Articles

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Transition-State Volumes in Solvent Exchange. Water Exchange on the Aqueous Aquapentaammineruthenium(III) Ion

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The rate of water exchange on $Ru(NH_3)_5OH_2{}^{3+}$ in aqueous CF_3SO_3H (0.01 mol L^{-1}) is characterized by $k^{298.2} = 2.30 \times 10^{-4}$ s^{-1}, $\Delta H^* = 91.5$ kJ mol^{-1}, $\Delta S^* = -7.7$ J K^{-1} mol^{-1}, and $\Delta V^* = -4.0$ cm^3 mol^{-1}. The order of lability of $M(NH_3)_5OH_2{}^{3+}$ in water exchange is (M=) Ru > Cr > Rh > Co ≫ Ir and is governed by ΔH^*. For substitution reactions of metal complexes involving "hard" leaving groups, the lability sequence first < second > third transition series may be general. For a series of related aqua complexes such as $M(NH_3)_5OH_2{}^{3+}$, variations in ΔV^* for water exchange and the molar volume of the complex as M is changed are largely compensatory, so that the molar volume of the transition state varies relatively little. This reflects reduced accessibility of the complex to associative attack as the central ion becomes smaller.

Introduction

Among complex ions of the type $M(NH_3)_5OH_2{}^{3+}$, rate data for the exchange of solvent water

$$M(NH_3)_5{}^*OH_2{}^{3+} + H_2O \rightarrow M(NH_3)_5OH_2{}^{3+} + H_2{}^*O \qquad (1)$$

are conspicuously lacking for the case M = Ru, despite the lively interest in the solution chemistry of ruthenium that has continued over the past quarter-century. This is largely due to the difficulties in preparing and handling pure salts or solutions of this ion; in particular, the standard general method of following reaction 1 through oxygen-18 exchange (by precipitation of halide or other salts of the aqua complex at appropriate intervals, followed by recovery of the coordinated water by heating on a vacuum line[2-4]) fails in the ruthenium case.[5] We now report success in measuring the rate of reaction 1 for M = Ru over a range of temperatures and pressures through following the rate of appearance of the oxygen-18 label from the complex in the solvent; this requires very precise isotope ratio measurements because of the limited solubility of salts of this ion.

Particular interest is attached to the volume of activation ΔV^* for the exchange of water on aquapentaammineruthenium(III), since a value of -5 ± 1 cm^3 mol^{-1} was predicted[6,7] on the basis of an inverse linear correlation between ΔV^* for reaction 1 (M = Co, Rh, Ir, Cr) and molar volumes of the aqueous ions $M(NH_3)_5OH_2{}^{3+}$. On the other hand, strongly negative volumes of activation were found[5] for both the reaction of chloride ion with $(NH_3)_5RuOH_2{}^{3+}$ (ca. -20 cm^3 mol^{-1}) and its reverse (-27 to -30 cm^3 mol^{-1}), which would suggest a ΔV^* value for the corresponding water-exchange reaction more negative than -20 cm^3 mol^{-1} in view of the absence of electrostrictive change in reaction 1. In this paper, we show that the prediction of the molar volume correlation is correct and consider the possible origins of such correlations and their implication that the molar volumes of the transition states for a series of solvent-exchange reactions are relatively insensitive to the nature of the central metal ion M.

Experimental Section

Trifluoromethanesulfonic acid (Eastman Kodak) was fractionally redistilled under reduced pressure.

Aquapentaammineruthenium(III) Trifluoromethanesulfonate. $[Ru(NH_3)_5Cl]Cl_2$ was purchased (Strem Chemicals) or made from $RuCl_3{\cdot}3H_2O$ (Aldrich) by a modification of the method of Allen et al.[8] and converted to $[Ru(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ with CF_3SO_3H at 95 °C.[9] This off-white solid was dissolved in the minimum amount of ^{18}O-enriched ^1H-normalized water (20–30% $H_2{}^{18}O$) containing ca. 0.01 mol L^{-1} CF_3SO_3H and was aquated by warming the solution briefly to about 40 °C (half-life ca. 8 s at 25 °C[9]). Solid, white, $H_2{}^{18}O$-labeled $[Ru(NH_3)_5OH_2](CF_3SO_3)_3$ was recovered by removal of the solvent on a vacuum line and was stored over P_2O_5. The optical spectrum of the pure material in acidic aqueous solution showed a single maximum at 268 nm with molar absorbance 720 ± 4 L mol^{-1} cm^{-1}, in excellent agreement with the definitive work of Sullivan et al.[10] (who report good elemental analyses). The isotopically normalized aqua-complex trifluoromethanesulfonate salt recovered from the kinetic experiments was purified by triple reprecipitation from 0.001 mol L^{-1} CF_3SO_3H by addition of the concentrated acid to the vigorously stirred solution at 0 °C and was relabeled by equilibrating it in solution in acidified ^{18}O-enriched water at 40 to 45 °C for about 24 h.

