

Linear Free Energy Relationships and Activation Volumes for Water Exchange Reactions as Measures of the Degree of Association in the Transition State for Octahedral Substitution Reactions

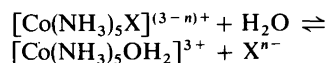
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The controversy which is encountered in the literature concerning the associative character of substitution reactions in the pentaamminechromium(III) series of complexes has been resolved by a redetermination of the association constant for $[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)]^{3+} + \text{Br}^-$ at 50 °C. Both linear free energy relationships and activation volumes then predict an increase in the associative character of substitution reactions along the series: $\text{Co}(\text{NH}_3)_5\text{X} < \text{Ir}(\text{NH}_3)_5\text{X} < \text{Rh}(\text{NH}_3)_5\text{X} < \text{Cr}(\text{NH}_3)_5\text{X} < \text{Cr}(\text{OH}_2)_5\text{X}$, where X is one of a number of single charged anions or water.

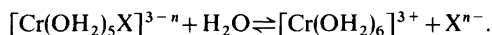
An important aspect of substitution reactions of metal complexes is the extent to which the entering and leaving ligands are associated with the metal center in the transition state. Several approaches to this problem have been made, two of the more successful being based upon determinations of volumes of activation for solvent exchange reactions, and investigations of the existence of linear free energy relations for series of similar complexes, respectively.

These two approaches have led to the same conclusions for both the pentaamminecobalt(III) and the pentaquachromium(III) series of complexes. In the former series of complexes the volume of activation for water exchange in the pentaammineaquacobalt(III) ion is positive, *viz.* $+1.2 \text{ cm}^3 \text{ mol}^{-1}$.¹ This indicates that *dissociation* of the reacting ligand is important in the formation of the transition state,¹ a conclusion which is further supported by the existence of a linear correlation (with slope, α , equal to 1.00) between ΔG^* and ΔG° for the process

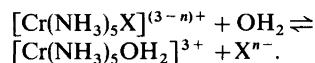


for a large number of X-ligands.²

Water exchange in the hexaaquachromium(III) ion is characterized by a negative volume of activation, *viz.* $-9.3 \text{ cm}^3 \text{ mol}^{-1}$.³ This indicates the importance of *association* of the reacting ligands in the transition state,^{1,3} and this conclusion is supported by the fact that α is 0.56⁴ for a variety of reactions of the type:



In the pentaamminechromium(III) series a different situation is encountered. The volume of activation for water exchange in the pentaammineaquachromium(III) ion is found to be $-5.8 \text{ cm}^3 \text{ mol}^{-1}$,⁵ a result which has been taken as evidence of significant association of the reacting ligands in the transition state.⁵ However, contrary to this an α value of 0.91 has been found and this has been taken as evidence of the operation of a dissociative mechanism for the series of reactions:⁶



The latter discrepancy would clearly appear to invalidate conclusions derived from the use of such data, and a closer examination of the agreement concerning the classification of reaction mechanisms reached on the basis of these two criteria was therefore of interest.

EXPERIMENTAL

Materials. Ion exchanged water, distilled from alkaline permanganate in an all-quartz apparatus, was employed throughout. HClO_4 (Merck 70 % *p.a.*) was used without further purification. NaBr (Merck, "reinst") was recrystallized once from water. $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ and $[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)]\text{Br}_3$ were prepared by literature methods.²⁰

Equilibrium measurements. Pentaammine chromium(III) complexes lose ammonia at a rate which renders equilibrium measurements in acid bromide solutions impractical. Instead, synthetic mixtures with varying $[\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+}/[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ ratios were prepared and solutions with negligible initial variation in absorbance at 270 nm as function of time were assumed to contain the pentaammine complex ions in their equilibrium concentrations. This assumption was supported by decreasing absorbances for ratios larger than the equilibrium value and increasing absorbances for smaller ratios. In aqueous 0.5 M $\text{NaBr} + 0.3 \text{ M HClO}_4$ solution with a total chromium(III) concentration of 3.5 mM the concentration equilibrium constant:

$$K = \frac{([\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+})}{([\text{Cr}(\text{NH}_3)_5(\text{OH}_2)]^{3+})(\text{Br}^-)}$$

was thus found to have the value $(0.019 \pm 0.002) \text{ M}^{-1}$ at 50 °C.

