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EFFECTS OF PROCEDURAL VARIABLES ON THE DEAQUATION—ANATION OF AQUAPENTAAMMINECOBALT(III) SALTS

H. EUGENE LEMAY, JR.

Department of Chemistry, University of Nevada, Reno, NV 89557 (U.S.A.)

MICHAEL W. BABICH

Department of Chemistry, Florida Institute of Technology, Melbourne, FL 32901 (U.S.A.)

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ABSTRACT

A kinetic investigation of the solid-phase deaquation—anation reactions of $[Co(NH_3)_5H_2O]X_3$, where $X^- = Cl^-$, Br^- or NO_3^- is reported. Because of the poor agreement in activation parameters reported in the literature for this series of reactions, this investigation includes a study of the effects of several experimental factors on these parameters. The factors studied include particle size, sample size, atmosphere, heating rate and compaction of the sample. Both isothermal and non-isothermal experiments are utilized and an investigation of the isokinetic relationship for these reactions is included. There is a linear correlation of $\Delta H^{\ddagger}$ with $\Delta S^{\ddagger}$ in the isothermal studies giving an isokinetic temperature of 362 ± 7 K. The results of this study suggest that previous assignment of an S_N2 type mechanism for this series based on variations in activation parameters is unwarranted.

INTRODUCTION

The solid-phase deaquation—anation reaction of aquapentaamminecobalt(III)

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

has been studied by several groups since 1959 [1—11]. The reaction appears to exhibit an entering group (or anion) effect. For example, the activation energies for this reaction are reported to vary with the anion [4,10]. Furthermore, the perchlorate salt does not undergo anation [5,6], although the perrhenate salt does [7]. Variations in activation parameters with anion are also reported for the deaquation—anation of aquapentaamminechromium(III) [12—14] and aquapentaammineruthenium(III) [15] salts. The usual interpretation of this apparent anion effect is that it signifies an S_N2 (or associative) ligand exchange between the leaving H_2O and the entering anion, X [5,6,12—15]. More recently, a defect-diffusion model has also been proposed to explain this anion effect [16].

In general, the activation parameters reported for such deaquation—anation reactions by different research groups are in poor agreement [17]. This fact suggests that the magnitudes of these activation parameters are influenced by experimental factors that have not been specified or controlled in experiments to date. Such factors could include particle size, sample-bed thickness, the packing of the solid on the sample holder, and the nature of the atmosphere around the sample. The existence of an isokinetic relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the deaquation—anation of both aquapentaamminechromium(III) [17] and aquapentaammineruthenium(III) [18] salts could also arise from such environmental or experimental factors. Thus, trying to assign mechanisms to these reactions on the basis of activation energies is a questionable practice.

In the present paper, we wish to report a kinetic investigation of the deaquation—anation of the chloride, bromide, and nitrate salts of aquapentaamminecobalt(III) that includes a study of the effects of experimental conditions on the activation parameters. This study involves both isothermal and non-isothermal experiments, and includes an investigation of the isokinetic relationship for these reactions.

EXPERIMENTAL

$[Co(NH_3)_5Cl]Cl_2$, prepared as described elsewhere [19], was the starting material for all $Co(NH_3)_5(H_2O)^{3+}$ salts. For each preparation, $[Co(NH_3)_5Cl]Cl_2$ was dissolved in a minimum of hot water to which a few drops of aqueous ammonia were added to promote base hydrolysis. The resulting red solution was then cooled in ice and the appropriate concentrated acid (HCl, HBr or HNO_3) added to precipitate the desired $Co(NH_3)_5(H_2O)^{3+}$ salt. This product was recrystallized, washed with absolute alcohol, then ether, and allowed to air dry.

Efforts to control particle size during precipitation by varying the temperature and speed at which the acid was added met with very limited success. Almost all preparations passed 200 mesh; in a few cases, a product was obtained that passed 60 mesh but was retained by a 100 mesh seive.