Kinetic Measurements. Typically, a weighed amount of the solid $H_2{}^{18}O$-labeled $[Ru(NH_3)_5OH_2](CF_3SO_3)_3$ was dissolved in deionized distilled water containing 0.01 mol L^{-1} CF_3SO_3H, to give a solution about 0.08 mol L^{-1} in Ru complex. For runs at ambient pressure, the solution was placed in a dark thermostated vessel from which a small portion could be briefly removed through a narrow-bore Teflon tube by means of a piston device at selected intervals for sampling. The liquid (some 0.05–0.1 mL) held up in the tube was rejected, and only about 0.004 mL of the solution was micropipetted out for conversion to CO_2, so that an initial solution volume of 0.5 mL sufficed for a complete run. The sample was pipetted into a cold (0 °C) 6 mm i.d. tube filled with dry nitrogen; the tube was connected to a vacuum line, and the solvent water was evaporated quickly in vacuo and recondensed onto carefully dried guanidine hydrochloride (30–40 mg, 99.99+% pure; Chemical Dynamics Corp. Ultralog reagent) in another 6 mm i.d. tube. The tube containing the condensate and guanidine hydrochloride was sealed off and heated for 20–36 h at 300–320 °C to convert the water to CO_2.[11]

The resulting CO_2 was freed of ammonia by exposure to concentrated sulfuric acid on a vacuum line and transferred to a high-precision isotope ratio mass spectrometer built around Micromass 903 components for measurement of the $^{12}C^{16}O^{18}O{:}^{12}C^{16}O^{16}O$ ratio of the sample relative to a "normal" CO_2 standard. The spectrometer readout expressed this conventionally as $\delta(^{18}O)$ (in parts per thousand):

$$\delta(^{18}O) = \{[(I_{46}/I_{44})_{sample}/(I_{46}/I_{44})_{std}] - 1\} \times 1000 \qquad (2)$$

where I_m is the ion current for singly ionized molecules of mass m. Triple

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Table I. Rate Constants k_{ex} for Water Exchange on $Ru(NH_3)_5OH_2^{3+}$ in Aqueous CF_3SO_3H[a]

$[Ru(NH_3)_5$-$OH_2^{3+}]$/ mol L^{-1}	press./ MPa	temp/ °C	$k_{ex}/10^{-5}$ s^{-1}[b]
0.0780	0.1	6.0	1.80 ± 0.02
0.0671	0.1	13.0	4.72 ± 0.02
0.0741	0.1	13.0	4.44 ± 0.10
0.0841	0.1	20.0	12.2 ± 0.1
0.0729	0.1	25.0	23.3 ± 0.2
0.1460	0.1	25.0	23.0 ± 0.7
	0.1	12.3	4.24[c]
0.0849	100.0	12.3	5.10 ± 0.03
0.0801	200.0	12.3	6.00 ± 0.23
0.0847	275.0	12.3	7.00 ± 0.14
0.0802	401.0	12.3	8.33 ± 0.16

[a] $[CH_3SO_3H]$ = 0.0118 mol L^{-1}. [b] Uncertainties are standard deviations of fit to eq 3. [c] Interpolated value.

collection of ion currents for m = 44, 45, and 46 permitted corrections for any minor variations in ^{13}C and ^{17}O abundances.

For kinetic measurements at elevated pressures, the reaction was carried out in a 20-mL glass syringe, enclosed in a thermostated pressure vessel, from which samples could be withdrawn with automatic maintenance of pressure (to within ±2 MPa at 400 MPa).[12] The general procedure was as described above except that 7–10 mL of solution was needed per run because holdup wastage was about 0.5 mL per sample and the thermal equilibration prior to taking the first sample took longer (30 min) so that a relatively low reaction temperature (12.3 °C) had to be used.

