Mechanistic Information from Pressure and Temperature Effects on the Rate of Transfer of Oxygen-18 from Aquopentaamminechromium(III) and Aquopentaamminerhodium(III) Ions to Solvent Water

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Abstract: The rates of exchange of bound water in $(NH_3)_5MOH_2^{3+}$ with solvent water are characterized by the activation parameters $\Delta V^* = -5.8 \pm 0.2$ cm^3 mol^{-1}, $\Delta H^* = 23.2 \pm 0.5$ kcal mol^{-1}, and $\Delta S^* = 0.0 \pm 1.6$ cal deg^{-1} mol^{-1} when M = Cr; the corresponding data for M = Rh are -4.1 ± 0.4 cm^3 mol^{-1}, 24.6 ± 0.3 kcal mol^{-1}, and $+0.8 \pm 1.1$ cal deg^{-1} mol^{-1}. These figures suggest an associative mechanism for both reactions. Some theoretical implications of this conclusion are discussed.

The pressure dependences of reaction rates yield the volume of activation, ΔV^*, which represents the difference between the molal volumes of the initial and transition states. In principle, ΔV^* data can serve to distinguish between various alternative mechanistic models, since the volume requirements of these can usually be rather readily visualized, but in many substitution reactions of complex ions in solution the interpretation is complicated by significant contributions to ΔV^* from changes in solvation, preassociation of the reactants, etc. These complications do not arise in the exchange reaction of solvo ligands with solvent molecules, as followed by isotopic labeling; here, no changes in formal charges are involved, the entering and leaving groups are identical and are merely the ubiquitous solvent molecules, and there is no net chemical reaction. Thus, solvent exchange reactions offer excellent opportunities for the determination of reaction mechanisms from ΔV^* measurements.

We recently reported[2] that ΔV^* is -9.3 cm^3 mol^{-1} for the reaction

$$Cr(H_2O)_6^{3+} + H_2{}^{18}O \longrightarrow Cr(H_2O)_5{}^{18}OH_2^{3+} + H_2O \quad (1)$$

and this constitutes evidence for an associative mechanism for reaction 1. Other data[3] relating to the anation and aquation of aquochromium(III) species also suggest an associative mechanism, presumably of the Langford–Gray[4] associative interchange (I_a) type. Thus it appears that the Eigen mechanism of complex formation,[5] which assumes dissociative activation in the rate-determining step, may be less generally applicable than has been hitherto believed.

On the other hand, replacement of the aquo group in $Co(NH_3)_5OH_2^{3+}$ seems to proceed by a dissociative interchange (I_d) mechanism,[4,6] and this is supported by the observation[7] that ΔV^* for the reaction is $+1.2$ cm^3

$$Co(NH_3)_5{}^{18}OH_2^{3+} + H_2O \longrightarrow Co(NH_3)_5OH_2^{3+} + H_2{}^{18}O \quad (2)$$

mol^{-1}. This raises the question of whether the strongly negative ΔV^* of reaction 1 and the apparent associative mode of activation of substitution reactions of chromium(III)–aquo species reflect some property of the Cr center, or whether they originate with the aquo ligands. We have therefore studied the pressure and temperature dependence of the reaction

$$Cr(NH_3)_5{}^{18}OH_2^{3+} + H_2O \longrightarrow Cr(NH_3)_5OH_2^{3+} + H_2{}^{18}O \quad (3)$$

in order to permit direct comparison with the analogous cobalt(III) system.

The mechanism of replacement of bound water in aqueous $Rh(NH_3)_5OH_2^{3+}$ might reasonably be expected to be similar to that of the Co(III) analog, yet Poë, *et al.*,[8] and Monacelli[9] have independently presented similar evidence favoring an associative interchange mechanism for the anation of the Rh(III) complex. We have therefore examined the pressure and temperature dependence of the rate of the reaction

$$Rh(NH_3)_5{}^{18}OH_2^{3+} + H_2O \longrightarrow Rh(NH_3)_5OH_2^{3+} + H_2{}^{18}O \quad (4)$$

with a view to obtaining independent mechanistic criteria.

