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Mechanistic Differentiation between Solvolysis Reactions of Pentaammine Trifluoromethanesulfonato-*O* Complexes of Cobalt(III), Chromium(III), and Rhodium(III)

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Volumes of activation (ΔV^*) for the solvolysis of $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (M = Co, Rh, Cr) were determined in acetonitrile and methanol. For each complex, the magnitude of ΔV^* does not depend significantly on the solvents studied. The values in acetonitrile are -3.1 ± 0.1, -7.8 ± 0.5, and -8.9 ± 0.5 cm^3 mol^{-1} for Co(III), Rh(III), and Cr(III) complexes, respectively, while those in methanol are -3.2 ± 0.1, -6.6 ± 0.1, and -10.5 ± 0.7 cm^3 mol^{-1}, respectively. The significantly less negative ΔV^* for the Co(III) complex as compared to those values for the Rh(III) and Cr(III) complexes is interpreted in terms of an I_d mechanism compared to an I_a mechanism for the last two. The important roles of the size of the anionic leaving ligand and the polarity of the solvent are discussed.

Introduction

Octahedral pentaammine complexes of Co(III), Cr(III), and Rh(III) have for many years been employed as model systems to investigate substitution and base hydrolysis reactions at such metal centers.[2-4] The large volume of kinetic information available enables a detailed description of the underlying reaction mechanisms and has contributed substantially to our general understanding of such processes. This success has encouraged various groups to study these systems in even more detail in order to resolve the fundamental reasons for the differing reaction mechanisms.

One of these aspects concerns the important role played by the leaving group in determining the activation parameters for aquation reactions of the pentaammine complexes. The fundamental difference in the substitution mechanisms is nicely demonstrated by the volumes of activation of +1.2, −5.8, and −4.1 cm^3 mol^{-1} for solvent exchange on $M(NH_3)_5H_2O^{3+}$, where M = Co(III), Cr(III), and Rh(III), respectively.[5,6] These data point toward the operation of an I_d mechanism for the Co(III) complex, compared to an I_a mechanism for the Cr(III) and Rh(III) complexes. Similar mechanistic differences were recently revealed for aquation reactions of a series of complexes of the type $M(NH_3)_5X^{3+}$, where X is a neutral leaving group.[7,8] An average volume of activation of $+1.9 \pm 1.0$ cm^3 mol^{-1} for the aquation of 10 Co(III) complexes, compared to a value of -6.0 ± 2.7 cm^3 mol^{-1} for seven Cr(III) complexes, clearly demonstrates this point as well as the high mechanistic discrimination ability of such data.[9] However, the situation becomes significantly more complicated when we are dealing with charged leaving groups. For instance the volumes of activation for aquation reactions of $M(NH_3)_5Cl^{2+}$ were reported to be -10.6 ± 0.4, -10.8 ± 0.3, and -14 ± 5 (determined in an indirect way) cm^3 mol^{-1} for M = Co(III), Cr(III), and Rh(III), respectively.[10-13] Although it is believed that the underlying mechanism does differ for Co(III) as compared to Cr(III) and Rh(III),[10-13] the interpretation of the volume of activation data is complicated by large changes in electrostriction associated with the release of an anionic ligand. An overall negative volume of activation can result from an intrinsic volume decrease due to bond formation in terms of an I_a mechanism or from a solvational volume decrease due to an increase in electrostriction during the release of an anionic ligand in terms of an I_d mechanism. As the results of this investigation will demonstrate, it was rather a coincidence that such similar volumes of activation were found for the aquation of $M(NH_3)_5Cl^{2+}$ complexes, a matter of fine balance between intrinsic and solvational volume changes. The latter should strongly depend on the nature and size of the leaving group and especially the polarity of the solvent.

