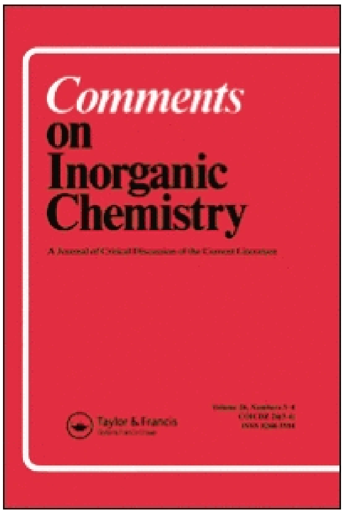

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Mechanistic Information from the Effect of Pressure on Thermal and Photochemical Substitution Reactions

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Mechanistic Information from the Effect of Pressure on Thermal and Photochemical Substitution Reactions

The effect of pressure on some typical thermal and photochemical substitution reactions is discussed to illustrate the general applicability of this method in the elucidation of reaction mechanisms. The selected examples include square planar solvolysis, octahedral complex formation, base hydrolysis and photosolvolysis reactions. A critical evaluation is given and general trends are discussed.

INTRODUCTION

Thermal and photochemical substitution reactions of inorganic and organometallic complexes are of fundamental interest since they often form the basis for catalytic, biological, environmental and energy related processes. The application of high pressure kinetic techniques in the elucidation of the underlying reaction mechanisms has received considerable attention in recent years.[1] This development is partly due to the more general availability of equipment that enables kinetic measurements in the milli-, micro- and nanosecond time range at pressures up to 300 MPa. Such equipment includes stopped-flow, temperature-jump, NMR and pulsed laser instrumentation. Furthermore, the determination of volumes of activation from the pressure dependence of rate constants, i.e. $\Delta V^{\ddagger} = -RT(\partial \ln k/\partial P)_T$, and combining such data with the partial molar volumes of reactant and product species, leads to the construction of a reaction volume profile, which is a pictorial view of

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the thermal or photochemical reaction on the basis of volume changes. This technique has been applied to almost all types of chemical reactions, and the mechanistic insight obtained in this way is quite remarkable. It does not only assist in the elucidation of the reaction mechanism, but also adds a further dimension to the kinetic parameters such that the suggested mechanism must also account for these effects.

In this contribution the effect of pressure on some typical thermal and photochemical substitution reactions will be discussed to illustrate the general ability of this technique to differentiate between various possible reaction mechanisms. A critical evaluation of this method, including a comparison with conventional kinetic parameters, will be given, and general trends will be discussed.

SUBSTITUTION MECHANISMS

Consider a substitution reaction of the type given in (1).

$$ML_nX + Y \longrightarrow ML_nY + X \qquad (1)$$

Such reactions are generally discussed in terms of a dissociative (D), interchange (I) or associative (A) mechanism, depending on the degree of bonding of X and Y in the transition state of the process. The pictorial view presented in Fig. 1 is useful to visualize the intimate nature of these mechanisms. If bond making is predominant, a significant decrease in molar volume of the reactants is expected (negative $\Delta V^\ddagger$), compared to a significant increase in volume for a dissociatively activated process (positive $\Delta V^\ddagger$). In the case of an interchange process, bond breakage and bond formation occur to varying degrees and small effects are expected, i.e., a slightly negative $\Delta V^\ddagger$ for I_a and a slightly positive $\Delta V^\ddagger$ for I_d. This interpretation is solely based on considering intrinsic volume contributions originating from changes in bond lengths and bond angles. Unfortunately, many substitution reactions are accompanied by changes in charge distribution, dipole moment and dipole–dipole interactions, such that volume changes due to electrostriction effects must also be considered. This so-called solva-

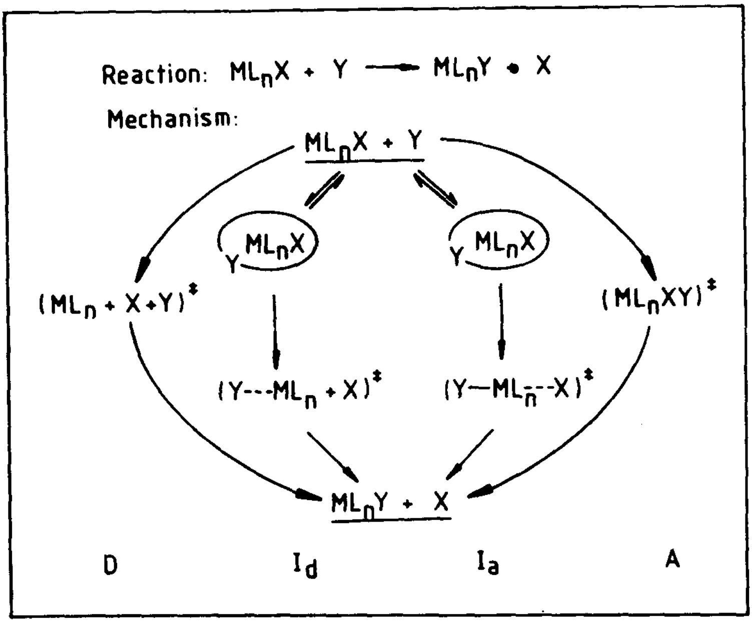


FIGURE 1 Pictorial view of the different types of substitution mechanisms.

