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# POSSIBLE TESTS FOR THE MECHANISMS OF LIGAND EXCHANGE IN SOLIDS

## THE DEAQUATION-ANATION OF $[Cr(NH_3)_5(H_2O)]X_3$ SALTS

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### ABSTRACT

The possibility of using correlations of $\Delta H^{*}$ and $\Delta H$, and of $\Delta H^{*}$ and $\Delta S^{*}$ to gain insight into the mechanisms of ligand-exchange reactions in solids are discussed. These correlations are tested using literature values for the deaquation–anation reactions of $[Cr(NH_3)_5(H_2O)]X_3$, where $X^- = Cl^-, Br^-, I^-$ or $NO_3^-$. The poor agreement in the activation parameters reported in the literature precluded a meaningful test of the $\Delta H$–$\Delta H^{*}$ correlation. This poor agreement suggests that these activation parameters are strongly influenced by experimental factors that have not been controlled in studies to date. Nevertheless, there is a linear correlation of $\Delta H^{*}$ and $\Delta S^{*}$ which gives an isokinetic temperature of 367 ± 11 K. This isokinetic behavior suggests that the same mechanism is operative throughout the series.

### INTRODUCTION

Kinetic investigations of the reactions of solids have focused primarily on gaining insight into those aspects of the reactions that are peculiar to solids. The concerns have been primarily to develop kinetic models in terms of nucleation and growth of interphase boundaries, to assess the roles of lattice defects, and to understand these phenomena in terms of both the microscopic and molecular-level structures of the solids[2]. However, little attention has been paid to the kinetic effects of specific bond-breaking and bond-making processes in the solid.

We therefore became interested in several solid-phase ligand-exchange reactions for which $S_N1$ or $S_N2$ mechanisms have been assigned[2–10]. These studies have involved the displacement of a volatile ligand such as $H_2O$ or $NH_3$ from the coordination sphere of a complex ion and its replacement by an anion from the crystal lattice. For example, studies have been performed on the deaquation–anation reactions of aquopentaammine complexes of cobalt(III)[3,4,11], chromium(III)[5–7,12] and ruthenium(III)[9]:

$$[M(NH_3)_5(H_2O)]X_3(s) \rightarrow [M(NH_3)_5X]X_2(s) + H_2O(g) \qquad (1)$$

There are two features of these studies that have especially caught our attention. First, the agreement in activation parameters reported by different groups is poor. This feature is alarming because the mechanisms have been assigned on the basis of activation parameters. Second, the mechanisms proposed for these reactions do not always agree with those proposed for similar ligand-exchange processes in solution. For example, the ligand-exchange reactions of cobalt(III) complexes in solution are now generally believed to involve no bond-making between cobalt and the incoming ligand in the transition state; the mechanism is therefore described as being $S_N1$ or dissociative[13-15]. The mechanism(s) for ligand-exchange at other tripositive centers is currently subject to more debate, but anation of $[Cr(NH_3)_5(H_2O)]^{3+}$ in water also appears to be dissociative[16]. It would be very interesting, therefore, if the mechanism for the same ligand-exchange in solids is $S_N2$ or associative in character as proposed for some of these complexes.

In this paper, we wish to discuss two tests that can be applied to aid in assessing the activation parameters for solid-phase ligand-exchange reactions and to assist in drawing mechanistic conclusions from these parameters. The first test involves a possible correlation between $\Delta H^{\neq}$ and $\Delta H$; the second involves a possible correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$. These two tests are applied to data reported in the literature for the anation of complexes in the $[Cr(NH_3)_5(H_2O)]X_3$ series. Application of these ideas to the $[Co(NH_3)_5(H_2O)]X_3$ and $[Ru(NH_3)_5(H_2O)]X_3$ series will be reported in forthcoming papers.

## CAUTIONARY COMMENTS

Since it is our intent to look more closely at the possible mechanistic insight that can be obtained from activation parameters, it is useful first to summarize several warnings that have already appeared in the literature. There are many potential problems associated with the use and interpretation of activation parameters for solid-phase reactions[17]. Some of these are related to the problem of finding valid kinetic descriptions. There is often considerable uncertainty in the choice of appropriate rate equations. In many cases, a single rate expression is not sufficient to describe the reaction through either the entire reaction or over the entire temperature range selected to evaluate the activation parameters. Since the choice of rate law can have a dramatic effect on the magnitudes of the activation parameters[18], the validity of reported activation parameters is often questionable. However, even where the question of rate-law is satisfactorily resolved, there still remains the question of the meaning of the activation parameters, whether they reflect chemical processes inherent to the sample or are dependent on experimental conditions such as sample-bed thickness, particle size or atmosphere. Activation parameters obtained by non-isothermal methods, in particular, are often suspect because the questions raised above are generally left unresolved. Because of these problems, Garn has suggested that the term "temperature coefficient of reaction" be used instead of "activation energy", a term that brings with it a well-defined meaning in homogeneous kinetics that might not be valid for solid-phase kinetics[19]. Nevertheless, we maintain the use of the term activation energy in our following discussion.