We have now studied the pressure dependence of the solvolysis of a series of (trifluoromethanesulfonato)pentaamminemetal(III) complexes in methanol and acetonitrile. These complexes were recently synthesized,[14,15] and their solvolysis reactions were studied in a wide range of solvents at ambient pressure.[16] The conventional activation parameters (ΔH^* and ΔS^*) do not allow a clear mechanistic distinction, although ΔS^* does become more negative from an average value of -31 ± 12 to -42 ± 17 and -62 ± 26 J K^{-1} mol^{-1} for a series of Co(III), Rh(III), and Ir(III) complexes, respectively. This trend was interpreted in terms of a gradual changeover from I_d to I_a along the series with the major contribution arising from an increase in electrostriction.[16]

Experimental Section

Materials. The complexes $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (M = Co, Rh, Cr) were prepared by reacting $[M(NH_3)_5Cl]Cl_2$ with anhydrous trifluoromethanesulfonic acid under a steady stream of nitrogen according to the methods described before.[14,15] UV–vis spectroscopic data were in good agreement with those reported before.[14,15] Analytical reagent grade solvents were used throughout this study: acetonitrile was dried over aluminum oxide; methanol was distilled over magnesium.

Measurements. UV–vis absorption spectra, repetitive-scan spectra, and kinetic runs at ambient pressure were recorded in the thermostated cell compartment of a Shimadzu UV-250 spectrophotometer. A Zeiss PMQ II spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure cell[17] was used for kinetic measurements at pressures up to 150 MPa. The solvolysis reactions were monitored at 540, 510, and 345 nm for the Co(III), Cr(III), and Rh(III) complexes, respectively. A drop of triflic acid was added to the reaction mixture in methanol.[16] No salt was added to adjust the ionic strength of the medium. The observed pseudo-first-order rate constants (k_{obsd}) were calculated from plots of ln $(A_t - A_\infty)$ versus time, which were linear for at least 3 half-lives of the reaction. All plots of ln k_{obsd} versus pressure were linear within the experimental error limits, and the volumes of activation (ΔV^*) were calculated from the slope of such plots ($= -\Delta V^*/RT$) in the usual way

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Table I. Pressure Dependence of the Rate Constant for Solvolysis of $M(NH_3)_5(OSO_2CF_3)^{2+}$ in Acetonitrile

M[a]	P, MPa	10^4k_{obsd},[b] s^{-1}
Co(III)[c]	5	4.42 ± 0.12 (2)
	50	4.70 ± 0.04 (3)
	100	4.98 ± 0.05 (2)
	150	5.31 ± 0.10 (2)
Rh(III)[d]	5	4.83 ± 0.13 (3)
	50	5.39 ± 0.09 (3)
	100	6.51 ± 0.07 (2)
	150	7.42 ± 0.06 (3)
Cr(III)[e]	5	5.15 ± 0.04 (2)
	50	6.00 ± 0.07 (2)
	100	7.46 ± 0.02 (2)
	150	8.55 ± 0.21 (2)

[a] [Complex] = (0.6–1.0) × 10^{-2} M. [b] Mean value of the number of kinetic runs indicated in parentheses. [c] T = 25.2 °C. [d] T = 34.6 °C. [e] T = 25.2 °C.

Table II. Pressure Dependence of the Rate Constant for Solvolysis of $M(NH_3)_5(OSO_2CF_3)^{2+}$ in Methanol

M[a]	P, MPa	10^4k_{obsd},[b] s^{-1}
Co(III)[c]	5	3.63 ± 0.10 (3)
	50	3.85 ± 0.08 (2)
	100	4.11 ± 0.13 (3)
	150	4.40 ± 0.15 (3)
Rh(III)[d]	5	5.84 ± 0.03 (2)
	50	6.59 ± 0.11 (3)
	100	7.50 ± 0.17 (3)
	150	8.62 ± 0.20 (3)
Cr(III)[e]	5	2.36 ± 0.15 (3)
	50	2.95 ± 0.21 (3)
	100	3.73 ± 0.15 (3)
	150	4.37 ± 0.14 (3)

[a] [Complex] = (0.6–1.0) × 10^{-2} M. [b] Mean value of the number of kinetic runs indicated in parentheses. [c] T = 17.4 °C. [d] T = 25.0 °C. [e] T = 20.0 °C.

by using a least-squares fit of the data.

