_6^{3+}$ itself, while k_{OH}, the corresponding rate coefficient for water exchange on $Cr(H_2O)_5OH^{2+}$, is given by k_{-1}/K_a with sufficient accuracy at the total acidities listed in Table I. Table III lists values of k_0 and k_{-1} obtained by fitting k_{obsd} at selected pressures

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Table I. First-Order Rate Coefficients k_{obsd} for the Exchange of $H_2{}^{18}O$ between $Cr^{III}(aq)$ and Solvent Water at Ionic Strength 0.7 mol kg^{-1} [a]

T/°C	P/MPa	$[Cr(ClO_4)_3]$/ mol kg^{-1}	$[H^+]_{occ}$/ mol kg^{-1}	$[H^+]_{added}$/ mol kg^{-1}	$[H^+]_{total}$/ mol kg^{-1}	k_{obsd}/10^{-5} s^{-1}
25.0	0.1	0.0206	0.003 93	0.111 3	0.115 3	0.245 ± 0.006
			0.003 93	0.005 87	0.009 96	0.374 ± 0.008
			0.004 15	0.002 17	0.006 56	0.439 ± 0.013
35.0	0.1	0.0206	0.002 32	0.112 6	0.115 0	1.152 ± 0.041
				0.008 86	0.011 41	1.817 ± 0.024
				0.002 68	0.005 47	2.808 ± 0.040
				0	0.003 15	4.03 ± 0.13
45.0	0.1	0.1017	0.009 61	0.113 8	0.123 6	4.30 ± 0.21
		0.0206	0.002 32	0.018 12	0.020 64	6.50 ± 0.10
				0.008 86	0.011 54	9.27 ± 0.27
				0.002 68	0.005 72	14.98 ± 0.37
	101	0.1017	0.009 61	0.113 8	0.123 6	5.89 ± 0.04
	100	0.0206	0.004 53	0.005 87	0.010 85	11.45 ± 0.38
				0.002 17	0.007 36	13.50 ± 0.70
				0	0.005 43	17.59 ± 0.97
	197	0.1017	0.009 61	0.113 8	0.123 6	8.15 ± 0.09
	200	0.0206	0.002 69	0.008 86	0.012 01	13.79 ± 0.32
				0.002 60	0.006 26	17.85 ± 0.38
				0	0.004 07	24.96 ± 0.97
	246	0.1017	0.009 61	0.113 8	0.123 6	9.63 ± 0.29
	327					13.19 ± 0.28
	325	0.0206	0.003 44	0.005 87	0.009 99	19.58 ± 0.60
				0.002 17	0.006 62	23.73 ± 0.81
				0	0.004 83	27.83 ± 0.57
	401	0.1017	0.009 61	0.113 8	0.123 6	16.60 ± 0.20
55.0	0.1	0.0206	0.003 93	0.111 3	0.115 3	18.10 ± 0.60

[a] $HClO_4/Cr(ClO_4)_3$, for $[Cr(ClO_4)_3]$ = 0.1017 mol kg^{-1}; $NaClO_4/HClO_4/Cr(ClO_4)_3$ otherwise.

Table II. Rate Coefficients for Water Exchange on $Cr(H_2O)_6{}^{3+}$ (k_0) and $Cr(H_2O)_5OH^{2+}$ (k_{OH}) at Ionic Strength 0.7 mol kg^{-1} and 0.1 MPa Pressure

T/°C	k_0/10^{-5} s^{-1}	k_{-1}/10^{-7} mol kg^{-1} s^{-1} [a]	k_{OH}/ 10^{-4} s^{-1} [b]
25.0	0.234 ± 0.004	0.136 ± 0.004	1.83
35.0	1.05 ± 0.04	0.942 ± 0.022	7.65
45.0	3.61 ± 0.18	6.48 ± 0.18	32.6
55.0	14.8 ± 0.6[c]	(36.9 ± 1.0)[d]	(119)[d]

[a] Equation 1. [b] $k_{OH} = k_{-1}/K_a$ (K_a from eq 4). [c] Calculated from k_{obsd} by extrapolated k_{-1} value. [d] Extrapolated from lower temperatures.

Table III. Pressure Dependence of Rate Coefficients for Water Exchange on Aqueous Cr(III) at 45.0 °C and Ionic Strength 0.7 mol kg^{-1}

P/MPa	k_0/10^{-5} s^{-1}	k_{-1}/10^{-7} mol kg^{-1} s^{-1}
0.1	3.61 ± 0.13	6.48 ± 0.18
100	5.29 ± 0.49	6.49 ± 0.40
200	7.60 ± 0.60	6.92 ± 0.39
325	12.47 ± 0.22	7.39 ± 0.16

to eq 1, while k_0 values over a wider pressure range, obtained by subtracting the small recalculated k_{-1} contribution from k_{obsd} values at $[H^+]$ = 0.1017 mol kg^{-1} and 45 °C, are collected in Table IV. The data of Table II and III, combined with $\Delta V_a = -3.8 \pm 0.4$ cm^3 mol^{-1} for reaction 2,[9] yield the activation parameters summarized in Table V, if enthalpies and entropies of activation are taken to be independent of temperature and volumes of activation to be independent of pressure. Indeed, ln (k/T) and ln k are linear functions of $1/T$ and pressure, respectively, to within the experimental uncertainty.