Experimental Section

Materials. Aquopentaamminerhodium(III) perchlorate was made by refluxing aqueous chloropentaamminerhodium(III) chloride (Alfa Inorganics) with a slight (<2%) excess of silver perchlorate solution and filtering periodically until no further silver chloride was precipitated. Precipitation of the product was assisted with the addition of 72% perchloric acid, and the pale yellow solid was recrystallized, first from the minimum of boiling water and then again from 1.5% $H_2{}^{18}O$ (Bio-Rad Laboratories, low in D), after refluxing in this solvent for 2 hr to ensure maximum enrichment of the aquo ligand with oxygen-18. *Anal.* Calcd for $[Rh(NH_3)_5$-

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[9] F. Monacelli, *Inorg. Chem. Acta*, **2**, 263 (1968).

$OH_2](ClO_4)_3$: N, 13.9; H, 3.0; Cl, 21.1; Rh, 20.4. Found: N, 13.6; H, 3.2; Cl, 21.4; Rh, 20.3.

Aquopentaamminechromium(III) perchlorate was made essentially according to published methods[10,11] except that acetone was used in place of ethanol or ether to avoid contamination of the product with species of mass numbers 45 or 46. (Note well: the perchlorate salt is appreciably soluble in acetone.) Oxygen-18 labeling of the aquopentaamminechromium(III) ion was achieved by warming a solution of the perchlorate salt (17 g) in 75 ml of 1.3% $H_2{}^{18}O$ (0.02 *M* in $HClO_4$) at 52–54° for 0.5 hr, cooling it to 0° for 3 hr, filtering, and drying the resulting orange crystals *in vacuo* over silica gel. *Anal.* Calcd for $[Cr(NH_3)_5OH_2](ClO_4)_3$: N, 15.5; H, 3.8; Cl, 23.5. Found: N, 15.8; H, 3.8; Cl, 23.6.

Perchloric acid (Baker Analyzed 72%) was used without further purification.

Kinetic Measurements. (a) Effect of Pressure. Typically, a weighed amount of the pulverized complex was dissolved in water (usually 50.0 ml) of normal isotopic composition containing a known concentration of perchloric acid. The solution was quickly brought to the temperature of the thermostat bath and then transferred to a syringe made of polystyrene and Teflon which was promptly immersed in the thermostated pressure vessel described elsewhere[2] and brought to the desired pressure with an Enerpac handpump. At least 20 min were allowed to ensure full thermal equilibration before samples (6.8–8.6 ml) were run out for analysis; the first 1.0–1.3 ml prior to the sample were rejected as "hold-up." Either a stainless steel or a platinum–iridium alloy capillary tube was used, in conjunction with a stainless steel needle valve, to withdraw these samples; the kinetic results were the same in either case. Pressures were measured with a Budenberg Bourdon gauge accurate to ±1%; temperatures quoted in the following tables are considered accurate to ±0.03°.

Runs conducted in the pressure assembly at atmospheric pressure gave the same results (within experimental uncertainty) as control experiments carried out with the solution in stoppered Pyrex vessels darkened with aluminum foil, nor was there any detectable difference between duplicate runs using different preparations of the complex salts.

The withdrawn aliquots were chilled at once to 0°, care being taken to avoid excessive frictional heating of the solution as it ran through the capillary. In the experiments on the rhodium complex, the complex cation was precipitated as the tribromide by addition of an equal volume of 48% hydrobromic acid,[12] while the aquopentaamminechromium(III) ion was precipitated as shining orange crystals of the tribromide by stirring the sample at 0° with two and one-half times its volume of an ice-cold mixture of equal volumes of acetone and 48% hydrobromic acid. In either case, the tribromide was filtered, washed thoroughly with acetone, and dried *in vacuo* over silica gel. The coordinated water was driven off at about 160° in a vacuum line, condensed onto dry guanidine hydrochloride in a break-seal tube, and converted to carbon dioxide by heating in the sealed tube at 300–320° for at least 12 hr[13] (shorter reaction times gave inadequate yields of carbon dioxide). The resulting carbon dioxide was treated with concentrated sulfuric acid and then analyzed for ${}^{12}C^{16}O^{18}O$ content relative to ${}^{13}C^{16}O_2$, using a Hitachi Perkin-Elmer RMU-6D mass spectrometer. The 46:45 mass ratios adopted were the mean of at least ten measurements, with typical standard deviations of ±1.4%, and were corrected as necessary for the small background present in some cases.