## POSSIBLE RELATIONSHIPS BETWEEN $E_a$ AND $\Delta H$

For the sake of our present discussion, let us assume that the solid-phase reactions under discussion have well-defined transition states with associated activation energies. Now consider a series of compounds of the type $[L_nMY]X$, where M is a metal, Y a volatile ligand, L a non-exchanging ligand of which $n$ are required to complete the coordination sphere, and X is an anion outside the coordination sphere. The reaction that we are concerned with is one in which the volatile ligand is expelled from the coordination sphere and replaced by the anion, X, as shown in eqn (2):

$$[L_nMY]X(s) \rightarrow [L_nMX](s) + Y(g) \tag{2}$$

It is reasonable to believe that some insight into the mechanism of the X–Y ligand exchange can be gained by studying a homologous series of compounds in which only X varies through the series. One such series consists of compounds of the type $[Cr(NH_3)_5(H_2O)]X_3$; another is $[Co(DMG)_2py_2]X$, where DMG is the dimethylglyoximato anion and py is pyridine.

### *Dissociative ligand exchanges*

If we are dealing with a homologous series of gaseous complexes and a dissociative mechanism is operative, the activation energy, $E_a$ will be constant through the series, because the transition state reflects only the M–Y bond strength. This constancy of $E_a$ will also be found for the corresponding reactions in a given solvent; indeed, the constancy of $E_a$ has been used as a test of this mechanism[20, 21]. However, when we place the $[L_nMY]$ ion within a crystal lattice, the constancy of $E_a$ is no longer assured, because each crystal lattice within the series can be and often is unique.

For the sake of our discussion, let us picture the $[L_nMY]$ ion as being placed in several different reaction cavities, formed by the surrounding array of ions in the crystal lattices. The activation energy will be constant through the series only if the interaction in each case between the complex and its surrounding lattice (the walls of its reaction cavity) is the same in the transition state as in the starting complex; that is, there is no change in the interaction between the complex and the surface of the reaction cavity as the transition state is formed*. It seems reasonable that, for a dissociative mechanism, the change in interaction would be minimal through the series unless perhaps the leaving group itself interacts strongly with the walls of the cavity. Thus, a fairly constant $E_a$ through a homologous series implies a dissociative mechanism; however, the mechanism can be dissociative without there being a constant $E_a$. We might further note that the broader the range of the enthalpy changes,

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* The reader should note that it is not necessary that the $[L_nMY]$ ion interact equally with the walls of the different reaction cavities in order to obtain a constant $E_a$ through the series of compounds.

$\Delta H$, over which $E_a$ is constant, the more convincing the dissociative mechanism becomes, because the range of $\Delta H$ values implies a range of different types of reaction cavities.

### *Associative ligand exchanges*

If we were dealing with solution reactions, we would expect $E_a$ to vary within a homologous series if the ligand exchange were associative. Furthermore, since $E_a$ reflects changes in M–X bond stability, we would anticipate a correlation of $E_a$ with $\Delta H$. Swaddle has reviewed the application of linear-free-energy relationships to octahedral substitution reactions in solution[15]. He has noted that a plot of $E_a$ vs. $\Delta H$ with a slope close to 0.5 should be found for associative mechanisms in which bond-making is essentially synchronous with bond-breaking. However, reactions in solids will reflect the interaction between the complex and its reaction cavity during the course of the reaction.

If the interaction between the transition state and its reaction cavity is identical to that between the product and the cavity, then a plot of $E_a$ vs. $\Delta H$ will have a slope of 1.0. Thus, such correlations of $E_a$ with $\Delta H$ would offer evidence for an associative mechanism and should be sought. However, the absence of such a correlation would not rule out the associative mechanism, but could merely reflect an irregular trend in the interaction of the complex with its reaction cavities as the transition state forms. In the absence of a linear correlation of $\Delta H$ and $E_a$, it would be informative to seek a series of compounds that are isostructural with each other. In such a series the reaction cavities would be similar, and the likelihood of $\Delta H$ reflecting changes in $E_a$ would be enhanced.