tional contribution could in extreme cases even overrule the intrinsic effects. A pictorial presentation of $\Delta V^{\ddagger}_{\text{intr}}$ and $\Delta V^{\ddagger}_{\text{solv}}$ is given in Fig. 2. Much of the discussion of the interpretation of $\Delta V^{\ddagger}$ data therefore focuses on the actual contribution of $\Delta V^{\ddagger}_{\text{intr}}$, since this is the mechanistic indicator.[2]

SUBSTITUTION REACTIONS OF SQUARE-PLANAR COMPLEXES

In general, substitution reactions of square-planar complexes follow an associative mechanism, and only a few exemptions have been reported in the literature.[3] Steric effects, for instance, are argued to hinder the attack by the entering ligand and the system is forced into a dissociative reaction mode. A well-known example concerns the solvolysis reaction of *cis*-$Pt(PEt_3)_2$(mesityl)Br in methanol, which was reported to proceed according to a dissocia-

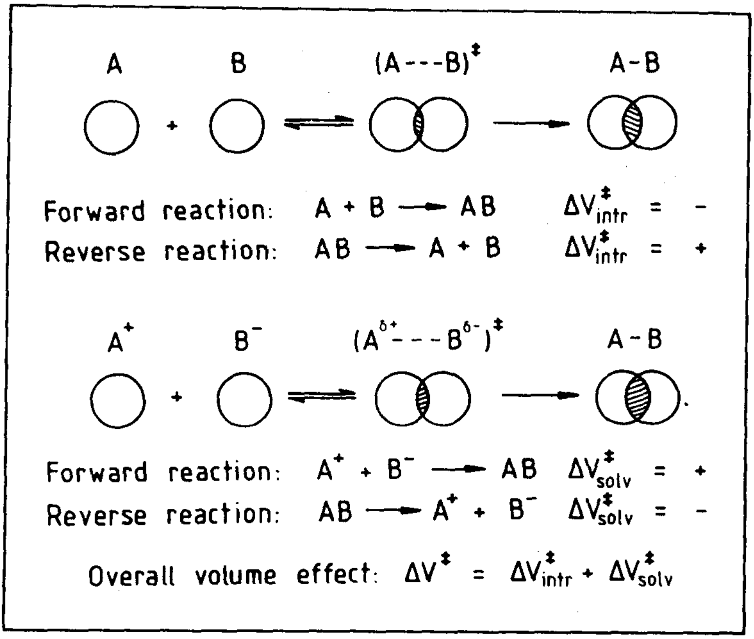
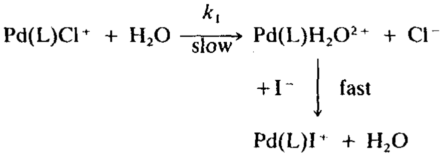


FIGURE 2 Pictorial presentation of $\Delta V^{\ddagger}_{\mathrm{intr}}$ and $\Delta V^{\ddagger}_{\mathrm{solv}}$.

tive mechanism.[4] However, the volume of activation for this reaction was found[5] to be -14.1 ± 0.5 cm^3 mol^{-1}, which clearly underlines the associative nature of the process. Solving such mechanistic discrepancies usually results in some disagreement in the literature.[6,7] Nevertheless, we have good reasons to believe that steric hindrance alone cannot induce a changeover in mechanism from associative to dissociative. This is very nicely demonstrated by the data in Table I.[8] The gradual increase in steric hindrance on the dien ligand is accompanied by a drastic decrease in the solvolysis rate constant (k_1) of up to five orders of magnitude. It is significantly more difficult for the water molecule to enter the coordination sphere as reflected by the gradual increase in $\Delta H^{\ddagger}$, but the mechanism remains associative throughout the series as seen from the fairly constant and negative values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$. The average volume of activation of -12 ± 2 cm^3 mol^{-1} is close to the maximum value expected for the associative entrance of a water molecule into the coordination sphere of an octahedral complex ion.[9] Moreover, $\Delta V^{\ddagger}$ is expected to mainly represent the

TABLE I

Kinetic parameters for the reaction



$$\begin{tikzcd}
\mathrm{Pd(L)Cl^{+} + H_2O} \arrow[r, "k_1", "\text{slow}"'] & \mathrm{Pd(L)H_2O^{2+} + Cl^{-}} \arrow[d, "+\mathrm{I}^{-}"', "\text{fast}"] \\
 & \mathrm{Pd(L)I^{+} + H_2O}
\end{tikzcd}$$

L[a]	k_1 at 25 °C s^{-1}	$\Delta H^‡$ kJ mol^{-1}	$\Delta S^‡$ J K^{-1} mol^{-1}	$\Delta V^‡$ at 25 °C cm^3 mol^{-1}
dien	43.8 ± 0.5	43 ± 3	−69 ± 12	−10.0 ± 0.6
1,4,7-Me_3dien	25.0 ± 4.2	38 ± 4	−87 ± 15	−9.2 ± 0.6
1,4,7-Et_3dien	10.0 ± 0.1	41 ± 5	−86 ± 18	−10.8 ± 1.0
1,1,7,7-Me_4dien	0.99 ± 0.02	49 ± 1	−79 ± 3	−13.4 ± 1.9
1,1,4-Et_3dien	0.77 ± 0.01	51 ± 1	−76 ± 3	−14.5 ± 1.2
1,1,4,7,7-Me_5dien	$(2.76 \pm 0.04) \times 10^{-1}$	50 ± 1	−88 ± 3	−10.9 ± 0.3
1,1,7,7-Et_4dien	$(2.1 \pm 0.4) \times 10^{-3}$	69 ± 2	−67 ± 8	−14.9 ± 0.2
4-Me-1,1,7,7-Et_4dien	$(6.8 \pm 0.1) \times 10^{-4}$	66 ± 7	−84 ± 25	−14.3 ± 0.6
1,1,4,7,7-Et_5dien	$(6.7 \pm 0.1) \times 10^{-4}$	59 ± 3	−106 ± 9	−12.8 ± 0.8

[a] dien = diethylenetriamine.

intrinsic component since major changes in electrostriction are not expected to occur during associative solvolysis.