(b) Effect of Temperature. For temperatures of 25° and above, the solutions were thermostated in stoppered, darkened Pyrex flasks, and samples were pipetted out as required. For runs at 0°, 7-ml aliquots of the ice-cold solution were sealed into Pyrex test tubes and placed in a light-tight dewar vessel containing a well-mixed slurry of ice and water; tubes were removed at selected intervals and analyzed promptly.

(c) Effect of Light. The aquo exchange rates at 50° of two aquopentaamminerhodium(III) solutions (each 0.040 *M* in Rh and 0.010 *M* in perchloric acid) were measured with one solution in a darkened Pyrex vessel and the other in a similar clear flask exposed (under 7 cm of clear Ondina 17 bath oil) to a 100-W pearl tungsten lamp at 37 cm, without reflector, in addition to normal room fluorescent lighting. The exchange rates were found to be identical, within the experimental uncertainty.

A significant photochemical effect can be anticipated for the chromium complex, by analogy with the hexaaquochromium(III) case,[14] and this effect was therefore not specifically sought for, although it was noted that solid samples of aquopentaamminechromium(III) bromide changed gradually from orange to crimson on exposure to indirect daylight, presumably because of photosubstitution of the aquo ligand by bromide. Appropriate precautions were therefore taken when dealing with the aquopentaamminechromium(III) system.

Results

Aquopentaamminechromium(III) Ion. The rate of disappearance of oxygen-18 from the complex was first order in complex, and the rate coefficients *k*, calculated on the basis of a theoretical final ${}^{12}C^{16}O^{18}O/{}^{13}C^{16}O_2$ ratio of 0.372, were obtained with an average standard deviation of 2.6%. Most of these experiments were duplicated (with agreement within the standard deviation cited), and Table I lists the weighted mean *k* values and their mean standard deviations.

Table I. First-Order Rate Coefficients for Reaction 3[a]

T, °C	P, kbars	10^5k, sec^{-1}
0.00	0.001	0.145 ± 0.009
25.00	0.001	5.24 ± 0.17
	0.55	6.12 ± 0.12
	1.03	6.71 ± 0.10
	1.59	7.64 ± 0.22
	2.07	8.62 ± 0.32
29.72	0.001	11.5 ± 0.3[b]
37.01	0.001	26.7 ± 0.6

[a] [Cr(III)] = 0.050 *M*, $[HClO_4]$ = 0.100 *M*. [b] Reference 15.

A linear relationship between log *k* and the pressure *P* represents the data to well within the experimental uncertainty, and gives $\Delta V^* = -5.8 \pm 0.2$ cm^3 mol^{-1}. If a quadratic in *P* is nevertheless used, $(\partial \Delta V^*/\partial P)_T$ is found to be $(+2.7 \pm 7.0) \times 10^{-4}$ cm^3 bar^{-1} mol^{-1}, which is not significant, and ΔV_0^* (1 bar) $= -6.1 \pm 0.7$ cm^3 mol^{-1}.

A plot of ln (k/T) *vs.* $(1/T)$ at 1 bar is linear and passes close to the datum for 29.72° given by Duffy and Earley.[15] These authors also give some relatively imprecise *k* values for 14.96 and 45.11°, but these deviate appreciably from our straight line and, unlike the 29.72° value, have not been included in our calculations of ΔH^* and ΔS^* (see Table III, below).