High-pressure UV–visible spectra of solutions of $[Ru(NH_3)_5Cl]Cl_2$ in aqueous HCl (0.01 mol L^{-1}) were obtained over the range 0.1–300 MPa with a le Noble–Schlott cell as previously described.[5]

Results

In a typical kinetic experiment, the value C_t of $\delta(^{18}O)$ at time t rose from about −40 at the arbitrary t = 0 to +40 at "infinite" time, with a reproducibility of better than ±0.3. Since the ^{18}O content of the solution was only about 0.2%, the pseudo-first-order rate coefficient k_{ex} for water exchange on the ruthenium complex is given by eq 3.

$$k_{ex}t = -\ln [(C_\infty - C_t)/(C_\infty - C_0)] \qquad (3)$$

The exchange reaction was followed over at least 3 half-lives, and C_t values obeyed eq 3 accurately, in all cases. The rate data, summarized in Table I, can be represented by the following Eyring activation parameters: $\Delta H^* = 91.5 \pm 1.3$ kJ mol^{-1}; $\Delta S^* = -7.7 \pm 4.4$ J K^{-1} mol^{-1}; $k_{ex}(298.15\ K) = 2.30 \times 10^{-4}$ s^{-1}; $\Delta V^* = -4.04 \pm 0.14$ cm^3 mol^{-1}. There was no detectable pressure dependence of ΔV^*; i.e., ln k was a linear function of the pressure P, over the range 0.1 to 400 MPa. This is typical of solvent-exchange reactions.[13]

The main and lowest lying (327 nm) band[14] in the visible–UV spectrum of aqueous $Ru(NH_3)_5Cl^{2+}$ was found to be shifted to shorter wavelengths as the pressure was increased. In terms of the wavenumber ν of the absorption maximum in cm^{-1}, this pressure dependence over the range 0.1–300 MPa can be described by eq 4 for pressure P in MPa.

$$\nu = 30\,630 + 1.2P \qquad (4)$$

Discussion

The most striking feature of the kinetic data for the general reaction (1) (Table II) is that the ruthenium(III) complex is the most labile of the $M(NH_3)_5OH_2^{3+}$ ions studied to date, despite having the least favorable ΔS^*. Fairlie and Taube[17] have pointed out that the common perception of ruthenium(III) ammines as being more substitutionally inert than (e.g.) their cobalt(III) analogues derives from the observation of relatively slow aquation rates of halopentaammineruthenium(III) ions and has no general validity. Indeed, Table III shows that rates of chloride anation of $M(NH_3)_5OH_2^{3+}$ parallel those of water exchange quite closely, while the aquation rates and formation constants of $M(NH_3)_5Cl^{2+}$ show the expected increased preference of M for "soft" Cl over "hard" H_2O as we descend the periodic table. Furthermore, the rates of aquation of the "hard" trifluoromethanesulfonate ion from $M(NH_3)_5O_3SCF_3^{2+}$[9] show the same qualitative trend with M as is found for reaction 1.

Table II. Activation Parameters for Water Exchange on $M(NH_3)_5OH_2^{3+}$ in Dilute Acidic Solution

M	k_{ex}(298 K)/ 10^{-5} s^{-1}	ΔH^*/kJ mol^{-1}	ΔS^*/J K^{-1} mol^{-1}	LFAE[a]/kJ mol^{-1}
Ru[b]	23.0	91.5	−8	0.86Dq = 35
Cr	5.2	97.1	0	2.00Dq = 50
Co	0.57	111.3	+28	4.0Dq = 108
Rh	0.87	102.9	+3	4.0Dq = 158
Ir	0.0061	117.6	+11	4.0Dq = 193

[a] Ligand field activation energy for an assumed square-pyramidal transition state;[15] Dq values estimated from spectroscopic data in ref 16. [b] This work; other data from sources named in ref 4.

Table III. Rate Constants for Formation (k_{an}) and Aquation (k_{aq}) of $M(NH_3)_5Cl^{2+}$[a]

M	$k_{aq}/10^{-6}$ s^{-1}	k_{an}[b]$/10^{-5}$ L mol^{-1} s^{-1}	K[c]/L mol^{-1}
Ru	0.88[d]	12.0 (0.10)[e]	136
Cr	6.8	0.35 (0.10)	0.51
Co	1.7	0.28 (0.10)	1.6
Rh	0.042	0.68 (0.20)	162
Ir	0.64[f]	230 (0.03)[f]	3600[f]

[a] At 25.0 °C except as indicated; interpolated by using data from sources listed in ref 18–20. [b] Ionic strength (mol L^{-1}) in parentheses. [c] Formation constant ($=k_{an}/k_{aq}$) for chloro complex. [c] Data of ref 18 give ΔH_{aq}^* = 91.5 kJ mol^{-1}, ΔS_{aq}^* = −54.0 J K^{-1} mol^{-1}. [e] From K and k_{aq} values in ref 18, we calculate ΔH_{an}^* = 98.8 kJ mol^{-1} and ΔS_{an}^* = +11.4 J K^{-1} mol^{-1}. [f] At 95.0 °C; $k_{ex} = 5.9 \times 10^{-4}$ s^{-1}.

