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Static and Dynamic Volume Relationships in Aquation Reactions of the Pentaamminecobalt(III) Series

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For the acid-independent and acid-dependent aquation pathways of $Co(NH_3)_5SO_4^+$, the respective volumes of activation ΔV^*_0 (at zero pressure) and ΔV^*_H (pressure averaged over 100 MPa) are −18.3 and −3.5 cm^3 mol^{-1} at 35 °C and −19.7 and −3.9 cm^3 mol^{-1} at 55 °C, at ionic strength 1.0 mol kg^{-1}. The temperature dependence of ΔV^*_0 can be accounted for in terms of the solvational change indicated by its pressure dependence. Discrepancies between earlier high-pressure studies of this reaction can be traced to neglect of the pressure dependence of ΔV^*_0 and of the contribution of ΔV^*_H. The apparent molal volumes of several complexes of the type $[M(NH_3)_5X](ClO_4)_{3-n}$ have been redetermined in aqueous solution, and apparent thermodynamic inconsistencies in the application of these to calculate volume changes for aquation reactions have been resolved. The "volume profile" approach to the interpretation of octahedral substitution kinetics is vindicated, but the common supposition that the volumes of the penta- and hexacoordinate ammine complexes of the same metal ion are equal is shown to be seriously in error, e.g., by 17–20 cm^3 mol^{-1} for the cobalt(III) case.

Introduction

A decade ago, reports[1] from this laboratory described the effects of pressure on the rate of reaction 1 and showed these

$$Co(NH_3)_5X^{(3-n)+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + X^{n-} \qquad (1)$$

to be consistent with a dissociative interchange (I_d) mechanism. Subsequently, other observations and interpretations have been published,[2–6] which seem at first sight to be at variance with those of our report of 1972.[1] The purpose of the present article is to resolve these discrepancies and to develop further the model of 1972.

van Eldik et al.[2] report values of the volume of activation ΔV^* for aquation of the (sulfato)pentaamminecobalt(III) ion at 60 °C of −8.1 and −8.0 cm^3 mol^{-1} in 0.1 M (M = mol L^{-1}) $HClO_4$ and at pH 4.5 (ionic strength I = 0.1 M), respectively. These values stand in sharp contrast to our limiting low-pressure value $\Delta V^*_0 = -18.5$ cm^3 mol^{-1} at 25 °C and pH 4.3, a fact which van Eldik et al.[2] ascribe to the difference in temperature but which could also be due in some measure to neglect on their part of the pressure dependence of ΔV^* (cf. a similar neglect by Gay and Nalepa[3] for the case $X^{n-} = Cl^-$) or to failure on ours to collect sufficient low-pressure data to define ΔV^*_0 accurately. In any case, the effect of pressure on the *acid-catalyzed* pathway for the aquation of $Co(NH_3)_5SO_4^+$[7–9] was not investigated by van Eldik et al.[2] We have therefore investigated the pressure dependence of the rate of aquation of $Co(NH_3)_5SO_4^+$ as a function of $[H^+]$. The aquation of this complex was of further interest to us in connection with a theory of the temperature dependence of ΔV^*_0 for reactions similar to eq 1.

Our other major concern centers upon the suggestion, made by Stranks[4] in 1974, that the molar volumes $\bar{V}$ of cationic complexes ML_6 and ML_5 (specifically, M = Co(III) and L = NH_3) may be taken as being equal for some purposes such as facilitation of the computation of their relative compressibilities. A study of the volume profiles of the series of reactions of type 1 by Palmer and Kelm[5] seemed to confirm that $\bar{V}(Co(NH_3)_5^{3+}) = \bar{V}(Co(NH_3)_6^{3+}) = 55$ cm^3 mol^{-1} (on an "absolute" volume scale with $\bar{V}(H^+) = -4.5$ cm^3 mol^{-1}), and consequently the 1974 postulate has recently been reiterated[6] with an implication of general validity. A disquieting aspect of the case advanced by Palmer and Kelm, however, is that it was necessary for them to assume that $\bar{V}(H_2O) = 0$, rather than 18 cm^3 mol^{-1}, not only to make the aqua-exchange case fit the volume profile argument but also to make the volumes of reaction $\Delta\bar{V}$ for reaction 1, calculated from the algebraic sum $\sum_i \bar{V}_i$ of the molar volumes for all i species involved, agree with the values of $\Delta\bar{V}$ obtained by direct measurement.[10] It is a matter of thermodynamic exigency that $\sum_i \bar{V}_i$ shall equal $\Delta\bar{V}$ within the experimental uncertainty, and it is noteworthy that no such special assumption was necessary to obtain this equality for the Cr(III) series analogous to reaction 1. This suggests that there is some systematic error in the $\bar{V}_i$ reported[5] for the cobalt(III) series.

We have therefore also redetermined the apparent molar volumes ϕ_v of electrolytes relevant to reaction 1 and have reexamined the application of the concept of reaction volume profiles to this reaction.