The extent to which $\Delta V_0{}^*$ for water exchange on $Cr(H_2O)_6{}^{3+}$ is independent of pressure may be expressed statistically with the data of Table IV. If, instead of the linear equation

$$\ln k_0 = \ln k_0{}^0 - P\Delta V_0{}^*/RT \qquad (7)$$

the quadratic function

$$\ln k_0 = \ln k_0{}^0 - P\Delta V_0{}^*/RT + \Delta\beta_0{}^*P^2/2RT \qquad (8)$$

Table IV. Pressure Dependence of First-Order Rate Coefficients k_0 for the Exchange of Water on $Cr(H_2O)_6{}^{3+}$ Alone at 45.0 °C and I = 0.7 mol kg^{-1}

P/MPa	k_0/10^{-5} s^{-1}	P/MPa	k_0/10^{-5} s^{-1}	P/MPa	k_0/10^{-5} s^{-1}
0.1	3.78	196.9	7.59	326.9	12.60
101.3	5.35	245.9	9.06	400.7	16.0

Table V. Activation Parameters for Water Exchange on Aqueous $Cr(H_2O)_6{}^{3+}$ and $Cr(H_2O)_5OH^{2+}$ at Ionic Strength 0.7 mol kg^{-1}

	$Cr(H_2O)_6{}^{3+}$	$Cr(H_2O)_5OH^{2+}$
ΔH^*/kJ mol^{-1}	108.6 ± 2.7	111.0 ± 2.5
ΔS^*/J K^{-1} mol^{-1}	+11.6 ± 8.6	+55.6 ± 8.1
k(298.15 K, 0.1 MPa)/s^{-1}	2.36×10^{-6}	1.78×10^{-4}
ΔV^*/cm^3 mol^{-1}	−10.0 ± 0.1[a]	+2.7 ± 0.5

[a] From data of Table III. Definitive value, from data of Table IV, is −9.6 ± 0.1 cm^3 mol^{-1} (see text).

(where $\Delta\beta_0{}^*$ is the compressibility coefficient of activation)[19] is used, one obtains $\Delta V_0{}^* = -9.3 \pm 0.5$ cm^3 mol^{-1} and $\Delta\beta_0{}^* = +(1.6 \pm 2.3) \times 10^{-3}$ cm^3 mol^{-1} MPa^{-1}; $\Delta\beta_0{}^*$ is clearly not statistically different from zero and is in any event very small. Alternatively, if one chooses to express any nonlinearity of the ln k_0 vs. pressure plot in terms of the gain of x molecules of solvating water from bulk solvent on going to the transition state, fitting the data of Table IV to the equation proposed elsewhere[14] and amended here for 45 °C[20] with P in MPa

$$\ln k_0 = \ln k_0{}^0 - P\Delta V_0{}^*/RT - 9.41 \times 10^{-4}x((P + 308.1)\ln(1 + P/308.1) - P) \qquad (9)$$

gives $\Delta V_0{}^* = -9.2 \pm 0.6$ cm^3 mol^{-1} and $x = -0.3 \pm 0.4$. According to this analysis, then, there is no significant gain or loss of solvating water in the activation process.

Clearly, eq 7 expresses the pressure dependence of ln k_0 accurately up to 400 MPa at least and with it the data of Table IV gives a definitive value of $\Delta V_0{}^* = -9.6_4 \pm 0.1_3$ cm^3 mol^{-1} for water exchange on $Cr(H_2O)_6{}^{3+}$.

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Table VI. Rate Constants for the Reactions of $M(H_2O)_6{}^{3+}$ and $M(H_2O)_5OH^{2+}$ with X^{z-} in Water[a]

X^{z-}	$k_{CrOH^{2+}}$[b]	$k_{Cr^{3+}}$[b]	$k_{CrOH^{2+}}/k_{Cr^{3+}}$	$k_{FeOH^{2+}}$[b]	$k_{Fe^{3+}}$[b]	$k_{FeOH^{2+}}/k_{Fe^{3+}}$
H_2O	1.8×10^{-4}[c]	2.4×10^{-6}[c]	75	1.2×10^{5}[c]	1.6×10^{2}[c]	750
$SO_4{}^{2-}$	6.1×10^{-4}	1.1×10^{-5}	57	1.1×10^{5}	2.3×10^{3}	50
$\mathit{N}CS^-$	9.7×10^{-5}	1.7×10^{-6}	58	5.9×10^{3}	7.3×10	80
$NO_3{}^-$	1.5×10^{-4}	7.1×10^{-7}	211			
Cl^-	4.2×10^{-5}	3.0×10^{-8}	1400	5.5×10^{3}	4.8	1150
Br^-	2.7×10^{-5}	8.7×10^{-9}	3100	2.8×10^{3}	1.6	1750
$\mathit{S}CN^-$	2.1×10^{-5}	9.8×10^{-9}	2150			
I^-	4.6×10^{-6}	8.3×10^{-10}	5540			

[a] From sources cited in ref 7, 17, and 22–26 and this work. Ionic strengths approximately 1 mol L^{-1} at 298.2 K and 0.1 MPa. No allowances for ion association. [b] Units: L mol^{-1} s^{-1}, except as indicated. [c] Units: s^{-1}. Not directly comparable with anation rate data.