Results and Discussion

The aquation and solvolysis reactions of the complexes $M(NH_3)_5(OSO_2CF_3)^{2+}$ (M = Co(III), Cr(III), Rh(III)) are significantly faster than for the corresponding halide and related complexes. This is mainly due to the weaker coordination ability of triflate (trifluoromethanesulfonate). The aquation rate constants are such that they do not allow enough time for temperature and pressure equilibration following dissolution of the solid complexes, to enable kinetic measurements as a function of pressure. The reactions are significantly slower in acetonitrile and methanol and can be studied conveniently as a function of pressure. A typical example of a repetitive-scan spectrum for the solvolysis of $Rh(NH_3)_5OSO_2CF_3^{2+}$ in CH_3CN is presented in Figure 1, from which it follows that the reaction exhibits very clean isosbestic points and well-behaved kinetics. The results in Tables I and II clearly demonstrate that the pseudo-first-order rate constants increase with increasing pressure for all the investigated systems. The corresponding volumes of activation along with other rate and activation parameters, taken from the literature or determined in this study, are summarized in Table III.

The solvolysis rate constants in acetonitrile and methanol are significantly lower than those reported for water, dimethyl sulfoxide, dimethylformamide, and related solvents.[16] Although no simple correlation of these rate constants with solvent parameters such as dipole moment, dielectric constant, viscosity, and polarizability was found,[16] that data do clearly demonstrate the important role played by the solvent, especially its ability to accommodate ionic species and ionic reaction products. During the overall solvolysis reaction (1), charge creation accompanied by

$$M(NH_3)_5(OSO_2CF_3)^{2+} + \text{solvent} \rightarrow M(NH_3)_5(\text{solvent})^{3+} + CF_3SO_3^- \quad (1)$$

a significant increase in electrostriction must significantly affect the rate and activation parameters. It is therefore quite understandable that the solvolysis rate constants increase with increasing solvent polarity. On the other hand, the metal–triflate bond strength will also affect the solvolysis rate constant,[16] a factor that does not contribute significantly in the reactions studied in this investigation.

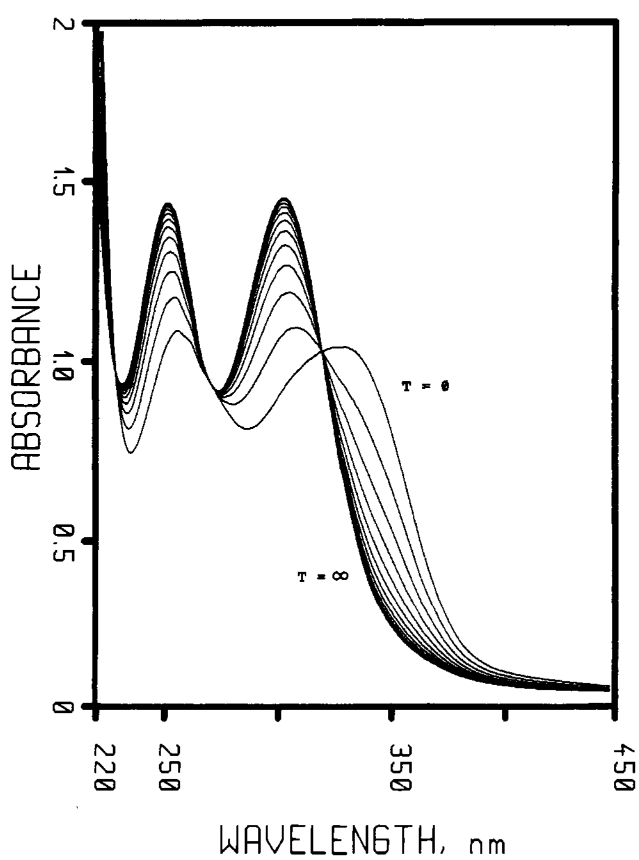

Figure 1. Repetitive-scan spectra for the reaction $Rh(NH_3)_5(OSO_2CF_3)^{2+} + CH_3CN \rightarrow Rh(NH_3)_5(CH_3CN)^{3+} + CF_3SO_3^-$: [Rh(III)] ≈ 1 × 10^{-2} M; T = 25 °C; optical path length 1 cm; Δt = 15 min.