Experimental Section

Materials. Distilled water was passed through Barnstead deionizer and organic removal cartridges before use. Baker Analyzed perchloric acid (70–72%) was used as received. Lithium perchlorate trihydrate was made from Baker Analyzed lithium carbonate and recrystallized from water. Sodium perchlorate monohydrate (Fisher Reagent) was recrystallized from water.

The salts $[M(NH_3)_5X^{(3-n)+}](ClO_4)_{3-n}$ (M = Co, Cr) in general were prepared as previously described.[1,9,11,12] The purity of complexes was verified by passing an aqueous solution of the complex through a column of Dowex 50W-X8 in the H^+ form and titrating the acid liberated to determine the formula weight and by comparing the visible absorption spectra with those previously recorded.[1] Samples having formula weights within 0.5% of the calculated value were considered acceptable for densimetry and kinetics.

In particular, the key compound $[Co(NH_3)_5Cl](ClO_4)_2$ was made by dissolving $[Co(NH_3)_5Cl]Cl_2$ in water at 21 °C, adding 70% $HClO_4$ with stirring such that the final $[HClO_4]$ did not exceed 4 M, and cooling the mixture to 0 °C. The precipitated solid was recrystallized in the same way, except that the final $[HClO_4]$ was limited to 1 M, and the product was dried in a vacuum desiccator. (Precipitation of $[Co(NH_3)_5Cl](ClO_4)_2$ by the usual method of filtering a saturated solution of the chloride into ice-cold 70% $HClO_4$ led to contamination of the product with $Co(NH_3)_6^{3+}$, which is almost always present in samples of the chloride.) Three different sources of $[Co(NH_3)_5Cl]Cl_2$

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were used (Ventron Corp., preparation as previously described,[1] and thermal deaquation of $[Co(NH_3)_5OH_2]Cl_3$), but in every case the formula weight of the product was 378 ± 3; cf. 378.4 calculated for anhydrous $[Co(NH_3)_5Cl](ClO_4)_2$. The X-ray diffraction patterns of $[Co(NH_3)_5Cl](ClO_4)_2$ samples used for densimetry showed no anomalous reflections attributable to impurities such as $[Co(NH_3)_6](ClO_4)_3$, $[Co(NH_3)_4Cl_2^+]$ salts, or unchanged $[Co(NH_3)_5Cl]Cl_2$ that might be anticipated on the basis of low solubilities. Samples did, however, gain slightly in weight on prolonged exposure to the air.

Kinetic Measurements. Experiments at atmospheric pressure were carried out by withdrawing samples of $[Co(NH_3)_5SO_4]ClO_4/HClO_4/LiClO_4$ solutions from thermostated (±0.01 °C), darkened flasks at times t, quenching them in ice, and subsequently monitoring the optical absorbance A_t at 280 nm with a Cary Model 17H spectrophotometer at room temperature. High-pressure runs at 35 °C were followed similarly, by withdrawing samples from a pressurized syringe[1] through a Teflon needle, while those at 55 °C were carried out in situ in the spectrophotometer using a modified Franck optical cell as previously described,[13] the temperature being monitored with thermistors, which were calibrated frequently against standardized mercury-in-glass thermometers.

Density Measurements. A Sodev 02D vibrating-tube densimeter, thermostated (±0.001 °C), was used in conjunction with a Systron-Donner 6150 frequency meter.

The volume of reaction ΔV for the aquation of $[Co(NH_3)_5SO_4]ClO_4$ was determined by measuring the densities of two aliquots of a solution of the complex (~0.01 M), one of which was base hydrolyzed and then reacidified, the other being prepared with the same amounts of alkali and acid added in reverse order; a reference solution without the complex salt was similarly prepared (cf. ref 13). This procedure was necessary because reaction 1 does not go to completion when $X^{n-} = SO_4^{2-}$ at the complex concentrations needed for reliable density measurements. For $[Co(NH_3)_5Cl](ClO_4)_2$, however, it was possible to measure ΔV by both direct aquation and base hydrolysis; the results agreed within the experimental uncertainty.

Results

Kinetics of Aquation of $Co(NH_3)_5SO_4^+$. The relatively high acidities and low complex concentrations used ensured that aquation went to effective completion (through extensive protonation of the liberated sulfate ion). The final optical absorbances A_∞ were generally measured directly for experiments using the sample method and calculated for those using the pressurized optical cell, but these procedures were shown to be equivalent. Excellent first-order kinetics (rate coefficients k_{obsd}) were observed over at least two half-periods of the reaction in all cases, according to the equation

$$-\ln [(A_t - A_\infty)/(A_0 - A_\infty)] = k_{obsd}t \tag{2}$$

It was found that k_{obsd} is accurately a linear function of $[H^+]$ at a given temperature T and pressure P:

$$k_{obsd} = k_{aq} + k_H[H^+] \tag{3}$$

Examination of the values of k_{aq} and k_H collected in Table I will show that, although the relatively slight dependence of $\ln k_H$ upon P may be taken as linear within the experimental uncertainty, plots of $\ln k_{aq}$ against P are unmistakably curved. The pressure dependence of $\ln k_{aq}$ was equally well described (correlation coefficients 0.997 at 35 °C and 0.996 at 55 °C) by either a quadratic equation

$$\ln k_{aq} = \ln k_{aq}^0 - (\Delta V^*_0/RT)P + CP^2 \tag{4}$$

or the modified Tait equation

$$\ln k_{aq} = \ln k_{aq}^0 - P(\Delta V^*_0)/RT - (18.0\rho x/2.303RT)[(\Pi + P)\ln(1 + P/\Pi) - P] \tag{5}$$

in which ΔV^*_0 is the volume of activation for the spontaneous aquation of $Co(NH_3)_5SO_4^+$ at atmospheric (effectively, zero) pressure, C is a constant, Π and ρ are the Tait parameters for water at the appropriate temperature T, and x is the number of solvating water molecules *added* en route to the transition state.[1] The values of ΔV^*_0, C, and x so obtained were very close to those of Jones et al.,[1] and since the latter were obtained over a much wider pressure range, the value of $x = 8.0$ reported by Jones et al.[1] was inserted into eq 5 to allow precise evaluation of ΔV^*_0 from the new data. Thus we have for the acid-dependent pathway $\Delta V^*_H = -3.5 \pm 0.6$ and -3.9 ± 0.5 cm^3 mol^{-1} and for the spontaneous aquation pathway $\Delta V^*_0 = -18.3 \pm 0.4$ and -19.7 ± 0.8 cm^3 mol^{-1}, at T = 35.0 and 55.0 °C, respectively, at ionic strength $I = 1.0\ m$ (m = mol kg^{-1}).

Table I. Temperature and Pressure Dependence of Rate Coefficients for Spontaneous and Acid-Catalyzed Aquation Pathways of $Co(NH_3)_5SO_4^{+\,a}$

temp, °C	pressure, MPa	10^6k_{aq}, s^{-1}	10^6k_H, kg mol^{-1} s^{-1}
34.99	0.1	3.39 ± 0.08	6.36 ± 0.17
	25.5	4.22 ± 0.11	6.48 ± 0.20
	50.5	4.87 ± 0.04	6.70 ± 0.07
	75.6	5.55 ± 0.08	7.02 ± 0.13
	99.1	6.20 ± 0.07	7.61 ± 0.13
	149.6	7.90 ± 0.08	7.59 ± 0.14
54.99	0.1	35.0 ± 0.5	99.3 ± 0.9
	25.0	43.0 ± 0.9	102 ± 2
	50.0	50.9 ± 0.9	107 ± 2
	75.0	56.3 ± 0.8	113 ± 2
	100.0	65.9 ± 0.9	113 ± 2

[a] $[Co(NH_3)_5SO_4^+] = 5.5 \times 10^{-4}$ mol kg^{-1}; ionic strength = 0.95 mol kg^{-1} ($LiClO_4/HClO_4$).

Density Measurements. Using the equation

$$\Delta V = 1000(d_{CoSO_4} - d_{CoOH_2})/cd_0 \tag{6}$$

where d_{CoSO_4}, d_{CoOH_2}, and d_0 are the measured densities of the reactant, product, and reference solutions, respectively, and c is the concentration of complex, we found the volume of reaction for the aquation of $Co(NH_3)_5SO_4^+$ (reaction 1, $X^{n-} = SO_4^{2-}$) from multiple determinations to be -23.7 ± 0.7 cm^3 mol^{-1} at 35 °C and $I = 0.08\ m$ (final $[H^+] = 7 \times 10^{-4}\ m$). Attempts to measure ΔV for the same reaction at $I = 1.0\ m$, for direct comparison with the kinetic results, gave poor reproducibility because of the sensitivity of the measurements to small differences in the concentration of the supporting electrolyte between samples. For the aquation of $[Co(NH_3)_5Cl](ClO_4)_2$ (~0.01 m) in the presence of 0.015 m $HClO_4$, ΔV was found to be -11.2 ± 1.0 cm^3 mol^{-1} at $I = 0.1\ m$ and -12.8 ± 1.0 cm^3 mol^{-1} at $I = 1.0\ m$ ($NaClO_4$), in good agreement with the data of Spiro et al.[10]

