

Leaving-Group Effects on Volumes of Activation for Dissociative Substitution Processes

Robert B. Jordan

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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A common, simplified picture for the rate-controlling step of a dissociative substitution reaction is shown in Figure 1(a). This picture has led to some unfulfilled expectations about activation volumes that this communication attempts to clarify.

With the assumption that the intermediate $\{ML_5\}$ in the dissociative process is close in structure to the transition state, the activation volume is given by eq 1.

$$\Delta V^* = \bar{V}^\circ(\{ML_5\}) + \bar{V}^\circ(Y) - \bar{V}^\circ(ML_5Y) \quad (1)$$

From Figure 1(a), it appears that ΔV^* should correlate with $\bar{V}^\circ(Y)$, on the basis of the implicit assumption that there is a fairly constant difference in partial molar volume between ML_5Y and $\{ML_5\}$. However, it is often observed^{1–6} that the activation volume is largely independent of $\bar{V}^\circ(Y)$, even in cases^{1–4} where other evidence strongly indicates a dissociative mechanism. This result has led to some perplexed comments from the observers.⁷

However, the visual concept in Figure 1(a) is probably not realistic for many systems. A better representation may be that, in Figure 1(b), where the leaving group (Y) is viewed as a cone with a volume component \bar{V}_b° extending beyond the spherical volume \bar{V}_s° , defined by the nonreacting ligands. In this representation, the partial molar volume of the reactant is $\bar{V}^\circ(ML_5Y) = \bar{V}_s^\circ + \bar{V}_b^\circ$ and that of the leaving group is $\bar{V}^\circ(Y) = \bar{V}_a^\circ + \bar{V}_b^\circ$.

The difference between Figure 1(a) and Figure 1(b) is that (a) implies that $\bar{V}^\circ(ML_5Y)$ is independent of $\bar{V}^\circ(Y)$, while (b) implies that $\bar{V}^\circ(ML_5Y)$ will change with Y because \bar{V}_b° will change. From Figure 1(b) one can deduce eq 2, which predicts

$$\bar{V}^\circ(ML_5Y) = \bar{V}_s^\circ + \bar{V}_b^\circ = \bar{V}_s^\circ - \bar{V}_a^\circ + \bar{V}^\circ(Y) \quad (2)$$

a linear plot of $\bar{V}^\circ(ML_5Y)$ versus $\bar{V}^\circ(Y)$ because $\bar{V}_s^\circ - \bar{V}_a^\circ$ is constant for a particular ML_5 system.

This prediction is confirmed in Figure 2 for a wide range of neutral Y ligands for $Co(NH_3)_5Y^{3+}$ and $Cr(NH_3)_5Y^{3+}$ complexes. It is further shown in Figure 2 that the more limited set of values for anionic Y^- ligands also fit eq 2. The variation of the intercepts ($\bar{V}_s^\circ - \bar{V}_a^\circ$) in Figure 2 can be attributed to the effect of solvent electrostriction which will make \bar{V}_s° larger for 2+ than for 3+ ions. Although \bar{V}_a° also will increase with \bar{V}_s° according to Figure 1(b), one can estimate for a 6-coordinate

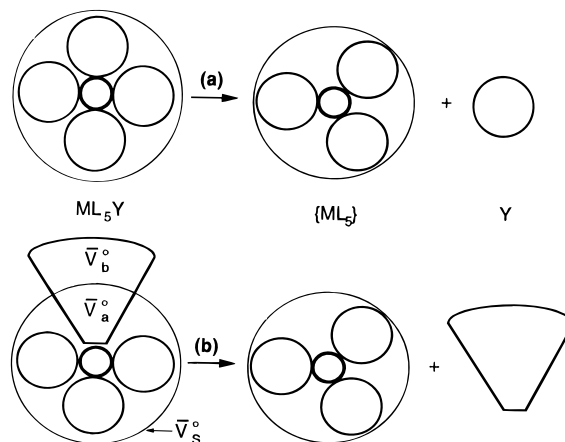


Figure 1. Two representations of the partial molar volume changes during dissociation of an ML_5Y complex to form $\{ML_5\} + Y$, shown in two dimensions for clarity, with the omission of the two nonreacting L ligands above and below the plane.