Discussion

The simplest interpretation of the volumes of activation $\Delta V_0{}^* = -9.6$ and $\Delta V_{OH}{}^* = +2.7$ cm^3 mol^{-1} is that they reflect a strongly associative mode of activation of solvent exchange on $Cr(H_2O)_6{}^{3+}$ and a predominantly (but not exclusively) dissociative one on $Cr(H_2O)_5OH^{2+}$.[17,21] The corresponding volumes of activation on $Fe(H_2O)_6{}^{3+}$ and $Fe(H_2O)_5OH^{2+}$ are −5.4 and +7.0 cm^3 mol^{-1},[8] so that the asssociative contributions to the activation processes may be said to be less significant for Fe(III) than for Cr(III). This is borne out by consideration of the rates of the reactions

$$M(H_2O)_6{}^{3+} + X^{z-} \rightarrow M(H_2O)_5X^{(3-z)+} + H_2O \qquad (10)$$

and

$$M(H_2O)_5OH^{2+} + X^{z-} \rightarrow M(H_2O)_5X^{(3-z)+} + H_2O \qquad (11)$$

listed in Table VI. It is clear that, for $z = 1$ at least (i.e., where ion-pairing effects are minimal), the selectivity[17] displayed by $Cr(H_2O)_6{}^{3+}$ is quite strong (cf. Espenson[22]) while that of $Cr(H_2O)_5OH^{2+}$ is weaker but still clearly discernible, consistent with the *small* positive value of $\Delta V_{OH}{}^*$. For the corresponding Fe(III) species, selectively is noticeably less. These observations are in accord withthe reactivity–selectivity principle, viz., that a series of fast reactions usually exhibits less selectivity than a comparable set of slow ones.[17]

The absence of any detectable pressure dependence of $\Delta V_0{}^*$ for water exchange on $Cr(H_2O)_6{}^{3+}$ translates (through eq 9) into the retention of the complete solvation sheath during the activation process; i.e., the kinetically significant displacements of water molecules occur cooperatively within the solvation sheath. Thus, the mechanism is aptly described as associative *interchange* (I_a) in the Langford–Gray nomenclature,[12] as suggested previously.[11] This is in accordance with the results of computer modeling of rare solvent-exchange process by Connick and Alder, who found that the two exchanging solvent molecules will both be located at intermediate positions between the first and second coordination shells in the transition state (implying at least some degree of associative activation) and that "exchange occurs by a highly collective motion involving very many small displacements of all the particles in the first two coordination shells".[27]

A hint as to the mechanism of water exchange on $Cr(H_2O)_5OH^{2+}$ comes from the difference ($\Delta V_{OH}{}^* - \Delta V_0{}^*$) between the volumes of activation for water exchange on $M(H_2O)_5OH^{2+}$ and $M(H_2O)_6{}^{3+}$. These differences are essentially the same (12.4 cm^3 mol^{-1}) for M = Cr as for M = Fe and are close to the limiting value of ~13 cm^3 mol^{-1} expected for the loss of one water molecule from the first coordination sphere of a typical aqueous metal cation to bulk solvent.[28] These coincidences suggest that the activation processes for solvent exchange on $M(H_2O)_6{}^{3+}$ and the corresponding $M(H_2O)_5OH^{2+}$ are very similar *except that* there is a step involving complete loss of one coordinated water molecule from $M(H_2O)_5OH^{2+}$ to bulk solvent somewhere along the reaction coordinate before the rate-determining transition state is passed. Such a loss of bound water to bulk solvent is tantamount to solvent exchange and so presumably comes last in any multistep activation process. Complete dissociative loss of a coordinated water from $M(H_2O)_5OH^{2+}$ cannot be the *only* significant step in the activation process, as this would lead to $\Delta V_{OH}{}^* \sim +13$ cm^3 mol^{-1} for any M,[28] which is not at all the case; otherwise, resemblances to the classic dissociative conjugate-base or S_N1CB mechanism[29] are evident. Details of the activation process in $M(H_2O)_5OH^{2+}$, however, remain matters for speculation.

Finally, we note from Table V that the approximately 75-fold higher reactivity of $Cr(H_2O)_5OH^{2+}$ relative to $Cr(H_2O)_6{}^{3+}$ is mainly entropic in origin, and so almost independent of temperature. Grant and Jordan,[7] however, found that the much larger (750-fold at 298 K) relative reactivity of $Fe(H_2O)_5OH^{2+}$ with respect to $Fe(H_2O)_6{}^{3+}$ was entirely due to a more favorable enthalpy of activation (42 as against 64 kJ mol^{-1}). The significance of this, if any, is obscure.

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Registry No. $Cr(H_2O)_6{}^{3+}$, 14873-01-9; $Cr(H_2O)_5OH^{2+}$, 27454-20-2.

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