The apparent molal volumes ϕ_v of various relevant electrolytes in aqueous solution, calculated in the usual way,[14] are collected in Table II. Reproducibility averaged ±0.8 cm^3 mol^{-1} for the complex salts, but for $[Co(NH_3)_5Cl](ClO_4)_2$, for which numerous measurements of ϕ_v were made upon samples prepared in various ways, a standard deviation of ±2.0 cm^3 mol^{-1} was found, and this may be taken to represent the uncertainty in ϕ_v for the other complexes more realistically. A sample of $[Co(NH_3)_5Cl](ClO_4)_2$ made by filtration of a solution of the chloride into 70% $HClO_4$ gave $\phi_v = 179._2$ cm^3 mol^{-1}, i.e., ~10 cm^3 mol^{-1} too high, probably in part because of $[Co(NH_3)_6](ClO_4)_3$ impurity. For all complexes of both Co(III) and Cr(III) listed in Table II, *with the exception of the (sulfato)-, chloro-, and bromopentaamminecobalt(III) perchlorates*, agreement of ϕ_v with the values of Palmer and Kelm[5] is excellent, as is that of ϕ_v for HCl and $HClO_4$ with the literature values[14] at the relevant ionic strengths. For the aqua complexes, ϕ_v was not detectably changed by the addition

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Table II. Apparent Molal Volumes (ϕ_V) of Electrolytes and Conventional Molal Volumes (V_c) of the Corresponding Complex Cations in Aqueous Solution at 25.00 °C[a]

solute	ϕ_V,[b,c] cm^3 mol^{-1}	ϕ_V,[d] cm^3 mol^{-1}	V_c,[c,e] cm^3 mol^{-1}
$[Co(NH_3)_6](ClO_4)_3$	207.6	207.1	72.6
$[Co(NH_3)_5OH_2](ClO_4)_3$	204.4	206.1	69.4
$[Co(NH_3)_5OH_2](ClO_4)_3$	210.6[f]	...	71.7
$[Co(NH_3)_5Cl](ClO_4)_2$	168.8	187.2[g]	78.8
$[Co(NH_3)_5Cl](ClO_4)_2$	179.4[f]	...	86.8
$[Co(NH_3)_5Br](ClO_4)_2$	(184.6)[g]	196.4[g]	(94.6)[g]
$[Co(NH_3)_5SO_4]ClO_4$	137.7	147.2[g]	92.7
$[Co(NH_3)_5NCS](ClO_4)_2$	195.3	195.2	105.3
$[Co(NH_3)_5N_3](ClO_4)_2$	180.2	181.4[h]	90.2
$[Cr(NH_3)_5OH_2](ClO_4)_3$	215.5	215.8[i]	80.5
$[Cr(NH_3)_5OH_2](NO_3)_3$[j]	171.4	170.4	
$[Cr(NH_3)_5Cl](ClO_4)_2$	183.4	184.7	93.4
HCl	18.7		
HCl[f]	21.1		
$HClO_4$	45.0		
$HClO_4$[f]	46.3		

[a] Concentration of specified solute = 0.01 mol kg^{-1}. [b] Mean of three or more determinations; reproducibility typically ±0.8 cm^3 mol^{-1}. [c] This work. [d] Reference 5. [e] Using the measured ϕ_V of $HClO_4$. Note that these are *conventional* molal volumes, defined in terms of $V_c(H^+) = 0$; they are related to the "absolute" molal volumes $\bar{V}$ defined in ref 5 by the relationship $\bar{V}(\text{cation}^{z+}) = V_c - 4.5z$ cm^3 mol^{-1}. [f] In 0.98 mol kg^{-1} $NaClO_4$. [g] Value inconsistent with measured ΔV for reaction 1.[10,12] [h] Calculated from value for chloride salt by using ϕ_V(HCl). [i] Calculated from value for nitrate salt by using V_c for NO_3^-.[14] [j] Misprinted as the perchlorate in ref 5.

of small amounts of $HClO_4$ to suppress hydrolysis.

Table II also lists values of the *conventional* molal volumes V_c of the complex cations, derived from ϕ_v with the assumption that $V_c(H^+) = 0$ for ionic strengths in the appropriate range. This convention avoids the unnecessary assignment of an estimated "absolute" volume to the aqueous proton, the ionic strength dependence of which could be significant. When these data are compared with those of Palmer and Kelm,[5] their use of "absolute" molar volumes based on the assumption $\bar{V}(H^+) = -4.5$ cm^3 mol^{-1} must be recognized.

Discussion

Aquation Kinetics of $Co(NH_3)_5SO_4^+$. A minor extrapolation of the new ΔV^*_0 values for reaction 1 with $x^{n-} = SO_4^{2-}$ at ionic strength $I = 1.0$ *m* gives $\Delta V^*_0 = -17.5$ cm^3 mol^{-1} at 25.0 °C, which is very close to our previous value[1] of -18.5 cm^3 mol^{-1} at $I = 0.1$ M. The marked pressure dependence of ΔV^* previously reported[1] for this reaction is confirmed and accounts in large part for the difference between our values of ΔV^*_0 and the pressure-averaged ΔV^* of -8 cm^3 mol^{-1} (60 °C, $I = 0.1$ M) reported by van Eldik et al.[2]