Aquopentaamminerhodium(III) Ion. The rate of loss of oxygen-18 was again first order and yielded rate coefficients (based upon a theoretical final oxygen-18 content as before) with typical standard deviations of 3.2%. Rate coefficients for a given pressure were measured at least in duplicate in all cases, and the data of Table II are the weighted means of the *k* values.

The value of *k* for 35.0° and 1 bar is about 20% lower than that obtained by interpolation of the data of Monacelli and Viel,[12] which were measured by essentially the same procedure except that the solutions were exposed to low and variable levels of room lighting during runs.[16] However, we have found no evidence for a photochemical effect, so this modest discrepancy remains unexplained.

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Table II. First-Order Rate Coefficients *k* for Reaction 4[a]

T, °C	*P*, kbars	10^5k, sec^{-1}
25.00	0.001	0.841 ± 0.018
35.00	0.001	3.22 ± 0.06
	0.55	3.43 ± 0.08
	1.03	3.63 ± 0.18
	1.59	4.12 ± 0.19
	2.07	4.54 ± 0.19
49.98	0.001	22.5 ± 0.8

[a] [Rh(III)] = 0.040 *M*, [$HClO_4$] = 0.0100 *M*.

In a plot of log *k vs. P*, at 35°, a representative straight line, corresponding to $\Delta V^* = -4.1 \pm 0.4$ cm^3 mol^{-1} and *k* (1 bar) = 3.18×10^{-5} sec^{-1}, passes comfortably within the stated error limits for each *k* value. A more elaborate analysis is thus superfluous, but it may be remarked that the log *k* data are well represented (presumably fortuitously so) by a quadratic in *P*, such that $(\partial \Delta V^*/\partial P)_T = (-2.0 \pm 0.6) \times 10^{-3}$ cm^3 bar^{-1} mol^{-1}, with $\Delta V_0^* = -2.2 \pm 0.6$ cm^3 mol^{-1} and $k_0 = 3.22 \times 10^{-5}$ sec^{-1} at 1 bar.

A plot of ln (k/T) *vs.* $(1/T)$ is linear within the experimental uncertainty, and the activation parameters listed in Table III compare satisfactorily with those recalculated by Poe, *et al.*,[17] from the data of ref 12.

Table III. Activation Parameters for the Reaction $ML_5{}^{18}OH_2{}^{3+} + H_2O = ML_5OH_2{}^{3+} + H_2{}^{18}O$

ML_5	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}	ΔV^*, cm^3 mol^{-1} (temp, °C)
$Co(NH_3)_5$[a]	26.6 ± 0.3	+6.7 ± 1.0	+1.2 ± 0.2 (25, 35)
$Rh(NH_3)_5$	24.6 ± 0.3	+0.8 ± 1.1	−4.1 ± 0.4 (35)
$Cr(NH_3)_5$	23.2 ± 0.5	0.0 ± 1.6	−5.8 ± 0.2 (25)
$Cr(H_2O)_5$[b]	26.2 ± 0.3	+0.3 ± 1.0	−9.3 ± 0.3 (45)

[a] Reference 7. [b] Reference 2 (referring to the exchange of *one* aquo ligand).

Discussion

Because the interpretation of the ΔV^* values for these simple, symmetrical reactions is not complicated by electrostrictive effects arising from changes in formal charge, the negative volumes of activation found for reactions 1, 3, and 4 can be taken to indicate associative mechanisms for all three, while reaction 2, with its positive and numerically smaller ΔV^*, is evidently dissociatively activated. Furthermore, the entropies of activation for reactions 1, 3, and 4 are the same, within the experimental uncertainty, whereas that for reaction 2 is markedly more positive, again supporting the view that the rhodium and chromium complexes react by a similar mechanism but the cobalt complex reacts by a different process involving looser binding in the transition state.