It must, however, be kept in mind that solvolysis reactions as those in Table I could be accompanied by significant changes in dipole moment since the leaving group is a charged species. Recent measurements[10] on similar solvolysis reactions with NH_3 and py as leaving groups resulted in $\Delta V^‡$ values of between −3 and −4 cm^3 mol^{-1}. Furthermore, $\Delta V^‡$ for solvent exchange on $Pd(H_2O)_4^{2+}$ and $Pt(H_2O)_4^{2+}$ was found to be −2.2 and −4.6 cm^3 mol^{-1}, respectively.[11,12] It follows that the intrinsic component can in fact be so small and that the more negative values observed for charged leaving groups could be due to dipole effects. Further investigations to account for this apparent difference are presently underway. However, this will not affect the mechanistic interpretation referred to above.

We also investigated[13] a series of anation reactions of the type outlined in (2),

$$Pd(L)H_2O^{2+} + X^{-} \longrightarrow Pd(L)X^{+} + H_2O \qquad (2)$$

and found a good correlation between $\Delta V^\ddagger$ and the size of X^-, *viz.* more negative $\Delta V^\ddagger$ for larger X^-. In this case solvational changes due to charge neutralization definitely contribute towards $\Delta V^\ddagger$, although the overall value remains significantly negative. To exclude this complication, anation reactions with neutral entering ligands are presently being studied, and the preliminary results do underline the expected tendencies.

SUBSTITUTION REACTIONS OF OCTAHEDRAL COMPLEXES

High pressure techniques have been used to investigate numerous substitution reactions of octahedral complexes.[1] Two representative systems have been selected to illustrate the mechanistic discrimination ability of this technique, *viz.* solvent exchange and complex formation reactions of first-row transition-metal elements, and base hydrolysis reactions of pentaamminecobalt(III) complexes. These systems represent reactions where, on the one hand, mainly intrinsic volume changes occur and, on the other hand, large solvational changes contribute towards the observed $\Delta V^\ddagger$.

In a series of papers Merbach and co-workers[14] reported volumes of activation for solvent exchange reactions on divalent octahedral first-row transition-metal ions (Table II). The trend in the $\Delta V^\ddagger$ data was interpreted in terms of a gradual mechanistic changeover from I_a to I_d along these elements. This phenomenon is a property of the central metal ion rather than of the solvent. Up to then only a few pressure dependence studies of fast complex formation re-

TABLE II

$\Delta V^\ddagger$ for solvent exchange on MS_6^{2+} ions[a]

Solvent	V^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
H_2O	−4.1	−5.4	+3.8	+6.1	+7.2
CH_3OH		−5.0	+0.4	+8.9	+11.4
CH_3CN		−7.0	+3.0	+7.7	+9.6
DMF				+6.7	+9.1

[a] Data taken from Ref. 14.

actions of these metal ions had been reported, and the available data for Ni(II) and Co(II)[15] seemed to be in good agreement with the solvent exchange data (Table III). A crucial experiment was to measure $\Delta V^\ddagger$ for complex formation of Mn(II) to determine whether a similar changeover would be observed as in the case of solvent exchange reactions. The first data came from a high pressure temperature-jump study of the complex formation of Mn(II) with bipyridine,[16] which was later extended to complexation by terpyridine.[17] The presently available results (Table III) clearly demonstrate that $\Delta V^\ddagger$ for complex formation reactions parallel those for solvent exchange, and underline the earlier suggested changeover in mechanism along the first-row transition-metal ions. In some cases it was possible to measure $\Delta V^\ddagger$ for the reverse aquation process, which then enables the construction of a reaction volume profile (see the example in Fig. 3). Prior to this work nobody had ever seriously questioned the dissociative nature of such reactions, i.e., the traditional "Eigen–Wilkins" (or I_d) mechanism. However, the discussed $\Delta V^\ddagger$ data strongly supports an I_a substitution mechanism for the earlier members of the series. Such a mechanistic assignment could never have been made on the basis of entropy of activation data since these are usually not that reliable (see further discussion).

Volumes of activation and reaction volume profiles not only reveal significant mechanistic detail for relatively simple systems such as those described above, but also for more complicated processes. One of these concerns the base hydrolysis reactions of Co(III) complexes, which are generally accepted to proceed according to a S_NICB mechanism as outlined in (3).

$$\begin{aligned}
&\mathrm{Co(NH_3)_5X^{(3-n)+} + OH^- \overset{K}{\rightleftharpoons} Co(NH_3)_4(NH_2)X^{(2-n)+} + H_2O}\\
&\mathrm{Co(NH_3)_4(NH_2)X^{(2-n)+} \xrightarrow{k} Co(NH_3)_4NH_2^{2+} + X^{n-}}\\
&\mathrm{Co(NH_3)_4NH_2^{2+} + H_2O \xrightarrow{fast} Co(NH_3)_5OH^{2+}}
\end{aligned} \qquad (3)$$