The remainder of this discrepancy cannot be ascribed to temperature difference, as van Eldik et al.[2] suggested, since we find that ΔV^*_0 becomes *more negative* as the temperature is increased. The extent of this temperature dependence of ΔV^*_0 can be accurately predicted by taking the bond-making/breaking component ΔV^*_b of ΔV^* for substitution reactions of cationic complexes to be both pressure and temperature independent within the experimental uncertainty (as data on solvent-exchange reactions affirm[15-17]) and ascribing the observed *P* and *T* dependence of ΔV^* entirely to solvational change. The pressure dependence of ΔV^* for $Co(NH_3)_5SO_4^+$, when analyzed by eq 5, can be interpreted to mean that eight molecules of water ($x = 8.0$) are added to the complex on going from the initial to the transition state;[1] this is reasonable, since the molar volume V_{el} of electrostricted water is ~3 cm^3 mol^{-1} less than for free water[1,18] (V_{H_2O}) at 0.1 MPa and one expects $\Delta V^*_b = \Delta V^*_0 - x(V_{el} - V_{H_2O})$ to be a small positive number for an I_d process. One can then calculate the change in ΔV^*_0 on going from temperature T_1 to T_2:

$$\Delta\Delta V^*_0 = [xV_{el} - xV_{H_2O}]T_2 - [xV_{el} - xV_{H_2O}]T_1 = x(V_{H_2O}(T_1) - V_{H_2O}(T_2)) \quad (7)$$

For $T_1 = 35$ °C, $T_2 = 55$ °C, and $x = 8$, $\Delta\Delta V^*_0$ should be $8(18.123 - 18.276) = -1.2$ cm^3 mol^{-1}; the observed $\Delta\Delta V^*_0$ is -1.4 ± 0.8 cm^3 mol^{-1}.

Another possible contributor to the discrepancy between our ΔV^*_0 value for the sulfato aquation reaction and the ΔV^* of van Eldik et al.[2] is the acid-catalyzed pathway, for which the pressure-averaged ΔV^*_H would be about -4 cm^3 mol^{-1} at 60 °C and $I = 1.0$ M, as against -19 cm^3 mol^{-1} for the acid-independent pathway. When this contribution and that arising from the pressure dependence of ΔV^* for the spontaneous aquation are taken into account, the data of van Eldik et al.[2] for 60 °C and $I = 2.0$ and 0.1 M, $[H^+] = 0.1$ M, indicate $\Delta V^*_0 \sim -16$ cm^3 mol^{-1}, which is in reasonable agreement with our values.

The linear correlation of unit slope between ΔV^*_0 values for reaction 1 in general with the volume of reaction ΔV shows that ΔV^*_0 is about 1 cm^3 mol^{-1} more positive than ΔV for mononegative X^- and $X = H_2O$, at least, the difference being accountable for as the conversion of a solvating water molecule to a coordinated one after passing through the transition state.[1] Evidently, the ions are essentially as fully solvated in the transition state as in the final state, even though the former is in effect an ion pair, if the I_d model is appropriate. The contribution of ion-pair character to the volume of the transition state is therefore probably not significant for mononegative X^- but might be observable for $X^{n-} = SO_4^{2-}$, in view of the evidence for ground-state ion pairing of $Co(NH_3)_5OH_2^{3+} + SO_4^{2-}$ with an associated positive, but rather variable, volume change.[8,10,19,20] Indeed, ΔV^*_0 is some 5 cm^3 mol^{-1} more positive than the redetermined ΔV for reaction 1 with $X^{n-} = SO_4^{2-}$ (-23.7 cm^3 mol^{-1} at 35 °C, $I \sim 0.1$), in reasonable agreement with $\Delta V^* = +2.3 \pm 1.8$ cm^3 mol^{-1} determined directly[20] for the reverse reaction at 60 °C.

Acid-Catalyzed Aquation of $Co(NH_3)_5SO_4^+$. For the reaction

$$Co(NH_3)_5SO_4^+ + H^+ + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + HSO_4^- \quad (8)$$

at 25 °C, $I \sim 0.07$ M, one may take $\Delta V_a = -21.5$ cm^3 mol^{-1} for the ionization of HSO_4^- under these conditions[21] and calculate $\Delta V = -23.7 - (-21.5) = -2.2$ cm^3 mol^{-1}. Then, if the case $X^{n-} = HSO_4^-$ is to fit the linear relationship between ΔV^*_0 and ΔV found for other X^- in reaction 1, ΔV^*_0 for the

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(20) van Eldik et al.[2] report that they find no *kinetic* evidence for the participation of such ion pairs in the reaction of $Co(NH_3)_5OH_2^{3+}$ with SO_4^{2-} under conditions of constant ionic strength, despite the findings of Posey and Taube.[8] The kinetic studies, however, were mostly done in the presence of 0.1 M $HClO_4$, so that a significant and varying fraction of the total sulfate, which ranged up to 0.6 M, would be present as HSO_4^-. For the same reason, the volume of activation reported for the reaction of $Co(NH_3)_5SO_4^+$ with sulfate ion is likely to be an underestimate, since increasing pressure will suppress protonation of sulfate and hence accelerate the anation reaction. There is also some question as to whether the ionic strength principle is valid at such high ionic strengths when a divalent anion is replacing a monovalent in major proportions.