The relative lability of $Ru(NH_3)_5OH_2^{3+}$ in water exchange clearly derives from a low enthalpy of activation (Table II), and the interpretation of this should be fairly straightforward since reaction 1 involves negligible solvational changes during the activation process (since ΔV^* shows no pressure dependence)[13] and no net free energy change. In the absence of a fully satisfactory theory, however, we note simply that the ligand field contributions to the activation enthalpy (LFAE) for reaction 1, calculated on the basis of an assumed dissociative (D) mechanism with a square-pyramidal intermediate,[15] explain the trend in ΔH^* *qualitatively* (Table II). If activation is indeed associative via an "octahedral wedge" geometry[19] (and negative ΔV^* and ΔS^* values suggest significant I_a character for all but the Co case[4]), additional assumptions regarding bond lengths and angles are required, but the result would not be greatly different. In any case, more factors than LFAE are involved, as the calculations for M = Rh and Ir, and also the generally high lability of Mo^{III} complexes relative to Cr^{III} analogues,[21,22] make clear.

Carbonyl and phosphine complexes of metals of the second transition series have been noted to be generally more labile in ligand substitution than corresponding complexes of the first or third series.[23] Thus, the relative lability of $Ru(NH_3)_5OH_2^{3+}$ and $Mo(H_2O)_6^{3+}$ (and, less markedly, $Rh(NH_3)_5OH_2^{3+}$) seems to be

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Table IV. Volume Properties Relating to Water Exchange on Aqueous $M(NH_3)_5OH_2^{3+}$ [a]

complex	$V_{abs}°$ [b]	ΔV^*	V^*
$Co(NH_3)_5OH_2^{3+}$	54.9	+1.2	56.1
$Rh(NH_3)_5OH_2^{3+}$	61.2	−4.1	57.1
$Ir(NH_3)_5OH_2^{3+}$	61.2	−3.2	58.0
$Ru(NH_3)_5OH_2^{3+}$	63.2[c]	−4.0	59.2
$Cr(NH_3)_5OH_2^{3+}$	65.3	−5.8	59.5

[a] In $cm^3\ mol^{-1}$; from ref 2, 6, and 7 and this work; $V_{abs}°$ for $H^+(aq)$ assumed to be $-5.4\ cm^3\ mol^{-1}$. [b] At 25 °C, infinite dilution. [c] Reference 5; extrapolation to infinite dilution on basis of averaged ionic strength effect found for M = Co, Rh, Ir, Cr.

part of a general phenomenon. It may be, however, that we need to explain, not why nucleophilic substitution is often unexpectedly *fast* at elements of the second transition series (fifth period),[22] but rather why it is often anomalously *slow* at fourth-period centers (e.g., Co^{III}[3,4]), an effect that is apparent in the reactivity sequence Si > Ge ≪ Sn in the alkaline cleavage of carbon–metal(loid) bonds.[24]

For the ion pair $[Ru(NH_3)_5OH_2^{3+},Cl^-]$, Fuoss-type calculations[25] give a formation constant K_{IP} of 5.3 L mol^{-1} and formation enthalpy of +2.2 kJ mol^{-1} at 25 °C and ionic strength 0.1 mol L^{-1}. If chloride anation of $Ru(NH_3)_5OH_2^{3+}$ proceeds by an interchange mechanism involving this precursor ion pair, then the rate constant k_i for replacement of coordinated water by chloride within the ion pair will be k_{an}/K_{IP}, or about $2.3 \times 10^{-5}\ s^{-1}$, with the corresponding $\Delta H_i^* = 96$–97 kJ mol^{-1} (see Table III). This is 10 times slower than water exchange on the free aqua complex, with an enthalpy of activation only slightly if at all higher (the accuracy of the calculations and extrapolations being limited). This conforms with expectations for predominantly dissociative activation (I_d mechanism), as favored by Fairlie and Taube[17] for substitution in ruthenium(III) ammines, but does not rule out significant associative contributions (I_a),[26] and in any event ionic strength effects are known to obscure the issue.[27] From this standpoint, $Ru(NH_3)_5OH_2^{3+}$ behaves much like its analogues with M = Cr, Co, Rh, and Ir.