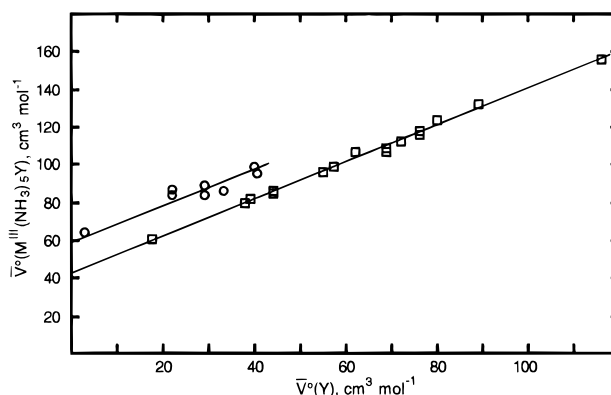


Figure 2. Variation of the partial molar volume of $M^{III}(NH_3)_5Y$ ($M = Co, Cr$) complexes with the partial molar volume of Y: \circ , anionic Y^- ; \square , neutral Y^0 .

complex that $\bar{V}_a^\circ \approx \bar{V}_s^\circ/6$, so that $\bar{V}_s^\circ - \bar{V}_a^\circ \approx 5\bar{V}_s^\circ/6$ and the intercept should increase with decreasing charge on the reactant as observed.

The correlation in Figure 2 was noted previously by Lawrance⁶ for cobalt(III) pentaammines, but the structural implication was not discussed. Instead, Lawrance and others^{4,6} focused on the rearranged version of eq 1, given by eq 3. This equation predicts

$$\bar{V}^\circ(ML_5Y) + \Delta V^* = \bar{V}^\circ(\{ML_5\}) + \bar{V}^\circ(Y) \quad (3)$$

that a plot of $\Delta V^* + \bar{V}^\circ(ML_5Y)$ versus $\bar{V}^\circ(Y)$ should be linear. However it was not emphasized that ΔV^* is essentially constant, and the plot is effectively one of $\bar{V}^\circ(ML_5Y)$ versus $\bar{V}^\circ(Y)$. The intercept of such plots is predicted to be $\bar{V}^\circ(\{ML_5\})$. It was recognized in the earlier work that this intercept was different for the $Co(NH_3)_5Y^{3+}$ and $Co(NH_3)_5Y^{2+}$ systems, with the implication that the partial molar volume of the $\{Co(NH_3)_5^{3+}\}$ intermediate depends on the charge of the leaving group. This would be inconsistent with a purely dissociative mechanism. This change of intercept seems to be more naturally accounted

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- Sample comments follow: from ref 1, the effect "calls for more detailed discussion" and "means that the extent of bond breakage in the transition state may vary with the nature of the leaving group"; from ref 2, "the reasons for the observed pattern will require more experimental results"; from ref 6b, "perhaps the covalent radius of the bonded atom alone is important in defining the volume change".

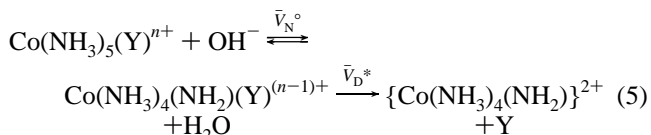
for in terms of the charge/electrostriction effect on \bar{V}_S° described in the preceding paragraph.

Substitution for $\bar{V}^\circ(\text{ML}_5\text{Y})$ from eq 2 into eq 3 gives eq 4, which predicts that ΔV^* should be independent of $\bar{V}^\circ(\text{Y})$ for a given ML_5 system for which \bar{V}_S° and \bar{V}_a° would be constant.

$$\Delta V^* = \bar{V}^\circ(\{\text{ML}_5\}) - (\bar{V}_S^\circ - \bar{V}_a^\circ) \quad (4)$$

Several systems that are believed to have a dissociative mechanism appear to conform to eq 4. For example, the ΔV^* values for substitution reactions of a series of $\text{Fe}(\text{CN})_5(\text{Y})^{3-}$ (Y = amine, substituted pyridine, and substituted pyrazine ligands) complexes^{1,2} are independent of the volume of Y when the latter changes from 25 to >100 $\text{cm}^3 \text{mol}^{-1}$. The substitution of L by 1-methylimidazole in $\text{Cr}^{\text{III}}(\text{TPP})(\text{Cl})(\text{L})$ in toluene⁸ has relatively constant ΔV^* values of 25.7, 23.8, and 19.6 $\text{cm}^3 \text{mol}^{-1}$ for L = pyridine, quinoline, and PPh_3 , respectively.