Table III. Rate Constants and Activation Parameters for the Solvolysis Reaction

$$M(NH_3)_5(OSO_2CF_3)^{2+} + \text{solvent} \rightarrow M(NH_3)_5(\text{solvent})^{3+} + CF_3SO_3^-$$

M	solvent	10^4k_{obsd}, s^{-1} (25 °C)	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	ΔV^*, cm^3 mol^{-1}
Co(III)[a]	CH_3CN	4.63	76.3 ± 1.3	−51 ± 4	−3.1 ± 0.1
	CH_3OH	9.50	83.1 ± 1.0	−23 ± 3	−3.2 ± 0.1
Rh(III)[a]	CH_3CN	1.65	75.1 ± 1.1	−66 ± 3	−7.8 ± 0.5
	CH_3OH	5.9	80.7 ± 1.0	−38 ± 3	−6.6 ± 0.1
Cr(III)	CH_3CN[b]	4.5	89 ± 1.3	−11 ± 4	−8.9 ± 0.5
	CH_3OH[c]	4.37	69.5 ± 0.5	−76 ± 2	−10.5 ± 0.7

[a] Rate constants, ΔH^*, and ΔS^* taken from ref 16. [b] Rate constant, ΔH^*, and ΔS^* from: Lawrance, G. A. Unpublished results, University of Newcastle, Newcastle, Australia. [c] 10^4k_{obsd} determined in this study (s^{-1} (°C)): 2.79 ± 0.31 (20.2); 4.37 ± 0.24 (24.9); 8.26 ± 0.23 (31.5); 13.2 ± 0.1 (36.5).

The role of solvent electrostriction during these solvolysis reactions is also clearly demonstrated by the significantly negative values of ΔS^* and ΔV^*. Although there is no direct correlation between the actual magnitude of the latter two parameters,[9,18] they do exhibit the same sign and can be interpreted along the same line of arguments. The results in Table III also clearly show that the quantitative agreement of the ΔV^* values for the different solvents is considerably better than for the ΔS^* values.

In contrast to the very similar ΔV^* values found for the aquation of $M(NH_3)_5Cl^{2+}$ (see Introduction),[10-13] the results for the solvolysis of the corresponding triflate complexes exhibit a significant

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trend along the series of complexes in Table III. ΔV^* becomes significantly more negative on going from Co(III) to Cr(III). This means that there is an increase in the intrinsic bond formation contribution along tthe series. In all cases charge creation will result in an increase in electrostriction accompanied by a decrease in volume, which can be complemented by bond-formation processes or offset by bond breakage. In light of all the arguments mentioned earlier, this trend in ΔV^* can be interpreted in terms of a gradual changeover from I_d to I_a along the series. This means that bond breakage accompanied by significant charge creation accounts for the overall small negative value found for the Co(III) complex, whereas mainly bond formation in terms of an I_a mechanism can account for the negative ΔV^* reported for the Cr(III) and Rh(III) complexes. The observation that ΔV^* values are very similar for the aquation reactions of the chloro complexes on the one hand but significantly different for the solvolysis of the triflate complexes on the other hand must be related to the nature of the leaving group and the properties of the solvents employed. In this respect it is important to consider the influence of π-bonding and M–L bond lengths on the value of ΔV^*. Both of these parameters will be significantly different for Cl^- and $CF_3SO_3^-$. The M–L bond strength is significantly lower for $CF_3SO_3^-$ than for Cl^- as demonstrated by the significantly higher solvolysis rate constants found for the triflate complexes.[16] Similarly, these rate constants do not exhibit a strong dependence on the nature of the metal center (Tables I–III), reflecting the weakness of the M–L bond and the associated lability of the complexes. Thus, we expect π-bonding and the M–L bond lengths to be very similar for the investigated complexes, such that these ground-state effects cannot account for the observed trends in ΔV^*.