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Table III. Comparison of Measured Volumes of Reaction ΔV_{obsd} for Reaction 1 with Those Calculated (ΔV_{calcd}) from the Conventional Molal Volumes V_c of Table II[a]

X^{n-} in $Co(NH_3)_5X^{(3-n)+}$	I, mol kg^{-1}	$V_c(X^{n-})$	ΔV_{calcd}[b]	ΔV_{obsd}[c]	ΔV^*_0[c]	V_c^R[b]
Cl^-	0.1	18.7	−9	−11.2 −11.6[d]	−10.6[e]	50
	1.0	21.1	−12	−12.8 −10.4[d]		
Br^-	0.1	25.1[f]	(−18)	−10.8[d,e]	−9.2[e]	
NCS^-	0.1	~41.5[g]	−12		−4[e,h]	⩽60
SO_4^{2-}	0.1	15.7[i]	−26	−23.7	−18.5[e]	59
	1.0	19.5[i]		−19.7[j]	−17.6[k]	
HSO_4^-	0.1	37.1	−2	−2.2[l]	−1[l]	53[l]
H_2O	0.6	18.0	0	0.0	+1.2[m]	53[n]

[a] All data from this work and at 25 °C, except where otherwise stated; all volumes in cm^3 mol^{-1}. [b] ±3 cm^3 mol^{-1}. [c] ±1.0 cm^3 mol^{-1}. [d] Reference 10. [e] Reference 1. [f] Estimated for HBr at $I \sim 0.06$ mol kg^{-1} from Masson equations for HCl, NaCl, and NaBr.[14] [g] Estimated for $I \sim 0.1$ from the data of: Fajans, K.; Johnson, O. *J. Am. Chem. Soc.* **1942**, *64*, 668. Padova, J. *J. Chem. Phys.* **1963**, *39*, 1552. These differ considerably from the $V_c°(NCS^-)$ value used in ref 5. [h] At 88 °C; average value is over the pressure range 0.1–255 MPa, so the true ΔV^*_0 value is more negative. [i] Reference 21. [j] Calculated by using an estimate by Spiro et al.[10] of effect of I. [k] Extrapolated from 35 and 55 °C. [l] Indirect estimate–see text. [m] Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642. [n] Using interpolated $V_c = 71.0$ for $I = 0.6$.

aquation of $Co(NH_3)_5HSO_4^{2+}$ must be about −1 cm^3 mol^{-1}, which is 2 cm^3 mol^{-1} more positive than for reaction 8.[22] Thus, ΔV_a for the reaction

$$Co(NH_3)_5HSO_4^{2+} \rightleftharpoons Co(NH_3)_5SO_4^+ + H^+ \qquad (9)$$

should be ~+2 cm^3 mol^{-1}, which is within the range of values of +3 to −4 cm^3 mol^{-1} reported[4,10,23-26] for several formally similar proton–dissociation reactions of cationic complexes of the types

$$M(NH_3)_5OH_2^{3+} \rightleftharpoons M(NH_3)_5OH^{2+} + H^+ \qquad (10)$$

and

$$M(H_2O)_6^{3+} \rightleftharpoons M(H_2O)_5OH_2^{2+} + H^+ \qquad (11)$$

so that the estimate of $\Delta V^*_0 \sim -1$ cm^3 mol^{-1} for reaction 1 with $X^{n-} = HSO_4^-$ seems valid.

Apparent Molal Volumes and Volumes of Reaction. Table II shows excellent agreement between our values of the apparent molal volumes ϕ_v of the complex salts for both Co(III) and Cr(III) and those of Palmer and Kelm, with the prominent exceptions of $[Co(NH_3)_5Cl](ClO_4)_2$, $[Co(NH_3)_5Br](ClO_4)_2$, and $[Co(NH_3)_5SO_4]ClO_4$. This indicates that the methods of measurement of ϕ_v used by Palmer and Kelm in Frankfurt-am-Main and by ourselves in Calgary are completely compatible, so that the discrepancies in the ϕ_v measurements for these three salts must have originated in their chemical composition at the time they were weighed out as solids. We find (cf. Hynes et al.[27]) that $[Co(NH_3)_5Cl]Cl_2$ is almost always contaminated with other cobalt(III) ammines, which have low solubility in aqueous perchlorate media and so are difficult to remove from the solid product by recrystallization of $[Co(NH_3)_5Cl](ClO_4)_2$ (made from the chloride) using relatively concentrated $HClO_4$ as precipitant. Similarly, Po and Jordan[28] report that the older methods of making $[Co(NH_3)_5SO_4]ClO_4$ gave products containing up to 20% aqua complex. Conventional chemical analyses tend to be falsely reassuring of purity in such cases; e.g., the N contents of pure $[Co(NH_3)_5Cl](ClO_4)_2$ and $[Co(NH_3)_6](ClO_4)_3$ are 18.5 and 19.0%, respectively; ion-exchange formula weight determinations are rather more discriminating in this respect and indicated that the complexes used in the Calgary ϕ_v and ΔV measurements were the pure, anhydrous compounds as formulated in Table II.