The expected volume profile for this scheme is given in Fig. 4. The quantities $\Delta V^\ddagger_{exp}$ and $\Delta \overline{V}_0$ are expected to strongly depend on the nature of the leaving group, since charge creation occurs when

TABLE III

$\Delta V^{\ddagger}$ for complex formation of first-row transition-metal elements in aqueous solution

Entering Ligand	V^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Ref.
NH_3				+4.8 ± 0.7	+6.0 ± 0.3	15
pada[a]				+7.2 ± 0.2	+7.7 ± 0.3	15
2,2′-bipyridine		−1.2 ± 0.2[b]		+4.3 ± 1.0	+5.5 ± 0.3	18[d]
				+7.5 ± 1.4	+5.1 ± 0.4	18[e]
2,2′ : 6′,2″-terpyridine		−3.4 ± 0.7[c]	+3.4 ± 0.6	+4.5 ± 0.8	+6.7 ± 0.2	18[d]
			+3.7 ± 0.8	+3.7 ± 1.3	+4.5 ± 0.4	18[e]
SCN^-	−2.1 ± 0.8					19

[a] pada = pyridine-2-azo(p-dimethylaniline).

[b] Ref. 16.

[c] Ref. 17.

[d] Experimental conditions such that [L] >> [M].

[e] Experimental conditions such that [M] >> [L].

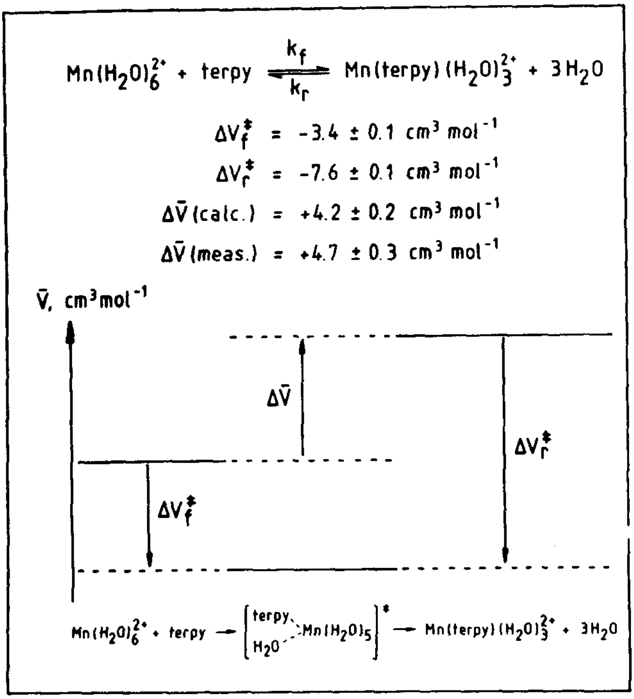


FIGURE 3 Typical example of a volume profile for a complex formation reaction.

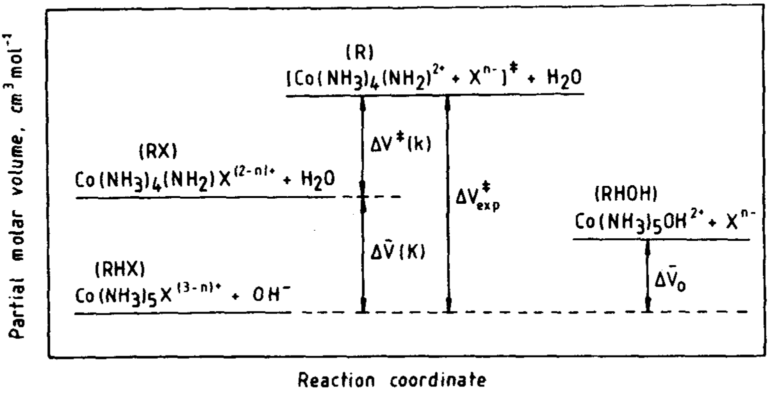


FIGURE 4 Volume profile for the base hydrolysis of $Co(NH_3)_5X^{(3-n)+}$ according to a S_NICB mechanism.

X is a charged species. We[20] measured these quantities for different X^{n-}, *viz.* F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-} and Me_2SO, and found $\Delta V^{\ddagger}_{\mathrm{exp}}$ values ranging from 22.2 ($X^{n-} = SO_4^{2-}$) to 40.2 ($X^{n-} = Me_2SO$) $cm^3\ mol^{-1}$ at 25 °C. Reaction volumes for neutralization reactions similar to the formation of a conjugate base species exhibit a similar tendency.[21]

More interesting, however, is the fact that if the suggested mechanism is really valid it should be possible to estimate the partial molar volume of the five-coordinate intermediate on the assumption that the rate-determining step has a late (product-like) transition state. Furthermore, this volume should be independent of the nature of X^{n-}. The adopted volume equations are given in (4) and the data are plotted in Fig. 5.

$$\begin{aligned} \Delta V^{\ddagger}_{\mathrm{exp}} &= \overline{V}_{\ddagger} + \overline{V}_{\mathrm{H_2O}} - \overline{V}_{\mathrm{RHX}} - \overline{V}_{\mathrm{OH}} \\ &\sim \overline{V}_{\mathrm{R}} + \overline{V}_{\mathrm{X}} + \overline{V}_{\mathrm{H_2O}} - \overline{V}_{\mathrm{RHX}} - \overline{V}_{\mathrm{OH}} \\ \therefore \Delta V^{\ddagger}_{\mathrm{exp}} + \overline{V}_{\mathrm{RHX}} &= \overline{V}_{\mathrm{R}} + \overline{V}_{\mathrm{H_2O}} - \overline{V}_{\mathrm{OH}} + \overline{V}_{\mathrm{X}} \end{aligned} \tag{4}$$

