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Note

The deaquation-anation reaction of aquopentaammineruthenium(III) complexes and some observations on the kinetic compensation effect

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During the past several years, there have been a number of studies of the deaquation–anation reactions of aquopentaammine complexes, viz.

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

Complexes of cobalt, chromium and ruthenium have been examined with a variety of anions, X, including, especially, nitrate and halides. Work has focused on both the thermodynamic and kinetic aspects of these reactions, and a wide range of thermoanalytical techniques has been employed[1–15].

In a recent article in this journal, we discussed the deaquation–anation of aquopentaamminechromium(III) salts[15]. It was noted that the activation parameters reported by different research groups are in poor agreement. However, there is one unifying feature to all the kinetic data; the activation parameters exhibit the isokinetic relationship (or kinetic-compensation effect), $\Delta H^{\neq}$ being linearly correlated with $\Delta S^{\neq}$. In the light of this observation and recent discussions elsewhere concerning the application of the kinetic-compensation effect to solid-phase reactions[16–21], we thought it would be interesting to examine similarly the activation parameters for other aquopentaammine complexes. In this note we wish to report that the activation parameters for $[Ru(NH_3)_5(H_2O)]X_3$ also fit the isokinetic relationship and to comment further on this data and on the possible implications of the isokinetic relationship. Experimental work is presently in progress on the $[Co(NH_3)_5(H_2O)]X_3$ system in order to draw further comparisons among the aquopentaammine complexes.

EVALUATION OF DATA

The deaquation–anation of $[Ru(NH_3)_5(H_2O)]X_3$ complexes was studied by Ohyoshi et al.[14] who reported $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values for X = Cl, Br, I and NO_3. Both isothermal and nonisothermal studies (using the method of Freeman and Carroll)[31] were performed, but $\Delta S^{\neq}$ values are reported only for the isothermal studies, which were performed on a thermobalance under a dynamic helium atmosphere. It was suggested that the mechanism for the deaquation–anation of the $[Ru(NH_3)_5$-

$(H_2O)]X_3$ salts is of the S_N2 (or associative) type, because the activation parameters differ with different anions. However, the observed variations in these parameters could also be due to differences in reaction conditions and/or random errors as discussed below.

It can be shown[22] that the uncertainty in $\Delta H^{\neq}$, $\delta(\Delta H^{\neq})$, can be related to the uncertainties in the rate constants, δk, and in the temperatures, δT, and to the temperature range, $T_1 - T_2$, used to evaluate the activation parameters:

$$\delta(\Delta H^{\neq}) \simeq \frac{2RT_1T_2}{(T_1 - T_2 + 2\delta T)} \left(\frac{\delta k}{k}\right) \tag{2}$$

Since Ohysahi et al.[14] give temperatures only to the nearest degree, we assume $\delta T = 1°$. The ratio $\delta k/k$ is normally of the order of 0.05 for solution studies[22] and can be expected to be larger for solid-phase reactions. The data for the chloride salt at 63 °C in Fig. 2 of ref. 14 suggest that $\delta k/k$ could be as large as 0.5; a value of 0.2 seems to be a reasonable estimate for the entire set of experiments. The largest temperature range is 308–340 K (iodide salt). Thus we can estimate $\delta(\Delta H^{\neq})$ as being of the order of 2.4 kcal/mole ($\delta k/k = 0.2$, $\delta T = 1°$, $T_2 - T_1 = 32°$), though it is likely to be somewhat larger. The average activation energy for the four $[Ru(NH_3)_5(H_2O)]X_3$ salts studied by Ohysahi et al. is 23.0 kcal/mole with an average deviation from the mean of 2.0 kcal/mole, within the estimated uncertainty of the data. The conclusion that the identity of the anion determines the magnitude of the activation enthalpy and the interpretation of this conclusion in terms of a rate-determining S_N2 ligand exchange are not warranted by the quality of the data. From eqn. (2), it can be seen that larger temperature ranges and better temperature control (both of which should be possible) are needed to improve the data. Even then, the frequently noted question of the meaning of activation energy for solid-phase reactions must be seriously considered[23, 24].

