

Correlation of Volumes and Entropies of Activation for Racemization and Isomerization Reactions of Octahedral Metal Complexes: Evidence for a Twist Mechanism

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The application of the volume of activation (ΔV^\ddagger) determined from the pressure dependence of the reaction rates in solution to the elucidation of the reactions of metal complexes has been reviewed previously [1, 2]. Since ΔV^\ddagger is related to the difference between the partial molar volumes of initial and transition states, it has found application as a criterion for distinguishing between possible mechanisms through a comparison of experimental values with those predicted using simple volume models of the transition and precursor state for a particular mechanism. For reactions involving exchange of neutral ligands, it has been argued [1, 2] that associative mechanisms characteristically exhibit negative ΔV^\ddagger values and dissociative mechanisms positive ΔV^\ddagger values. In the case of racemization and isomerization reactions, twisting mechanisms offer an important alternative mechanism, and these have been argued to exhibit approximately zero ΔV^\ddagger values [3].

The experimental activation volume may be a composite of several contributions, and interpretation in terms of intrinsic volume changes in forming the transition state is often complicated by contributions from variation in solvent electrostriction [2]. This can be particularly important for reactions assumed to involve motion of charged ligands, where electrostrictive effects can dominate. In general, however, it is apparent that factors contributing to both the sign and size of ΔV^\ddagger lead to related changes in entropy between the initial and transition states, that is to ΔS^\ddagger . The anticipated relationship between ΔV^\ddagger and ΔS^\ddagger for a class of reactions [4] has been illustrated most recently for the case of acid aquation reactions of inert transition metal complexes [5].

Recently in our laboratories we have been involved in the determination of activation volumes for a range of racemization and isomerization reactions of octahedral metal complexes. For these types of reactions,

apart from various dissociative and associative mechanisms, intramolecular twist mechanisms can also be envisaged as pathways for interconversion between optical or geometrical isomers. Available mechanisms have been reviewed in detail recently [6]. While several labile metal complexes apparently rearrange via twist mechanisms [6], examples of racemization or isomerization reactions in relatively inert octahedral complexes proceeding by twisting mechanisms have not been unequivocally established.

Recently, strong support for a trigonal twist mechanism for racemization of $\text{Cr}(\text{nn})_3^{3+}$ and $\text{Cr}(\text{nn})_2(\text{ox})^+$ (nn = phen or byp) has been presented, based on ΔV^\ddagger data [3]. One point of interest regarding these complexes was the observation of large negative ΔS^\ddagger values while ΔV^\ddagger was approximately zero. The related complexes $\text{Cr}(\text{nn})(\text{ox})_2^-$ and $\text{Cr}(\text{ox})_3^{3-}$ also exhibited large negative ΔS^\ddagger values, but ΔV^\ddagger was large and negative in these cases. It appeared that ΔS^\ddagger was insensitive to a mechanistic change in the series clearly characterized by changes in the ΔV^\ddagger values. A qualitative $\Delta V^\ddagger - \Delta S^\ddagger$ relationship is observed for those reactions apparently proceeding via a ring-opening mechanism, but such a relationship breaks down in the case of the $\text{Cr}(\text{nn})_3^{3+}$ and $\text{Cr}(\text{nn})_2(\text{ox})^+$ complexes.

A trigonal twist mechanism, since it involves to a first approximation changes in bond angles and not bond lengths in generating the transition state, can be argued to proceed with no change in the intrinsic volume of the complex or to exhibit ΔV^\ddagger of approximately zero [3]. Provided the intramolecular twisting motion does not induce appreciable movement of solvent molecules about the ion to areas where they would exhibit markedly different partial molar volumes and compressibility coefficients, this argument remains valid. However, low frequency factors and thus negative activation entropies have long been argued as support for twist mechanisms [6–8], since the twist can only proceed when there is concerted motion of the chelate rings. On the other hand, a trigonal bipyramidal intermediate in an intramolecular dissociative mechanism, for example, requires a one-ended dissociation initially (contributing in the same sense to ΔV^\ddagger and ΔS^\ddagger) with subsequent rearrangement to the five-coordinate trigonal bipyramid possible through motion of only one ring. Dissociative and associative mechanisms for racemization and isomerization should exhibit the normal qualitative relationship of entropy and volume of activation, therefore. Thus a reasonable correlation of ΔV^\ddagger and ΔS^\ddagger for this type of reaction can be expected *except in the case of a twist mechanism*. For a twist mechanism, both a near-zero activation volume and an appreciably negative activation entropy are predicted.

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TABLE I. Activation Volumes and Entropies for Racemization and Geometrical Isomerization Reactions of Octahedral Metal Complexes in Solution.