Members of the Frankfurt group, however, have recently repeated ϕ_v measurements on samples of $[Co(NH_3)_5Cl](ClO_4)_2$ sent by us as well as their own and find values that were essentially the same (180 ± 3 cm^3 mol^{-1}) for all specimens but that were intermediate between their published value[5] and ours (private communication, J. von Jouanne and H. Kelm). This, combined with our observation that the desiccated solid slowly gained weight on exposure to air, suggests that the chemical integrity problem is simply one of hygroscopic behavior of $[Co(NH_3)_5Cl](ClO_4)_2$, especially since the absolute humidity in Calgary is extremely low by European standards in winter when our ϕ_v measurements were made. The same explanation probably applies to $[Co(NH_3)_5Br](ClO_4)_2$ and $[Co(NH_3)_5SO_4]ClO_4$, both of which have been reported[28,29] to analyze as monohydrates, contrary to our experience. In the case of the relatively reactive bromo complex,[29] contamination by other cobalt(III) ammines or significant aquation during ϕ_v measurement was also possible and so this ϕ_v value is probably inaccurate.

Calculation of volumes of reaction ΔV_{calcd} for reaction 1 by summing ϕ_v values algebraically involves the difference between two numbers (ϕ_v or V_c of the complex ions) that are some 10 times larger than ΔV_{calcd}, which is therefore subject to relatively large uncertainties. These uncertainties are further compounded if the small but significant medium dependence of ϕ_v is ignored (Table II); ϕ_v might be expected to vary with ionic strength in the same way for similar electrolytes, thus canceling ΔV to a large extent, but this is not always true in practice (cf. Wirth and Collier's study[30] of $HClO_4$ vis-à-vis $NaClO_4$). We have therefore attempted to present in Table II ϕ_v and V_c data for ionic strengths close to those of the kinetic studies and of the ΔV measurements of Spiro et al.[10] It will be seen from Table III that V_c data yield correct ΔV values for reaction 1, within the experimental uncertainties of ±3 cm^3 mol^{-1} in ΔV_{calcd} and ±1.0 cm^3 mol^{-1} in ΔV_{obsd}, with the exception of the case $X^{n-} = Br^-$ for which the preparation of pure $[Co(NH_3)_5Br](ClO_4)_2$ seems especially difficult. Clearly, whenever direct measurement of ΔV is practicable, it is to be preferred to estimation from ϕ_v data.

Also listed in Table III are values of ΔV^*_0, reemphasizing the linear relationship with ΔV noted earlier for neutral and

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(22) Since this value is numerically small, the effects of ionic strength and temperature differences and of assuming ΔV^* for reaction 8 to be constant over the limited pressure range should be negligible for purposes of this rough comparison.

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mononegative X^{n-} but now suggesting the presence of some ion-pair character in the transition state when $X^{n-} = SO_4^{2-}$, as noted above. This latter effect is less marked at the higher ionic strength, as expected for ion association.[8]

The Volume Profile Concept. The final column of Table III lists values of a parameter V_c^R which is analogous to Palmer and Kelm's V_R except that it is conventional rather than an absolute molal volume.

$$V_c^R = V_c(Co(NH_3)_5X^{(3-n)+}) + \Delta V^*_0 - V_c(X^{n-}) \quad (12)$$

This would equal the partial molal volume of an intermediate $\{Co(NH_3)_5^{3+}\}^*$ if an extreme dissociative (D) mechanism were operating, i.e., if X^{n-} were lost completely in the transition state and consequently had its normal bulk-solution molal volume. If, however, the mechanism of reaction 1 is dissociative interchange (I_d), as seems likely,[15] X^{n-} will be present in the outer sphere of $Co(NH_3)_5^{3+}$ with a molal volume appropriate to such an environment; thus, for $X^{n-} = H_2O$, $V_c(X^{n-})$ should be about 15 rather than 18 $cm^3\ mol^{-1}$.[1,4,18] The modest spread in V_c^R values in Table III is therefore quite consistent with an I_d process, especially since the more deviant sulfato case can be understood as explained above. In particular, it is now clear that the case of aqua exchange in reaction 1 ($X^{n-} = H_2O$) is entirely compatible with the others, whether one chooses $V_c(H_2O)$ to be 15 or 18 $cm^3\ mol^{-1}$; the zero value adopted in ref 5 is quite inappropriate. The use of the volume-profile approach, as advocated by Palmer and Kelm,[5] is vindicated by the present study, but is now seen to be less clear-cut than one would like, especially in view of the potential for error in V_c values for the complex ions.