A plot of $\Delta V^{\ddagger}_{\mathrm{exp}} + \overline{V}_{\mathrm{RHX}}$ versus $\overline{V}_{\mathrm{X}}$ (see Fig. 4 for notations) should be linear with unity slope and an intercept corresponding to $\overline{V}_{\mathrm{R}} + \overline{V}_{\mathrm{H_2O}} - \overline{V}_{\mathrm{OH}} = \overline{V}_{\mathrm{R}} + 17.5$. It follows that $\overline{V}_{\mathrm{R}}$ has an average value[20] of 71 ± 4 $cm^3\ mol^{-1}$, which is remarkably close to the value of 68 $cm^3\ mol^{-1}$ estimated for the six-coordinate $Co(NH_3)_5OH^{2+}$ species. It was concluded that these five- and six-coordinate species of similar charge have approximately the same molar volume.

A further interesting point is the fact that $\Delta V^{\ddagger}_{\mathrm{exp}} - \Delta\overline{V}_0$ should also be independent of the nature of X^{n-} since it only involves the reaction of H_2O with $Co(NH_3)_4NH_2^{2+}$ to produce $Co(NH_3)_5OH^{2+}$. This difference is indeed constant[20] and has an average value of 20 ± 2 $cm^3\ mol^{-1}$, which almost equals the molar volume of water, demonstrating that the water molecule is completely absorbed by the five-coordinate intermediate. This is also in agreement with the observation that the partial molar volumes of

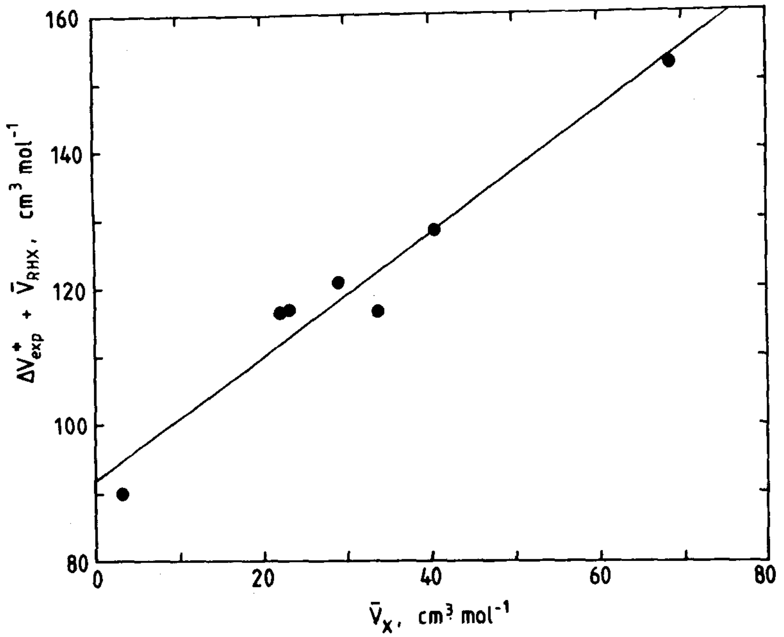
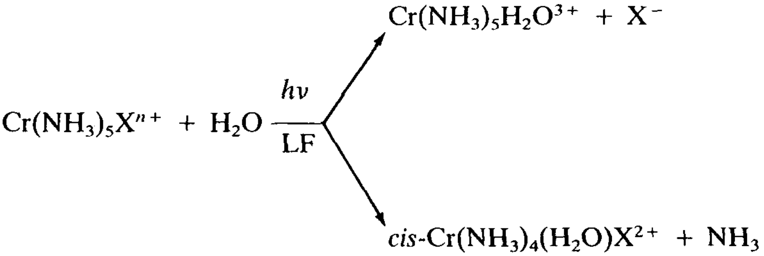


FIGURE 5 Plot of $\Delta V^{\ddagger}_{exp} + \overline{V}_{RHX}$ versus $\overline{V}_X$ according to Eq. (4).

$Co(NH_3)_4NH_2^{2+}$ and $Co(NH_3)_5OH^{2+}$ are almost similar. Recent measurements[22] on related systems of the type *cis*- and *trans*-$Co(NH_3)_4(NH_2R)Cl^{2+}$, where R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9 and *i*-C_4H_9, show exactly the same tendencies as those described above. The partial molar volume of the five-coordinate intermediate also equals that of the hydroxo product, and both quantities increase linearly with increasing size of R. The equality of partial molar volumes for five- and six-coordinate species will only hold for systems in which the sixth ligand is small like NH_3 or H_2O. In the case of larger ligands that cannot be fully accommodated by the sphere of the five-coordinate species, an increase in partial molar volume is bound to show up, similar to the correlation mentioned above. It follows that the volume profile in Fig. 4 presents an accurate and realistic description of the underlying reaction mechanism.