Thus, there is no new evidence to support our previous proposal of an extreme associative (A) mechanism for the formation of $Ru(NH_3)_5Cl^{2+}$ from the aqua complex and its reverse (aquation), the volumes of activation for which are both more strongly negative than that now reported for water exchange. The corresponding ΔS^* values (see footnotes to Table III) are not particularly unusual,[20] and it may be that the negative volumes of activation represent incursion of some pressure-induced secondary reaction pathway. Since formation of Ru^{II} and free halogen prevents measurement of the rates of aquation of $Ru(NH_3)_5Br^{2+}$ and $Ru(NH_3)_5I^{2+}$,[28] a similar redox process might provide activation for aquation of $Ru(NH_3)_5Cl^{2+}$ (and, by microscopic reversibility, for the reverse reaction) through formation of a (possibly transient) labile Ru^{II} intermediate. This can be ruled out on two grounds, however: (i) homolytic pathways for the decomposition of metal complex ions in water generally have markedly *positive* volumes of activation[29] and (ii) the energy of the presumed chloro-ligand-to-metal charge-transfer band at 327 nm in the spectrum of $Ru(NH_3)_5Cl^{2+}$[14] *increases* with increasing pressure (eq 4; the slope of this equation is equivalent to a volume change of +14 cm^3 mol^{-1}). Thus, increased pressure should *suppress* any pathway activated by a redox-like process.

The strongly negative volumes of activation for chloride anation of $Ru(NH_3)_5OH_2^{3+}$ and the reverse process[5] therefore remain puzzling, although a similarly surprising value of −11 $cm^3\ mol^{-1}$ has recently been reported for the thiocyanate anation of aqueous hexaaquamolybdenum(III) ion, for which conventional kinetic evidence indicates strongly associative activation.[21] Hambley and Lawrance[30] also find atypical, strongly negative entropies of activation for base hydrolysis of aqueous $Ru(NH_3)_5Cl^{2+}$ and *cis*-$Ru(en)_2(OH)Cl^+$ and suggest an associative mechanism of some kind. The question of the mechanism(s) of the anation and hydrolysis of Ru^{III} complexes therefore remains open.

Table IV shows that ΔV^* for reaction 1 correlates inversely with the "absolute" molar volume $V_{abs}°$ of aqueous $M(NH_3)_5OH_2^{3+}$ with a slope of about −0.7. This means that the molar volume V^* of the transition state ($= V_{abs}° + \Delta V^*$) increases only slowly with increasing $V_{abs}°$, spanning only about one-third of its range. This partial compensation between $V_{abs}°$ and ΔV^* may also be seen in water-exchange reactions of $M^{2+}(aq)$ and $M^{3+}(aq)$[6,7] (although lack of accurate $V_{abs}°$ data for the latter obscures the issue) and, as argued below, probably reflects the tendency of an interchange mechanism to take the least sterically restrive course.

We have stressed[31] that the *whole* assemblage (metal ion + first coordination sphere + outer sphere) must be considered when discussing substitution reactions of complex ions in solution. Thus, the limiting associative and dissociative extremes of the interchange mechanism for reaction 1, i.e., for solvent exchange within the assemblage $[M(NH_3)_5OH_2^{3+},(H_2O)_x]$, correspond to transition states having the compositions $[M(NH_3)_5(OH)_2^{3+},(H_2O)_{x-1}]$ and $[M(NH_3)_5^{3+},(H_2O)_{x+1}]$, respectively. Failure to include the x outer-sphere water molecules has led to misinterpretation,[32] although of necessity (since x is not accurately known) they are conveniently ignored when measured values of $V_{abs}°$ and hence also V^* are quoted. Computer modeling of the interchange mechanism for solvent exchange[33] clearly shows that the substitution process involves concerted movements of essentially *all* the inner-sphere ligands *and* the x solvent molecules of the outer sphere, with many collisions en route to the transition state. A large central ion, which will be associated with a large $V_{abs}°$ for a given coordination number,[6] will have a more open-structured first coordination sphere with easier avenues for associative attack than will a small ion, other factors (such as ionic charge) apart; thus, the larger $V_{abs}°$ values will usually be associated with the more negative ΔV^* within a series of solvent-exchange reactions, the transition-state volumes V^* being relatively invariant.

This last assertion can be supported, for the case of water exchange on simple hexaaquametal ions, by calculating[6] the volumes of seven- and five-coordinate $M^{z+}(aq)$ for ionic radii representing the limits of stability of six-coordination relative to increase and decrease of coodination number, respectively, on the traditional close-packing model. For water molecules of radius 138 pm, these ionic radii are 101.0 and 57.2 pm, respectively; for $z = 2$, the corresponding calculated V^* values are −32.5 and −30.7 $cm^3\ mol^{-1}$, which are very close to those observed[7,34] and remarkably similar in view of the 12.6 $cm^3\ mol^{-1}$ range observed and the 27 $cm^3\ mol^{-1}$ range theoretically possible[35] in ΔV^*, for water exchange on divalent metal aqua ions of the first transition series. Other choices of limiting radii etc. lead to qualitatively similar results.

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