If we take the aqua exchange case as being most likely to give a realistic value of $V_c(Co(NH_3)_5^{3+})$, this can be set at 53–56 $cm^3\ mol^{-1}$ on the *conventional* scale; this is 17–20 $cm^3\ mol^{-1}$ smaller than V_c for $Co(NH_3)_6^{3+}$ (Table II). We conclude that *Stranks' postulate*,[4] that these two quantities can be taken as equal, *is in error by an amount that exceeds most of the values of* $|\Delta V|$ *and* $|\Delta V^*_0|$ *so far recorded for reaction 1 and related series and must never be used in attempting to rationalize such values.*

We can infer from this that the effective molar volume of an ammine ligand coordinated to cobalt(III) is 17–20 $cm^3\ mol^{-1}$, whereas ϕ_v for NH_3 may be calculated from density data[31] for aqueous ammonia to be 24.5 $cm^3\ mol^{-1}$. Thus, the upper limit of ΔV^* for the $Co(NH_3)_6^{3+}$–NH_3 exchange reaction may be set at +7.5 $cm^3\ mol^{-1}$ for a D mechanism. Interestingly, in 1924, Birk and Biltz[32] used the densities of solid halides to estimate that the average molal volume of a coordinated ammonia in $M(NH_3)_6^{3+}$ (M = Co, Cr) is 20 $cm^3\ mol^{-1}$. Molar volumes of neutral ligands calculated from the densities of solids should be regarded only as upper limits for the solution values because of the effect of empty space in the lattice in some cases on the measured density; for example, the molar volume of ice-I_h is 19.6 $cm^3\ mol^{-1}$, as against 9.0 for the hypothetical closest packed structure,[33] while Birk and Biltz's "gleichräumiger Verbindungen" $[M(NH_3)_6]X_2$ and $[M(NH_3)_6]X_3$, in which interstices in the quasi-antifluorite lattice of the former are filled with additional anions X^- in the latter[34] to give equal apparent molar volumes,[32] provide fair warning. Nevertheless, the agreement between the present approach and that of Birk and Biltz is encouraging.

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Registry No. $[Co(NH_3)_6](ClO_4)_3$, 13820-83-2; $[Co(NH_3)_5OH_2](ClO_4)_3$, 13820-81-0; $[Co(NH_3)_5Cl](ClO_4)_2$, 15156-18-0; $[Co(NH_3)_5Br](ClO_4)_2$, 14591-65-2; $[Co(NH_3)_5SO_4]ClO_4$, 15156-23-7; $[Co(NH_3)_5NCS](ClO_4)_2$, 15663-42-0; $[Co(NH_3)_5N_3](ClO_4)_2$, 14283-04-6; $[Cr(NH_3)_5OH_2](ClO_4)_3$, 32700-25-7; $[Cr(NH_3)_5OH_2](NO_3)_3$, 19683-62-6; $[Cr(NH_3)_5Cl](ClO_4)_2$, 22478-30-4; $Co(NH_3)_5HSO_4^{2+}$, 15156-26-0; HCl, 7647-01-0; $HClO_4$, 7601-90-3.

Supplementary Material Available: A table showing the dependence of pseudo-first-order rate coefficients k_{obsd} for the aquation of $Co(NH_3)_5SO_4^+$ on temperature, pressure, and acidity (2 pages). Ordering information is given on any current masthead page.

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Theoretical Study of the Olefin Insertion Step in the Chlorotris(triphenylphosphine)rhodium(I)-Catalyzed Hydrogenation of Olefins

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Ab initio LCAO–MO–SCF calculations have been performed for the reaction $H_2RhCl(PH_3)_2(C_2H_4) \rightarrow HRhCl(PH_3)_2(C_2H_5)$. This reaction stands as a model for the first hydrogen transfer in the dihydrido olefinic intermediate involved in the $RhCl(PPh_3)_3$-catalyzed hydrogenation of olefins. It is found that the early stages of the process, up to the transition state, are best described as an ethylene insertion into the Rh–H bond. The calculations indicate that some polytopal rearrangements occur simultaneously with relaxation from the transition state. The whole insertion process is computed to be exothermic with a rather moderate energy barrier. In connection with the origin of this barrier the metal substitution pattern is discussed. The presence of a good π-donor ligand in the coordination sphere promotes the olefin insertion, as opposed to the hydrogen migration, and lowers the energy barrier. Finally, the directionality of the insertion for some substituted olefins is analyzed on the basis of the composition of the perturbed molecular orbitals.

Introduction

We recently undertook[1-2] a theoretical study of the hydrogenation of olefins catalyzed by the chlorotris(triphenylphosphine)rhodium(I) complex (the so-called Wilkinson complex $RhCl(PPh_3)_3$).[3] The key intermediate of the corresponding catalytic cycle is an octahedral dihydrido olefinic

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