ISOKINETIC RELATIONSHIP

The data reported for the deaquation–anation of $[Ru(NH_3)_5(H_2O)]X_3$ salts exhibits the kinetic compensation effect. The linear least-squares regression line through the plot of $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ gives a slope (the isokinetic temperature) of $T_i = 339 \pm 19$ K and an intercept of 24.9 ± 0.2 kcal/mole (the error limits are standard deviations obtained from the least-squares analysis). The correlation coefficient for the linear relationship is $R = 0.9967$. By comparison, for $[Cr(NH_3)_5(H_2O)]X_3$ the isokinetic temperature is 367.5 K, the intercept 26.9 kcal/mole and the correlation coefficient 0.9968[15]. The lower isokinetic temperature for $[Ru(NH_3)_5(H_2O)]X_3$ compared with $[Cr(NH_3)_5(H_2O)]X_3$ reflects the lower stability of the ruthenium complexes and consequently the lower temperatures at which studies of the ruthenium complexes were made.

The isokinetic relationship has been observed for many solution-phase reactions, and its possible significance has been discussed by many authors[22, 25–30]. The picture emerging from these discussions is that the isokinetic relationship can have either of two general origins. It can arise from random errors in evaluating $\Delta H^{\neq}$; errors in $\Delta H^{\neq}$ produce corresponding errors in $\Delta S^{\neq}$, which can give rise to an apparent correlation of $\Delta H^{\neq}$ with $\Delta S^{\neq}$. This situation is often associated with activation parameters that have been evaluated using a small temperature range[22, 25–27]. On the other hand, the isokinetic relation can arise from a common mechanism among the members of the series, the differences in activation parameters reflecting substituent effects (structural variables) or differences in reaction conditions (procedural variables)[28–30]. It seems to us that these same causes are also the likely ones for solid-phase reactions.

When the isokinetic relationship arises from compensating errors in $\Delta H^{\neq}$ and $\Delta S^{\neq}$, the isokinetic temperature is expected to be approximately the average temperature at which kinetic studies were performed[22, 25, 26]. However, a similar situation can prevail even when the $\Delta H^{\neq}$–$\Delta S^{\neq}$ correlation arises from a constant mechanism. Exner, focusing on solution reactions, states that the isokinetic temperature is characteristic of the reaction series and dependent on the experimental temperature range and that it has no immediate physical meaning and can be determined only with large uncertainty[25]. In contrast, Zsako, focusing on solid-phase reactions, suggests that the compensation parameters (from which the isokinetic temperature can be obtained) have an unknown physical significance that is independent of procedural variables and characteristic of the reaction itself[17]. The isokinetic temperatures for both the $[Ru(NH_3)_5(H_2O)]X_3$ and $[Cr(NH_3)_5(H_2O)]X_3$ series are at the high temperature limit of the temperatures over which the reactions were studied. Thus these isokinetic temperatures reflect the chosen temperature ranges; however, the temperature ranges were chosen on the basis of the thermal stabilities of the complexes, and at least in this sense they are characteristic of the reactions themselves. Whether they are intrinsically characteristic of the reactions remains to be shown.

In the case of $[Ru(NH_3)_5(H_2O)]X_3$, our analysis of the errors associated with the reported activation parameters (vide supra) indicates that the isokinetic relationship could easily arise from compensating errors in $\Delta H^{\neq}$ and $\Delta S^{\neq}$. In the case of $[Cr(NH_3)_5(H_2O)]X_3$, where more kinetic studies covering a wider range of experimental conditions have been reported, the case for the isokinetic relationship arising from differences in procedural variables such as heating rate, particle size, sample mass and sample atmosphere is stronger (though not compelling). Exner has pointed out some more statistically rigorous tests for the isokinetic relationship, which under favourable circumstances can show whether the $\Delta H^{\neq}$–$\Delta S^{\neq}$ correlation is genuine (indicating a common mechanism) or merely due to compensating errors[25]. Experiments are currently in progress applying these tests to the deaquation–anation of members of the $[Co(NH_3)_5(H_2O)]X_3$ series.

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