RESULTS AND DISCUSSION

In addition to the data for the various series of complexes already mentioned, data may be found in the literature which permit $\Delta G^*/\Delta G^\circ$ plots to be constructed for the aquation reactions of a limited number of pentaamminerhodium(III)⁷⁻⁹ and pentaammineiridium(III)^{10,11} complexes. These plots are shown in Fig. 1 and are found to have α -values of 0.72 and 0.85, respectively. As a measure of association in the transition state these values are consistent with volumes of activation for water exchange of $-4.1 \text{ cm}^3 \text{ mol}^{-1}$ ¹² and $-3.2 \text{ cm}^3 \text{ mol}^{-1}$ ¹³ for the pentaammineaquarhodium(III) and -iridium(III) ions, respectively. Additional evidence for the importance of association in the transition state in the reactions of pentaamminerhodium(III) and -iridium(III) complexes comes from studies of the chloride and bromide anation of the pentaammineaquarhodium ions, reactions which are found to be significantly faster than water exchange.^{7,14}

The value of α of 0.91 for aquation of the pentaamminechromium(III) series of complexes is derived from data obtained at 50 °C. A limited number of

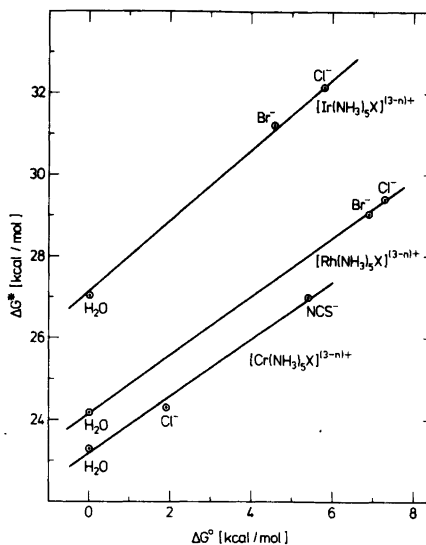


Fig. 1. Relationship between the free energy of activation, ΔG^* , and the free energy of reaction, ΔG° , for the acid-independent aquation of $\text{M}(\text{NH}_3)_5\text{X}^{(3-n)+}$ [$\text{M} = \text{Cr}(\text{III})$ (25 °C) $\text{Rh}(\text{III})$ (65 °C), and $\text{Ir}(\text{III})$ (95 °C)]. ΔG° values are calculated from

$$K = \frac{[\text{M}(\text{NH}_3)_5\text{OH}_2^{3+}][\text{X}^{n-}]}{[\text{M}(\text{NH}_3)_5\text{X}^{(3-n)+}][\text{H}_2\text{O}]}$$

with $[\text{H}_2\text{O}]$ taken as 55.5 M.

rate and equilibrium measurements which have been carried out at, or may be extrapolated to 25 °C^{12,15-18} may be found in the literature. These data are also shown in Fig. 1 and they yield an α value of 0.70. This is significantly lower than the value derived from data at 50 °C, and indicates a degree of association in the transition state which is in agreement with that predicted on the basis of the activation volume.

The temperature dependence of α may be evaluated from:¹⁹

$$\alpha_T = \gamma_H \times \frac{\beta^*(T - \beta^*)}{\beta^*(T - \beta^*)}$$

where γ_H is the slope of a plot of ΔH^* vs. ΔH° , and β^* and β° are the slopes of plots of ΔH^* vs. ΔS^* and ΔH° vs. ΔS° , respectively. For reactions of series of complexes for which all these quantities are known this equation predicts only a slight temperature dependence of α . Thus for the pentaamminechromium-

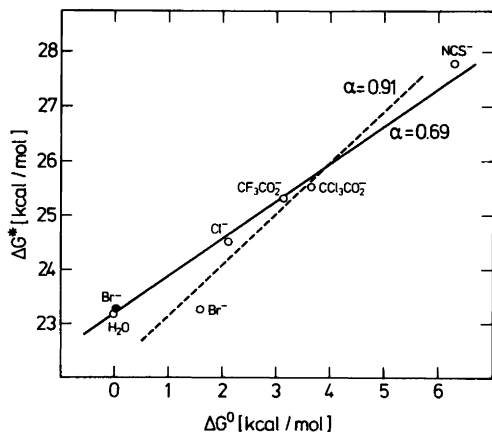
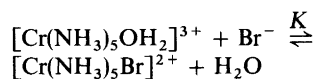