The partial molar volume of Cl^- is 21.8 compared to 80.4 cm^3 mol^{-1} for $CF_3SO_3^-$. This means that during bond breakage in terms of an I_d mechanism there will be a significantly larger increase in volume for the release of triflate than for chloride. This then results in the sufficiently more positive ΔV^* value reported here for the solvolysis of $Co(NH_3)_5OSO_2CF_3^{2+}$ as compared to the aquation of $Co(NH_3)_5Cl^{2+}$. On the other hand, the decrease in volume resulting from the increase in electrostriction during bond breakage will increase with increasing solvent polarity.[9,19] In this way we can further account for the more negative ΔV^* in H_2O as compared to CH_3CN and CH_3OH as solvent. We conclude from these arguments and the absolute magnitude of ΔV^* that the solvolysis reactions proceed according to an I_d mechanism for the Co(III) complex and an I_a mechanism for the Rh(III) and Cr(III) complexes, respectively. It is therefore quite understandable that ΔV^* becomes more positive with increasing partial molar volume of the leaving group in the case of the Co(III) complexes (ΔV^* increases from −10.6 to 4.0 cm^3 mol^{-1} along the series of leaving groups Cl^-, Br^-, NO_3, and NCS^-).[20] On the other hand, no such effect is observed for the Cr(III) complexes, where ΔV^* remains rather constant at approximately −10 cm^3 mol^{-1} in line with an I_a mechanism.

The trends in the rate constants and the thermal activation parameters (ΔH^* and ΔS^*) for the solvolysis reactions in Table III do not directly support the assigned mechanisms. For instance, in terms of an I_a mechanism, the Cr(III) reaction should be accelerated in CH_3OH, which is the better nucleophile, but according to the data this is not the case. Our earlier experience has shown that the rate data alone cannot give a clear mechanistic indication in the case of an interchange process.[9,13] This difficulty has in general led to the application of pressure as a mechanistic parameter.

At this point it is important to refer to possible effects caused by the nonparticipating ammine ligands. Increasing the steric hindrance on the metal center by introducing substituents on the amine ligand can have a meaningful influence on the substitution mechanism especially in cases where the crowding around the metal ion plays an important role. In this respect it is interesting to note that ΔV^* for the aquation of $Co(NH_2CH_3)_5L^{3+}$, where L = DMSO, DMF, and CH_3CN, is approximately +6 cm^3 mol^{-1}.[21] This slightly more positive value as compared to that for the pentaammine complexes merely reflects less participation of the incoming water molecule due to the increased steric crowding. A similar result was found for the aquation of the corresponding chloro complex: ΔV^* increases from −10.6 for the pentaammine to −2.3 cm^3 mol^{-1} for the pentakis(methylamine) complex,[22] which again underlines the importance of bond breakage on increasing the steric hindrance. In this respect there is no mechanistic changeover for the Co(III) complexes. However, in the case of the corresponding chloro complexes of Cr(III), ΔV^* also increases from −10.6 to +0.5 cm^3 mol^{-1} on going from the pentaammine to the pentakis(methylamine) complex.[22] It follows that an increase in steric hindrance can change the substitution mechanism on the Cr(III) center from I_a to I_d,[7,22] thus resulting in an I_d mechanism for the aquation of all $M(CH_3NH_2)_5Cl^{2+}$ complexes.[23,24] This is probably a unique example where steric crowding around the metal center can cause a changeover in mechanism and demonstrates the critical tuning of the molecular dynamics of octahedral complexes with the aid of steric hindrance.

We conclude that the aquation and solvolysis reactions of pentaamminemetal(III) complexes occur according to well-characterized interchange mechanisms. The important role played by the size of the metal center in controlling such interchange processes has been highlighted. The mechanistic changeover in going from Cr(III) to Co(III) along the first-row transition-metal elements can be reversed in going down the series from Co(III) to Rh(III). Increasing steric hindrance can force the Cr(III) complexes to change their mechanism, and it remains an open question whether the same effect can be achieved by increasing the steric hindrance on the Rh(III) or even the Ir(III) center. This study has demonstrated the feasibility of using pressure as a kinetic parameter and the important role played by solvent electrostriction in such substitution processes.

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Registry No. $[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 75522-50-8; $[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-57-9; $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-61-5; MeCN, 75-05-8; MeOH, 67-56-1.

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