In general, ligand field photolysis of Cr(III) and Rh(III) ammine complexes leads to the formation of solvolysis products. These substitution reactions, occurring from an electronic excited state, proceed via a transition state which can be visualized in a similar way as for thermal substitution reactions. Since so little is known about the reaction mode of such excited state species, it is of fundamental interest to develop a method to analyze the molecular nature of such reactions. In this respect the pressure dependence of the photochemical reaction step could reveal the intimate nature of the ligand substitution process. It must, however, be kept in mind that we are dealing with excited state species, and the interpretation of such data can be expected to be more complicated than for ground state species. Nevertheless, the results are very promising and worth including in this Comment.

Ligand field photolysis of Cr(III) ammine complexes occurs according to the reactions given in (5).

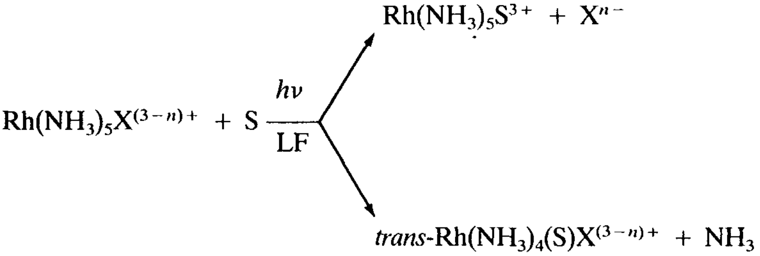


$$\mathrm{Cr(NH_3)_5X}^{n+} + \mathrm{H_2O} \xrightarrow[\mathrm{LF}]{h\nu} \begin{cases} \mathrm{Cr(NH_3)_5H_2O}^{3+} + \mathrm{X}^- \\ cis\text{-}\mathrm{Cr(NH_3)_4(H_2O)X}^{2+} + \mathrm{NH_3} \end{cases}$$

$(n = 2\text{: X} = \text{Cl, Br, NCS};\ n = 3\text{: X} = \mathrm{NH_3})$ (5)

The two photoreactions are thought to occur via different electronic excited states, their exact nature still being discussed in the literature. The pressure dependence of the photoaquation quantum yields[23] resulted in significantly negative volumes of activation, *viz.* an average value of -6 cm^3 mol^{-1} for aquation of NH_3, and between -10 and -13 cm^3 mol^{-1} for aquation of X^-. Since very little is known about the pressure dependence of the other deactivation processes, it was assumed that the apparent volumes of activation mainly represent that for the primary photochemical reaction. The results were interpreted[23] in terms of an I_a mechanism, the more negative values for aquation of X^- being ascribed to a solvational contribution originating from partial charge separation in the transition state.

Significantly more progress was made in studying the photosolvolysis reactions of Rh(III) ammine complexes[24-27] outlined in (6).



$$\mathrm{Rh(NH_3)_5X^{(3-n)+}} + \mathrm{S} \xrightarrow[\mathrm{LF}]{h\nu} \begin{cases} \mathrm{Rh(NH_3)_5S^{3+}} + \mathrm{X}^{n-} \\ trans\text{-}\mathrm{Rh(NH_3)_4(S)X^{(3-n)+}} + \mathrm{NH_3} \end{cases}$$

(S = solvent) (6)

Earlier studies by Ford and co-workers (see literature cited in Ref. 24) indicated that ligand field photolysis can be presented by the Jablonski diagram given in Fig. 6. The lowest energy excited state is a ligand field triplet state from which the primary photoreaction (k_p), nonradiative (k_n) and radiative deactivation (k_r) occur. Since $\phi_{ISC} \simeq 1$ and $k_r << (k_n + k_p)$, the expression for ϕ can be simplified as shown in (7).

$$\phi = \phi_{ISC} \frac{k_p}{k_p + k_n + k_r}$$

$$\simeq \frac{k_p}{k_p + k_n} = k_p \tau \qquad (7)$$

The pressure dependence of both ϕ and the lifetime (τ) of the excited state were measured,[24,27] such that the volume of activation for the primary photoreaction can be calculated using (8).

$$\Delta V_p^\ddagger = \Delta V_\phi^\ddagger + \Delta V_{\tau^{-1}}^\ddagger \qquad (8)$$

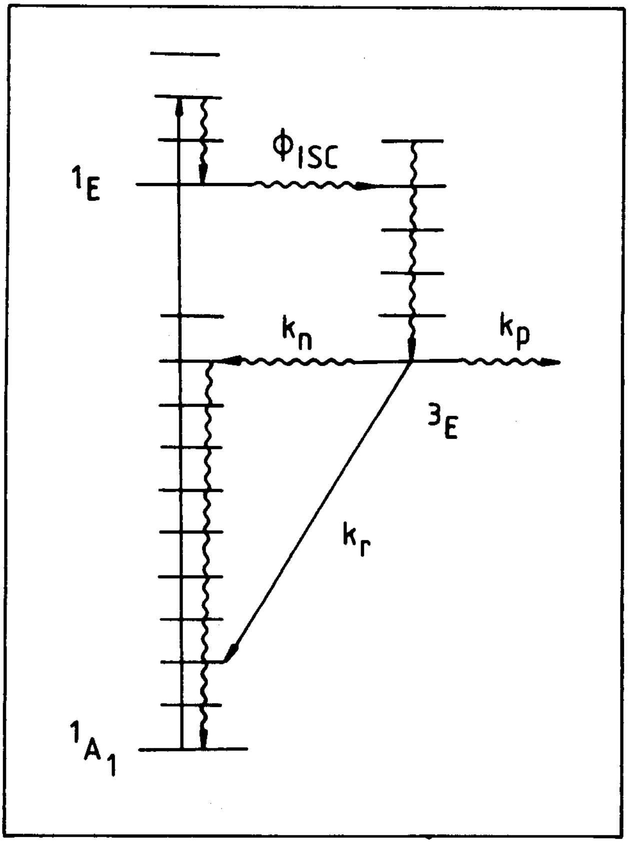


FIGURE 6 Jablonski diagram for the ligand-field photolysis of Rh(III) ammine complexes.