### *Application to $[Cr(NH_3)_5(H_2O)]X_3$*

Both $E_a$ and $\Delta H$ values have been reported for the deaquation–anation compounds in the $[Cr(NH_3)_5(H_2O)]X_3$ series. The fact that several groups have chosen to study these reactions offers additional insight into the uncertainty of these parameters. Literature values are summarized in Table 1. Tsuchiya et al.[5] obtained $E_a$ from non-isothermal DTA and TG studies by assuming the rate-law to be first order; they did not report values for $\Delta S^*$. Wendlandt and Bear[12] performed isothermal kinetic studies by following pressure changes using an isoteniscope. They reduced their data in terms of a first-order rate law. Nagase and coworkers[7] followed the reaction in the same way, but analyzed their results in terms of the Prout–Tompkins equation.

The agreement in $\Delta H$ values obtained in different research groups is reasonably good. However, the $\Delta H^*$ and $\Delta S^*$ values obtained by different workers show much less agreement. Part of the lack of agreement can be ascribed to differences in experimental procedures used to determine these parameters (isothermal vs. non-isothermal) and part to differences in rate laws used. However, when the $\Delta H^*$ values from a particular research group are plotted against $\Delta H$, no correlation is evident. The absence of such a correlation and the great variation in literature values for $\Delta H^*$

TABLE I

LITERATURE VALUES FOR $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ AND $\Delta H$ FOR THE DEAQUATION-ANATION REACTION OF $[Cr(NH_3)_5(H_2O)]X_3$

| *Anion*, $X^-$ | $\Delta H$ *(kcal mol*$^{-1}$*)* | $\Delta H^{\ddagger}$ *(kcal mol*$^{-1}$*)* | $\Delta S^{\ddagger}$ *(e.u.)* | *Ref.* |
|---|---|---|---|---|
| $Cl^-$ | 6.1 | 26 ± 2$^a$ | — | 5 |
| | 6.1 ± 0.5 | 16.8 ± 0.4$^b$ | −25.4 ± 0.8$^b$ | 12 |
| | 4.2 ± 0.4 | — | | 6 |
| | 6.7$^c$ | — | | 6 |
| | 6.5 | 26.4 | − 2.5 | 7 |
| $Br^-$ | 9.0 | 37 ± 1$^a$ | — | 5 |
| | 7.8 ± 0.6 | 22.6 ± 4.9 | −12.2 ± 3.4 | 12 |
| | 5.9 ± 0.4 | — | — | 6 |
| | 8.5$^c$ | — | — | 6 |
| | 6.3 | 29.7 | 9.2 | 7 |
| $I^-$ | 10.8 | 18 ± 1$^a$ | — | 5 |
| | 6.3 ± 0.5 | 15.6 ± 0.3 | −31.2 ± 0.7 | 12 |
| | 4.8 ± 0.4 | — | — | 6 |
| | 8.6$^c$ | — | — | 6 |
| | 7.0 | 32.7 | 15.4 | 7 |
| $NO_3^-$ | 11.9 | 16 ± 2$^a$ | — | 5 |
| | — | 15.9 ± 0.3 | −29.4 ± 0.9 | 12 |
| | 3.8 ± 0.4 | — | — | 6 |
| | 13.0$^c$ | — | — | 6 |
| | 12.3 | 25.1$^d$ | - 2.5 | 7 |
| | — | 34.5$^d$ | 20.2 | 7 |

[a] The values recorded for $\Delta H^{\ddagger}$ are actually average $E_a$ values from nonisothermal DTG and DTA studies; the error limits are average deviations from the mean.

[b] These values were calculated by least-square analysis from the rate constants given in ref. 12; error limits are the standard deviation using three rate constants.

[c] These values were calculated from sealed-tube DTA using $\Delta H$ for the vaporization of $H_2O$[22].

[d] Two crystalline forms of the nitrate were reported.

suggest that the activation energies are influenced by factors other than the rate of bond-making and bond-breaking. It appears that the activation parameters are strongly dependent on some uncontrolled experimental factor or factors rather than by intensive chemical processes inherent to the solids. Therefore, it has been sought to examine the data in light of Garn's observations of the kinetic compensation effect [19, 23].