One of the most studied dissociative reactions is the base hydrolysis of $\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{Y})$ complexes for which ΔV^* is $\sim 42 \text{ cm}^3 \text{mol}^{-1}$ for neutral Y (DMSO, DMA) and $\sim 32 \text{ cm}^3 \text{mol}^{-1}$ for anionic Y (Cl^- , Br^- , I^- , NO_3^-). This reaction is believed to proceed by the dissociative conjugate base mechanism, through the initial stages shown in eq 5. For this mechanism,



$\Delta V^* = \Delta \bar{V}_N^\circ + \Delta \bar{V}_D^*$, and $\Delta \bar{V}_N^\circ$ can be estimated from the empirical equation developed by van Eldik and co-workers^{4,9} as 27 and 22 $\text{cm}^3 \text{mol}^{-1}$ for neutral and monoanionic Y, respectively. Then $\Delta \bar{V}_D^*$ should follow eq 4, and $\bar{V}_S^\circ - \Delta \bar{V}_a^\circ$ can be estimated as 58 $\text{cm}^3 \text{mol}^{-1}$ for neutral Y (from intercept of Figure 2 for 2+ complexes since the conjugate base has 2+ charge) and 69 $\text{cm}^3 \text{mol}^{-1}$ for monoanionic Y (assuming \bar{V}° for $\text{Co}(\text{NH}_3)_5\text{SO}_4^+$ follows eq 2). Then $\bar{V}^\circ(\{\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}\})$ is estimated to be 73 and 79 $\text{cm}^3 \text{mol}^{-1}$ from the neutral and anionic systems, respectively, in satisfactory agreement with previous estimates⁴ of $74.4 \pm 3.4 \text{ cm}^3 \text{mol}^{-1}$.

The mechanism for the aquation of $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Y}$ complexes is less well established but seems to be I_d . It is noteworthy that the ΔV^* for aquation of a number of the complexes with neutral leaving groups is nearly constant ($2 \pm 2 \text{ cm}^3 \text{mol}^{-1}$) and independent of $\bar{V}^\circ(\text{Y})$. For anionic Y, Jones et al.¹⁰ originally suggested a correlation of ΔV^* and ΔV° for the reaction, but subsequent volume measurements indicate that Y = NCS^- would not fit this correlation, and it may be more realistic to say that these ΔV^* values are also constant at $-7 \pm 3 \text{ cm}^3 \text{mol}^{-1}$. For Y = SO_4^{2-} , $\Delta V^* = -17 \text{ cm}^3 \text{mol}^{-1}$ continues the pattern of variation of ΔV^* with charge observed for base hydrolysis. From eq 4 and the values of $\bar{V}_S^\circ - \bar{V}_a^\circ$ for various charges used above, one can assume a dissociative mechanism

and calculate values for $\bar{V}^\circ(\{\text{Co}(\text{NH}_3)_5^{3+}\})$ of 44, 51, and 52 $\text{cm}^3 \text{mol}^{-1}$ for Y^0 , Y^- , and Y^{2-} , respectively. The same calculation for $\text{Cr}^{\text{III}}(\text{NH}_3)_5\text{Y}$ (with ΔV^* of ~ -5 and $-7 \text{ cm}^3 \text{mol}^{-1}$ for Y^0 and Y^- , respectively) gives $\bar{V}^\circ(\{\text{Cr}(\text{NH}_3)_5^{3+}\})$ of 37 and 51 $\text{cm}^3 \text{mol}^{-1}$, respectively. These estimates indicate that, for cobalt(III) and chromium(III), ΔV^* is ~ 7 and 14 $\text{cm}^3 \text{mol}^{-1}$, respectively, more negative for the Y^0 systems than expected for the Y^- and Y^{2-} complexes. The implications are that the $\text{M}(\text{NH}_3)_5\text{Y}^{3+}$ complexes have more associative character than their lower charged analogues and that the Co(III) and Cr(III) systems are aquating by similar mechanisms, as argued previously by Lay¹¹ from structural, ΔH^* , and ΔS^* information.