A typical example of the photosolvolysis quantum yield as a function of pressure is given in Fig. 7. Furthermore, the volume of activation for the nonradiative deactivation process can also be obtained from this data using Eq. (9).

$$\Delta V^{\ddagger}_{n} = \Delta V^{\ddagger}_{\tau^{-1}} - \frac{\phi_1 \Delta V^{\ddagger}_{\phi_1} + \phi_2 \Delta V^{\ddagger}_{\phi_2}}{1 - \phi_1 - \phi_2} \tag{9}$$

These measurements were performed for different leaving groups X^{n-} [24–26] and solvents.[27] The results, summarized in Table IV, reveal some important and consistent tendencies.

The nonradiative deactivation process exhibits a rather small pressure dependence, such that earlier assumptions regarding this step are now justified. Throughout the series of pentaammine complexes the solvolysis of NH_3 is accompanied by a positive $\Delta V_p^\ddagger$ value, whereas the solvolysis of X^{n-} exhibits negative values for $\Delta V_p^\ddagger$ (see Fig. 7 and Table IV). This remarkable difference also shows up in the other investigated solvents. The interpretation of the data for the solvolysis of NH_3 is rather straightforward since the positive volumes of activation clearly underline the dissociative

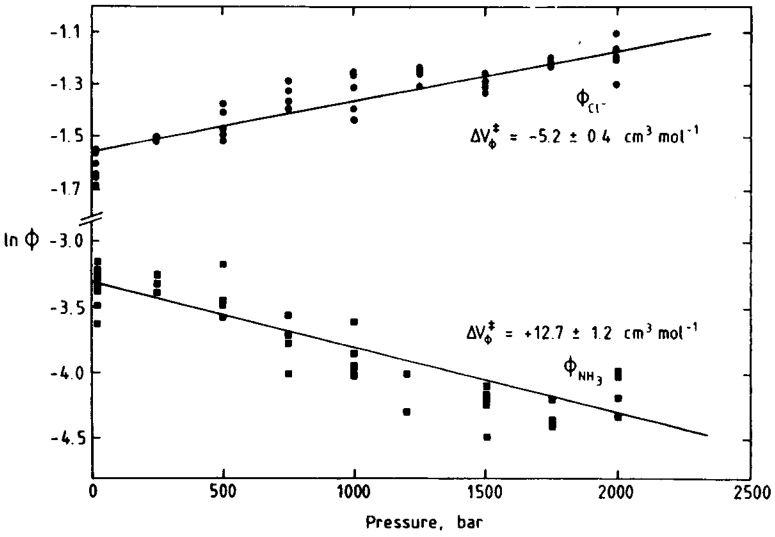
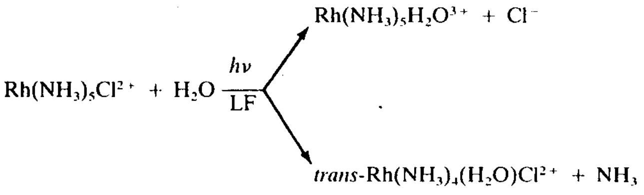


FIGURE 7 Pressure dependence of the reaction



$$Rh(NH_3)_5Cl^{2+} + H_2O \xrightarrow[LF]{h\nu} \begin{cases} Rh(NH_3)_5H_2O^{3+} + Cl^- \\ \textit{trans}\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} + NH_3 \end{cases}$$

TABLE IV

Volumes of activation from photochemical and photophysical measurements on the photosolvolysis reactions of Rh(III) ammine complexes at 25 °C