No.	Complex ^a	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	ΔV^\ddagger (cm ³ mol ⁻¹)	Reference
1	Cr(ox) ₃ ³⁻	-76 (± 8)	-16.3 (± 0.4)	3
2	Cr(ox) ₂ (phen) ⁻	-69 (± 7)	-12.3 (± 0.3)	3
3	Cr(ox) ₂ (bpy) ⁻	-79 (± 9)	-12.0 (± 0.3)	3
4	Cr(ox)(phen) ₂ ⁺	-64 (± 6)	-1.5 (± 0.3)	3
5	Cr(ox)(bpy) ₂ ⁺	-69 (± 4)	-1.0 (± 0.2)	3
6	Cr(phen) ₃ ³⁺	-56 (± 8)	+3.3 (± 0.3)	3
7	Cr(bpy) ₃ ³⁺	-63 (± 8)	+3.0 (± 0.3)	3
8	Fe(phen) ₃ ²⁺	+89 (± 8) ^b	+15.6 (± 0.3)	9
9	"	+104 (± 10) ^c	+14.2 (± 0.3)	9
10	Ni(phen) ₃ ²⁺	+12 (± 3) ^b	-1.5 (± 0.3)	9
11	"	+8 (± 5) ^c	-0.4 (± 0.2)	9
12	Ni(phen) ₂ (bpy) ²⁺	+16 (± 20) ^c	+0.6 (± 0.2)	10, 11
13	"	+7 (± 20) ^b	-0.1 (± 0.1)	10, 11
14	Ni(phen)(bpy) ₂ ²⁺	+13 (± 12) ^c	-1.9 (± 0.2)	10, 11
15	"	+16 (± 12) ^b	-5.2 (± 0.5)	10, 11
16	Co(Ph ₂ dte) ₃	-22 (± 10) ^d	-6.6 (± 0.6)	12, 13
17	<i>trans</i> -Cr(ox) ₂ (OH ₂) ₂ ⁻	-61 (± 5)	-16.6 (± 0.5)	14
18	<i>trans</i> -Cr(mal) ₂ (OH ₂) ₂ ⁻	+74 (± 5)	+8.9 (± 0.3)	14
19	<i>trans</i> -Co(en) ₂ (SeO ₃ H)(OH ₂) ²⁺	+53 (± 4)	+7.5 (± 0.2)	2, 15
20	<i>trans</i> -Co(en) ₂ (OH ₂) ₂ ³⁺	+103 (± 5) ^e	+14.3 (± 0.2)	16
21	"	+64 (± 4) ^b	+12.6 (± 0.8)	16
22	<i>trans</i> -Co(en) ₂ (acet)(OH ₂) ²⁺	+61 (± 9) ^e	+7.9 (± 0.3)	17
23	"	+47 (± 8) ^b	+5.6 (± 0.6)	17
24	<i>trans</i> -Co(en) ₂ (SeO ₃)(OH ₂) ⁺	+36 (± 10)	+7.3 (± 0.3)	18
25	<i>trans</i> -Co(en) ₂ (OH)(OH ₂) ²⁺	+100 (± 20)	+14.5 (± 1.1)	18
26	β -Co(edda)(tn) ⁺	+124 (± 10)	+19.9 (± 0.4)	19, 20
27	β -Co(edda)(en) ⁺	+174 (± 15)	+25.2 (± 0.5)	19, 20

^aNumbers 1 to 16 racemizations; remainder isomerizations. ^b1.0 M acid. ^c0.01 M acid. ^dChloroform solution. ^e0.05 M acid.

We have collected in Table I available data on separately determined activation volumes and activation entropies for a range of isomerization and racemization reactions of octahedral complexes [3, 9–20]. Much of this data was determined in these laboratories. When represented graphically, a line of best fit represented by the expression

$$\Delta S^\ddagger = 13.7 (\pm 5.8) + (5.4 (\pm 0.5) \times \Delta V^\ddagger)$$

can be drawn through the data points, as illustrated in Figure 1. Of the data considered, only for the complexes Cr(nn)₃³⁺ and Cr(nn)₂(ox)⁺ (nn = phen or bpy) do the points fall well outside the 90% confidence limits determined by least-squares analysis, consistent with the earlier assignment of a twist mechanism for racemization of these complexes.

Only one other complex in this series has been assigned a twist mechanism previously, namely racemization of Fe(phen)₃²⁺ [21–24]. For this complex, however, the mechanism is complicated by a low-high spin transition in forming the transition state which has been shown [9] to contribute significantly and positively to both ΔV^\ddagger and ΔS^\ddagger . Thus a relationship of these parameters is expected in this case,

though the strong correlation observed lends support to a dissociative mechanism. Other complexes in the series show a correlation consistent with the generally dissociative mechanisms previously assigned.

We contend that appreciable deviation from the ΔV^\ddagger – ΔS^\ddagger correlation illustrated in Figure 1 is indicative of a twist mechanism for racemization and isomerization reactions. Four examples of related chromium(III) complexes which appear to exhibit twist mechanisms have been presented. Confirmation of this empirical observation must await further experimental evidence. It is apparent that racemization studies of clathrate or 'cage' complexes where dissociative pathways are unlikely could offer the best experimental evidence in the future.

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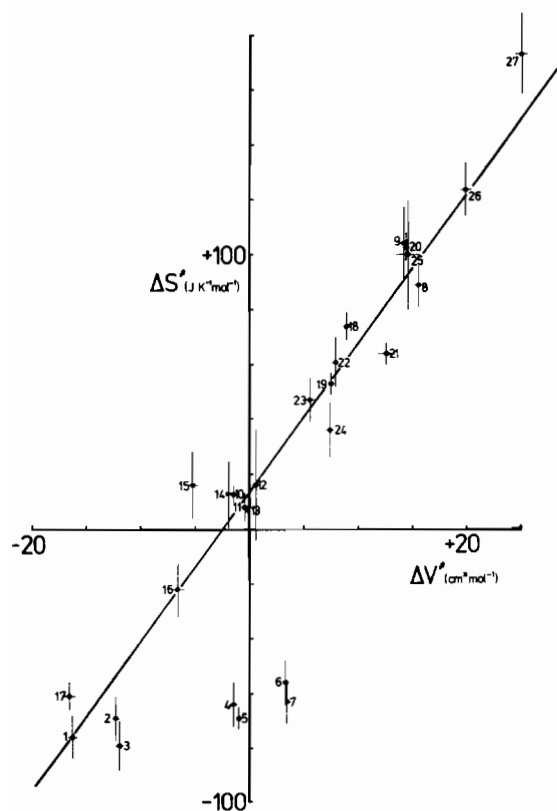


Figure 1. Graph of activation entropy versus activation volume for racemization and geometrical isomerization of octahedral complexes. Numbers refer to position of complex in Table I.

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