The negative volumes of activation obtained for the chromium and rhodium complexes are numerically larger than might be expected on the basis of water–metal bond formation alone.[6,7] The explanation[2] seems to be that ΔV^* encompasses not only a bond-making contribution (which may in any event be partially or wholly compensated for by concomitant bond breaking) but also the creation of a vacancy in the solvation sheath of the complex when the attacking water molecule is removed from this region to the first coordination sphere of the central ion. On this basis, a complex ion having a large, well-structured solvation sheath would be expected to give a more strongly negative ΔV^* in an associative mechanism than would an ion having a less extensive, poorly structured solvation sheath. The hexaaquochromium(III) ion will fall in the former category because of the ability of its relatively acidic and numerous aquo protons to hydrogen-bond solvent molecules, while the ammine complexes, with their very weakly acidic ammine protons, will form relatively poorly structured solvation sheaths, that of the rhodium complex being presumably even less extensive than for aquopentaamminechromium(III) because of the larger size and consequent lower electrostatic potential of the central Rh^{3+} ion.[18]

In principle, values of $(\partial \Delta V^*/\partial P)_T$ for solvent exchange processes can be used to distinguish I_a from A mechanisms,[2] depending upon whether the observed value is respectively much less than or comparable with the mean molar compressibility of water over the pressure range employed (about 7×10^{-4} cm^3 bar^{-1} mol^{-1} in these cases). For reaction 3, $(\partial \Delta V^*/\partial P)_T$ is calculated to be 3×10^{-4} cm^3 bar^{-1} mol^{-1}, but unfortunately the *standard deviation* of this quantity is comparable with the molar compressibility of water and so a definite distinction between I_a and A cannot truly be made on the basis of the data of Table I; the same is true of our data[2] for reaction 1.[19] Similarly, the somewhat cruder data obtained for reaction 4 do not warrant pronouncements regarding the possible pressure-dependence of ΔV^*, although the plot of log *k vs. P* does show a curvature (concave *upwards*) which persisted despite duplication of all the data points and for which the only obvious explanation would be that I_a and I_d mechanisms operate competitively in this case, the former predominating at high and the latter at low pressures.

While the Eigen mechanism,[5] involving a rate-determining I_d step, has rather generally been assumed to be operative in ligand substitution processes of trivalent as well as divalent metal ions in solution, associative reaction mechanisms for many of the former ions might have been anticipated, since it has long been recognized[20] that the greater the charge of the central metal ion the greater should be the tendency toward associative rather than dissociative activation. The data of Table III suggest that associative activation may actually be *the norm* in substitution reactions of cationic complexes of trivalent metal ions, with cobalt(III) complexes being anomalous. This generalization need not apply to anionic complexes[20] such as reineckate or aquopentachlororhodate(III), and the validity of the

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(17) H. L. Bott, A. J. Poe, and K. Shaw, *J. Chem. Soc. A*, 1745 (1970).

(18) The relative hydrated radii of cations of the same net charge can be qualitatively gauged by comparing their relative ease of elution from a cation exchange resin; thus, the familiar elutability sequences $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ and $Lu^{3+} > Yb^{3+} > Tm^{3+} >$ etc. are considered to reflect decreasing *hydrated* ionic radii from left to right. We find that hexaaquochromium(III) ion is eluted from Dowex 50W-X4 resin by 1.0 *M* perchloric acid about five to six times more rapidly than are aquopentaammine-chromium(III) or –rhodium(III); of the latter two, the rhodium ion appears to be slightly more firmly held by the resin. Thus, the hydrated radii apparently fall in the series $Cr(H_2O)_6{}^{3+} \gg Cr(NH_3)_5OH_2{}^{3+} \geq Rh(NH_3)_5OH_2{}^{3+}$.

(19) We thank Dr. M. W. Grant for bringing this oversight to our attention.

(20) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 1st ed, Wiley, New York, N. Y., 1958, p 102.

dissociative Eigen mechanism for reactions of divalent transition metal ions such as nickel(II) and cobalt(II) has recently received support by the observation[21] that their substitution reactions with some uncharged ligands are characterized by markedly positive ΔV^*.