Solvent	Complex	Photosolvolysis Product	$\Delta V^\ddagger_\Phi$	$\Delta V^\ddagger_{\tau^{-1}}$	$\Delta V^\ddagger_p$	$\Delta V^\ddagger_n$	Ref.
H_2O	$Rh(NH_3)_5Cl^{2+}$	$Rh(NH_3)_5H_2O^{3+}$	-5.2 ± 0.4	(-3.4)[a]	-8.6 ± 1.6	(-2.6)[a]	24
		trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	$+12.7 \pm 1.2$		$+9.3 \pm 1.9$		
D_2O	$Rh(ND_3)_5Cl^{2+}$	$Rh(ND_3)_5D_2O^{3+}$	-4.2 ± 0.5	-3.5 ± 1.1	-7.7 ± 1.6	-2.6 ± 1.0	24
		trans-$Rh(ND_3)_4(D_2O)Cl^{2+}$	$+9.5 \pm 1.6$		$+6.0 \pm 2.2$		
H_2O	$Rh(NH_3)_5Br^{2+}$	$Rh(NH_3)_5H_2O^{3+}$	-10.3 ± 1.2	$(+3.5)$[a]	-6.8 ± 1.6	$(+2.5)$[a]	24
		trans-$Rh(NH_3)_4(H_2O)Br^{2+}$	$+4.6 \pm 0.6$		$+8.1 \pm 1.2$		
D_2O	$Rh(ND_3)_5Br^{2+}$	$Rh(ND_3)_5D_2O^{3+}$	-9.4 ± 1.5	$+4.1 \pm 0.6$	-5.3 ± 1.8	$+2.5 \pm 1.2$	24
		trans-$Rh(ND_3)_4(D_2O)Br^{2+}$	$+3.4 \pm 0.5$		$+7.5 \pm 1.1$		
H_2O	*trans*-$Rh(NH_3)_4Cl_2^+$	*trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$	$+2.5 \pm 0.5$	b	$+2.8 \pm 0.6$	~0[a]	25
H_2O	*trans*-$Rh(NH_3)_4Br_2^+$	*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	$+3.4 \pm 0.7$	b	$+2.9 \pm 0.7$	~0[a]	25
H_2O	$Rh(NH_3)_6^{3+}$	$Rh(NH_3)_5H_2O^{3+}$	$+3.7 \pm 0.5$	b	$+3.9 \pm 0.5$	~0[a]	26
H_2O	$Rh(NH_3)_5I^{2+}$	*trans*-$Rh(NH_3)_4(H_2O)I^{2+}$	$+0.3 \pm 0.1$	b	$+1.4 \pm 0.9$	~0[a]	26
H_2O	$Rh(NH_3)_5SO_4^+$	$Rh(NH_3)_5H_2O^{3+}$	-2.7 ± 0.4	b	-3.9 ± 0.6	~0[a]	26
FMA	$Rh(NH_3)_5Cl^{2+}$	$Rh(NH_3)_5FMA^{3+}$	-4.6 ± 0.7	-0.3 ± 0.4	-4.9 ± 1.1	$+0.2 \pm 0.5$	27
		trans-$Rh(NH_3)_4(FMA)Cl^{2+}$	$+4.2 \pm 0.9$		$+3.9 \pm 1.3$		
DMF	$Rh(NH_3)_5Cl^{2+}$	*trans*-$Rh(NH_3)_4(DMF)Cl^{2+}$	$+6.3 \pm 0.9$	$+1.3 \pm 0.2$	$+7.6 \pm 1.1$	$+0.7 \pm 0.3$	27
Me_2SO	$Rh(NH_3)_5Cl^{2+}$	$Rh(NH_3)_5Me_2SO^{3+}$	-7.8 ± 1.8	-1 ± 1	-8.9 ± 2.7	-1 ± 1	27
		trans-$Rh(NH_3)_4(Me_2SO)Cl^{2+}$	$+4.4 \pm 0.9$		$+3.3 \pm 1.8$		

[a] Assumed value—see reference.

[b] Not measured—see discussion.

nature of the process. The relatively low values may be due to a parallel decrease in volume of the excited state on going to the transition state.[24] However, the negative volumes of activation for the solvolysis of X^{n-} can either be due to an associative attack by the solvent molecule, or dissociative release of X^{n-} accompanied by a large negative contribution from electrostriction due to charge creation. The latter interpretation is also in line with more positive values of $\Delta V_p^\ddagger$ for aquation of *trans*-$Rh(NH_3)_4X_2^+$ (X = Cl, Br), since electrostriction is expected to be smaller than in the case of the pentaammine complexes, *viz.* 1+ going to 2+ and 1−, compared to $(3 - n)+$ going to 3+ and $n-$.

The cited results demonstrate the ability of this technique to obtain mechanistic information on ligand field photochemical processes. The method can equally well be applied to study charge transfer photochemistry as illustrated by some recent studies performed in our laboratories.[28-30] These studies present the first efforts to understand the chemical dynamics of such excited state species.

CONCLUDING REMARKS

The correlation between $\Delta V^\ddagger$ and $\Delta S^\ddagger$ for a particular series of reactions has been referred to by different investigators.[2,31,32] For example the data in Table I would fit in with such a correlation for square-planar substitution reactions. However, there is no thermodynamic equation that links $\Delta V^\ddagger$ and $\Delta S^\ddagger$ directly, and it could be rather misleading to use such a generalized correlation to interpret the observed data. There are numerous examples where no such correlation exists and where $\Delta V^\ddagger$ and $\Delta S^\ddagger$ have opposite signs.[1,2,33] Furthermore, $\Delta S^\ddagger$ data are usually subjected to large error limits since they are determined via an extrapolation to $1/T \rightarrow 0$. In contrast, $\Delta V^\ddagger$ can usually be determined fairly accurately since it is estimated from the slope of a plot, similar to $\Delta V^\ddagger$. In addition, the interpretation of $\Delta V^\ddagger$ offers a pictorial presentation of the chemical process on a volume basis, which usually simplifies the mechanistic interpretation. The occurrence of large solvational contributions does complicate the interpretation of $\Delta V^\ddagger$ and additional measurements in other solvents or for differently charged species are usually required to enable a definite interpretation of the data.

A major advantage of $\Delta V^{\ddagger}$ data is the ability to solve mechanistic discrepancies and to provide information on the size (volume) of intermediate and/or transition state species. This is not only true for the discussed substitution reactions, but for almost any type of reaction. In some instances good correlations with theoretically expected values are found. Our more recent activities focus on the substitution behavior of organometallic species, especially those in which neutral ligands of low oxidation state metal complexes are substituted thermally and photochemically, and mainly intrinsic volume changes are observed.

As kineticists it is our goal to understand the intimate mechanism of a chemical reaction. High pressure kinetic data adds an additional dimension to the information obtained from conventional kinetic data measured at ambient pressure. It has almost become a necessity for the realistic assignment of the underlying reaction mechanism.

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