## THE ISOKINETIC RELATIONSHIP

Linear correlations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (or $E_a$ and log $A$) have been widely used, especially in organic chemistry, to provide insight into the role of substituent effects on reactions in solution[24]. In this context, they have been referred to as isokinetic relationships. Recently, Garn has pointed out the same correlation for several

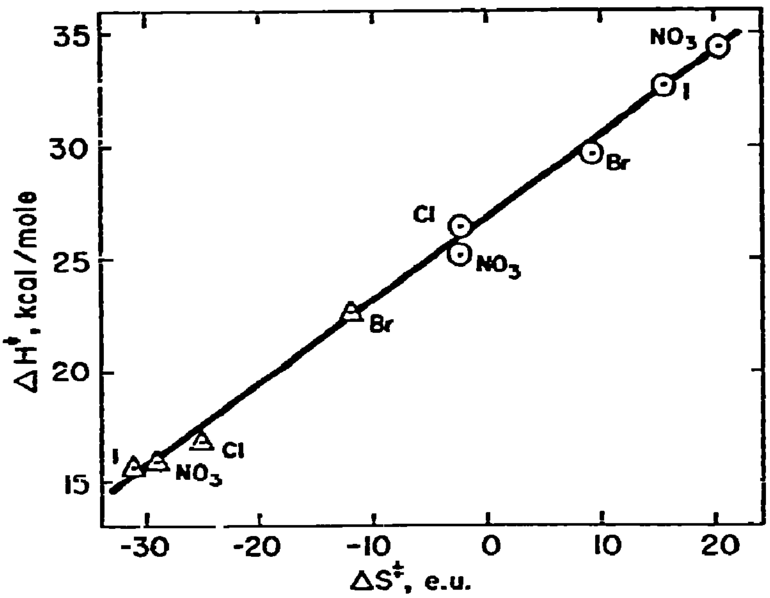

Fig. 1. Isokinetic plot for the deaquation–anation of $[Cr(NH_3)_5(H_2O)]X_3$; △ = data from ref. 12; ○ = data from ref. 7. Slope = $T$ = 367.5 ± 0.4 K; intercept = $\Delta G^{\ddagger}$ = 26.8 ± 0.2 kcal mol$^{-1}$.

solid-phase reactions, drawing comparisons from studies of heterogeneous catalysis, and has referred to the correlation as the kinetic-compensation effect[19, 23].

For reactions in solution, the existence of a linear correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ through a homologous series of compounds has been taken to mean that the same reaction mechanism is operative throughout the series[24, *]. The slope of the linear plot of $\Delta H^{\ddagger}$ (as ordinate) vs. $\Delta S^{\ddagger}$ (as abscissa) has units of absolute temperature, because it represents the temperature at which all of the reactions represented on the line occur at the same rate. Below this temperature, the reaction rate is controlled primarily by $\Delta H^{\ddagger}$ while, above this temperature, $\Delta S^{\ddagger}$ is the dominant factor. The former situation normally occurs when electronic effects are paramount, while the latter occurs when solvent effects dominate.

Figure 1 shows that the deaquation-anation reaction of $[Cr(NH_3)_5(H_2O)]X_3$ shows the isokinetic behavior. A linear least-squares regression analysis of the data gives an isokinetic temperature of 367 ± 11 K, where the error limit is the standard deviation. The correlation coefficient for the line is 0.9968. There are two additional features of the correlation that are interesting. First, the fact that two different rate-laws were used to obtain rate-constants does not appear to affect the correlation. Second, only one kinetic study was performed above the isokinetic temperature. That single study was performed at 94.5°C (367.7°C) by Wendlandt and Bear on the iodide salt[12].

The existence of isokinetic behavior strongly suggests that the mechanism is the

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[*] In studying substituent effects in organic reactions, a linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ further indicates that the same interaction mechanism between substituent and the reactive center is operative throughout the series.

same throughout the series (same rate-controlling process). However, it is not possible to say on this basis alone that the rate is controlled by ligand exchange. Indeed, the absence of a $\Delta H^{\neq}$–$\Delta H$ correlation indicates that other factors are involved in determining at least the magnitude of $\Delta H^{\neq}$. The existence of the isokinetic relationship further underscores the unreliability of drawing mechanistic conclusions from either $\Delta H^{\neq}$ or $\Delta S^{\neq}$ trends alone. Furthermore, it supports our suggestion that there are experimental factors influencing activation parameters that have not been controlled in studying this series of reactions.

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