It should be noted that the value of ΔH^* for aquo exchange with $Rh(NH_3)_5OH_2^{3+}$ is actually 2.0 kcal mol^{-1} *less* than for the analogous reaction of $Co(NH_3)_5OH_2^{3+}$, whereas for any probable geometry of the transition states the ligand field contribution to ΔH^* should be at least 20 kcal mol^{-1} *greater* for Rh(III) than for Co(III).[22] This indicates that ligand field effects cannot be a major component of ΔH^* in substitution reactions at *both* Rh(III) and Co(III) centers. Our assignment of an associative mechanism for Rh(III) and a dissociative one for Co(III) provides an explanation for this observation, since the energy of bond formation between the incoming aqua nucleophile and the Rh(III) center could lower the activation enthalpy to a value less than that of the Co(III) substitution. The increased importance of the associative mechanism as one descends a periodic group can be attributed to the enhanced tendency of the larger central metal atom to engage in covalent bonding to the incoming nucleophile (as measured by the "Class B" character[23] or "softness"[24] of the metal atom), and to the reduced steric hindrance to the entry of the seventh ligand.

The factors favoring an associative mechanism for Cr(III) as opposed to a dissociative mechanism for Co(III) remain unresolved. Calculations of the ligand field contributions to ΔH^*, made by Spees, Perumareddi and Adamson[22] on the basis of assumed spin pairing in the transition state, do indeed suggest that a seven-coordinate transition state of local D_{5h} symmetry may be favored over alternative dissociative pathways for Cr(III), while a five-coordinate transition state may be favored, albeit marginally, for analogous Co(III) systems. However, the general observation[25] that stereochemical change is rarely encountered in Cr(III) substitutions is difficult to reconcile with a transition state of D_{5h} symmetry, and the Spees–Perumareddi–Adamson calculations indicate that the most likely alternative stereoretentive seven-coordinate transition state, which would have C_{2v} local symmetry, would involve a higher ligand-field contribution to ΔH^*. A further uncertainty arising from the Spees–Perumareddi–Adamson analysis is that the alternative assumption of a high-spin transition state for substitutions at Cr(III) leads to the result that ligand-field effects would favor a dissociative process.

We conclude that the analysis of ΔH^* values in terms of ligand-field effects, as in the Spees–Perumareddi–Adamson approach, involves significant uncertainties when applied to the problem of reaction mechanisms. While considerations of ΔS^* values are rather more definitive, in the case of the aquo exchanges there still remains the ambiguity from the unknown molecularity with respect to the solvent as a nucleophile. This uncertainty can involve even the sign of ΔS^* as well as its numerical magnitude. By contrast, the sign and values of ΔV^* appear to be more reliable in establishing reaction mechanisms for aquo exchange systems such as those described in this paper.

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Dynamic Stereochemistry of Polytopal Isomerization Reactions

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Abstract: Following the approach taken in studies of permutational isomerization reactions, polytopal isomerization reactions are defined in terms of permutation operations. The point group symmetry of the interconverting polytopal isomers is used to generate classes of symmetry equivalent reactions. Formulas for enumerating these classes are provided. Topological representations are then defined in a precise fashion and various properties are examined. The relationship between a polytopal isomerization reaction and the permutational isomerization reactions it implies is also discussed. Finally, some nonrigid inorganic, organic, and organometallic molecules are treated to show the usefulness of these formalisms.

The ligands or substituents of many molecules define polytopes, *i.e.*, polygons or polyhedra. Within this class of molecules, isomers defining different polytopes are designated polytopal isomers.[2] The concept of polytopal isomerism has proven to be useful in unifying seemingly diverse areas of structural chemistry. While the structural stereochemistry of poly-

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[2] As originally defined,[3] polytopal isomers are characterized by their idealized polytopal forms in order to maximize symmetry. In this paper, the "nonidealized" shape of polytopal isomers will be considered and the symmetry of each polytopal form will be the standard molecular point group symmetry.

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