Fig. 2. Relationship between the free energy of activation, ΔG^* , and the free energy of reaction, ΔG° , for the acid-independent aquation of $\text{Cr}(\text{NH}_3)_5\text{X}^{(3-n)+}$ complexes at 50 °C. The open circles are values calculated from data given in Refs. 5 and 6, and the filled circle is the value for bromide obtained in the present work. The dotted line is that obtained in Ref. 5, whereas the full line is obtained after correction of the association constant for the bromido complex.

(III) series of complexes, where α (25 °C)=0.56, a value for α (90 °C) of 0.57 may be computed.* This result casts doubt on the reality of the apparently large temperature dependence of α for the pentaamminechromium(III) series of complexes, and the agreement between the activation volume and the $\Delta G^*/\Delta G^\circ$ data at 25 °C focus attention primarily upon the $\Delta G^*/\Delta G^\circ$ data for 50 °C. The latter data are shown in Fig. 2 and have been supplemented with data for the water exchange reaction.⁵

Attempts in this laboratory to reproduce the reported⁶ association constant ($K=0.21 \text{ M}^{-1}$) for the process



were unsuccessful. An aqueous 0.5 M NaBr + 0.3 M HClO₄ solution with the chromium species cal-

* From data given in Ref. 4 values of $\gamma_{\text{H}}=0.45$, $\beta^*=-280 \text{ K}$ and $\beta^\circ=-190 \text{ K}$ are obtained. Neither ΔH^* vs. ΔS^* nor ΔH° vs. ΔS° gives a single straight line, two parallel lines being obtained in both cases. The data for the Cl^- , Br^- and I^- complexes lie one line and the data for the H_2O , NCS^- and NH_3 complexes on the other.

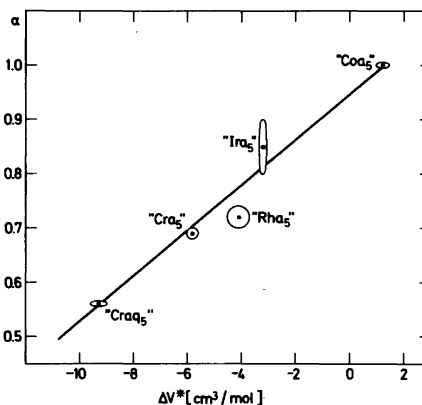
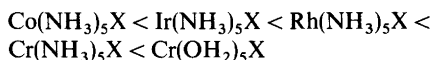


Fig. 3. Correlation between ΔV^* and α for the indicated series of complexes (see the text, $a=\text{NH}_3$ and $aq=\text{OH}_2$). Experimental values are indicated by contour ellipses of the probability density function drawn at the 68 % probability level.

culated from this constant to be at equilibrium showed a decreasing absorbance at 270 nm as function of time. From spectrophotometric measurements we find a value which is approximately 10 times smaller ($K \sim (0.019 \pm 0.002) \text{ M}^{-1}$). This new value brings the $\Delta G^*/\Delta G^\circ$ data for the pentaammineaquachromium(III) ion into agreement with the remaining data for the pentaamminechromium(III) series of complexes, the resulting value of α being 0.69 (Fig. 2). This value is in good agreement with that estimated from the data at 25 °C, Fig. 1.

Fig. 3 shows that a correlation exists between ΔV^* and α obtained from the corrected and the new data. Predictions based on the two types of criteria are thus in agreement and furthermore the degree of association of the reacting ligands in the transition state may be expected to increase along the series:



The degree of association in the transition state is therefore not only dependent on the central metal ion, but also on the non-reacting ligands.

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Note added in proof. Additional evidence for the assignment of an associative mechanism to the series of pentaamminechromium(III) complexes has recently been given: Palmer, D. A. and Kelm, H. *Inorg. Chem.* 16 (1977) 3139.

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