The relatively constant value of $\bar{V}^\circ(\{\text{M}(\text{NH}_3)_5^{3+}\}) = 51 \text{ cm}^3 \text{mol}^{-1}$ for Y^- and Y^{2-} might be taken as evidence for essentially dissociative behavior for these systems. However, the results in Figure 2 imply that $\bar{V}^\circ(\{\text{M}(\text{NH}_3)_5^{3+}\})$ might be $\sim 16 \text{ cm}^3 \text{mol}^{-1}$ smaller than $\bar{V}^\circ(\{\text{M}(\text{NH}_3)_4\text{NH}_2^{2+}\})$, so that $\bar{V}^\circ(\{\text{M}(\text{NH}_3)_5^{3+}\}) \approx 60 \text{ cm}^3 \text{mol}^{-1}$ is predicted for dissociative activation. The smaller value of 51 $\text{cm}^3 \text{mol}^{-1}$ implies that an interchange mechanism is a more appropriate assignment.

There have been a number of studies^{3,12-15} in which the nonreacting NH_3 is replaced by NH_2CH_3 with the apparent expectation that increased steric interactions will promote more dissociative behavior that will be evidenced by a more positive ΔV^* . Although Lay¹¹ has argued that the kinetic effect of NH_2CH_3 is due to solvation, $\text{M}^{\text{III}}(\text{NH}_2\text{CH}_3)_5$ systems typically do show a 0–7 $\text{cm}^3 \text{mol}^{-1}$ more positive ΔV^* than their $\text{M}^{\text{III}}(\text{NH}_3)_5$ analogues. The only exception¹³ is the base hydrolysis of $\text{Cr}(\text{NH}_2\text{CH}_3)_5\text{Cl}^{2+}$, for which $\Delta V^* = 34.8 \text{ cm}^3 \text{mol}^{-1}$, compared to 17.0 $\text{cm}^3 \text{mol}^{-1}$ for $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$. However, if one allows for the nonlinearity of the $\ln(k)$ versus P plot by including a P^2 term,¹⁶ then $\Delta V_0^* = 20.1 \pm 2 \text{ cm}^3 \text{mol}^{-1}$ for $\text{Cr}(\text{NH}_2\text{CH}_3)_5\text{Cl}^{2+}$. If the $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ results are corrected for aquation,¹⁷ then $\Delta V^* = 22.2 \pm 2 \text{ cm}^3 \text{mol}^{-1}$. These reanalyses make the small difference in ΔV^* between the NH_2CH_3 and NH_3 systems consistent with the others and emphasize that ΔV^* values may not be as firm as they appear. The revised ΔV^* for base hydrolysis of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ is identical to that for the iodo complex, thus removing any hint of a leaving-group effect on ΔV^* , just as observed with Co(III). It also removes the previously noted anomaly¹² that ΔV^* was smaller than $\Delta \bar{V}_N^\circ$.

Supporting Information Available: Table of partial molar, net reaction, and activation volumes with references to original sources (3 pages). Ordering information is given on any current masthead page.

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 (17) The data from ref 13 at $\mu = 1.0 \text{ M}$ were corrected using the aquation rate constant at $\mu = 1.0 \text{ M}$ from Rogers and Staples [Rogers, A.; Staples, P. J. *J. Chem. Soc.* **1965**, 6834] and the pressure dependence at $\mu = 0.1 \text{ M}$ from Guastalla and Swaddle [Guastalla, G.; Swaddle, T. W. *Can. J. Chem.* **1973**, 51, 821]. The correction changes from 4% to 17% as the pressure is increased because of the opposite pressure dependencies of aquation and base hydrolysis.