The enthalpy changes accompanying deaquation—anation were measured on a Perkin-Elmer Differential Scanning Calorimeter Model DSC-1B. The instrument was standardized against indium and all measurements were made on 10—20 mg samples at a heating rate of 5° min^{-1} under flowing N_2 gas (ca. 25 ml min^{-1}). The following enthalpy changes were measured: $[Co(NH_3)_5(H_2O)]Br_3$, $\Delta H = 5.81 \pm 0.26$ kcal $mole^{-1}$; $[Co(NH_3)_5(H_2O)]Cl_3$, $\Delta H = 4.63 \pm 0.10$ kcal $mole^{-1}$; $[Co(NH_3)_5(H_2O)](NO_3)_3$, $\Delta H = 5.91 \pm 0.10$ kcal $mole^{-1}$ (error limits are average deviations from the mean for three determinations). These results are in good agreement with those reported elsewhere [9,11].

Both isothermal and non-isothermal kinetic studies were performed on an automatic recording thermobalance which has been described elsewhere [20]. Unless otherwise stated, measurements were made on 10 mg (±1 mg) samples at 0.5 Torr.

RESULTS AND DISCUSSION

Isothermal studies

Isothermal kinetic studies were performed on the chloride, bromide, and nitrate salts of $[Co(NH_3)_5(H_2O)]^{3+}$. The iodide was not investigated because the dequation—anation reaction is accompanied by electron transfer between I^- and Co(III) with resultant loss of I_2 and NH_3 as well as H_2O from the sample.

The isothermal mass loss was found to fit the contracting-cube rate law, $(1 - \alpha)^{1/3} = 1 - kt$, typically over the range $\alpha = 0.15$—0.75. However, the "first-order" or random nucleation rate law, $-\log(1 - \alpha) = kt + c$, gave a slightly better fit (that is, over a longer range of α) on some occasions. Because of the small particle sizes involved, kinetic models were not tested by optical microscopy. The isothermal activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, that we cite in this paper were obtained using rate constants from the contracting-cube rate law. Wendlandt and Bear used the "first-order" rate law in their studies [4].

At least six rate constants were used to obtain each pair of activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$. Typically kinetic runs were made from 60 to 90°C. The largest set of data spanned eleven kinetic runs from 50 to 95°C. The effects of different sample preparations, entering group, and particle size were examined in a set of eleven determinations of activation parameters. When procedural variables (sample-bed thickness, particle size, and atmosphere) were held constant, the entering group seemed to be an insignificant variable. Table 1 compares the results for Cl^-, Br^- and NO_3^-. The data suggest that $\Delta H^\ddagger \simeq 20$ kcal mole^{-1} and $\Delta S^\ddagger \simeq 17$ e.u., regardless of anion.

The activation parameters were affected by particle size; $\Delta H^\ddagger$ and $\Delta S^\ddagger$ increased as particle size increased. Whereas the samples of $[Co(NH_3)_5(H_2O)](NO_3)_3$ that passed 200 mesh gave $\Delta H^\ddagger = 20.0 \pm 0.5$ kcal mole^{-1} and $\Delta S^\ddagger = -18.3 \pm 0.9$ e.u. (Table 1), two 60—100 mesh samples gave $\Delta H^\ddagger = 24.9 \pm 0.5$ kcal mole^{-1} and $\Delta S^\ddagger = -4.1 \pm 1.8$ e.u. Mechanical grinding of these larger particles caused a reduction in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ to give $\Delta H^\ddagger = 20.5$ kcal mole^{-1} and $\Delta S^\ddagger = -17.2$ e.u.

The activation parameters, obtained in these isothermal studies as well as

TABLE 1

Activation parameters obtained isothermally for the deaquation—anation of $[Co(NH_3)_5(H_2O)]X_3$ [a]

Anion (X^-)	$\Delta H^\ddagger$ (kcal mole^{-1})	$\Delta S^\ddagger$ (e.u.)
Cl^-	21.3 ± 1.0	—15.0 ± 2.0
Br^-	20.3 ± 1.3	—17.2 ± 3.6
NO_3^-	20.0 ± 0.5	—18.3 ± 0.9

[a] Error limits are average deviations from the mean for two determinations for Cl^- and NO_3^-, and four determinations for Br^-. All samples passed 200 mesh.

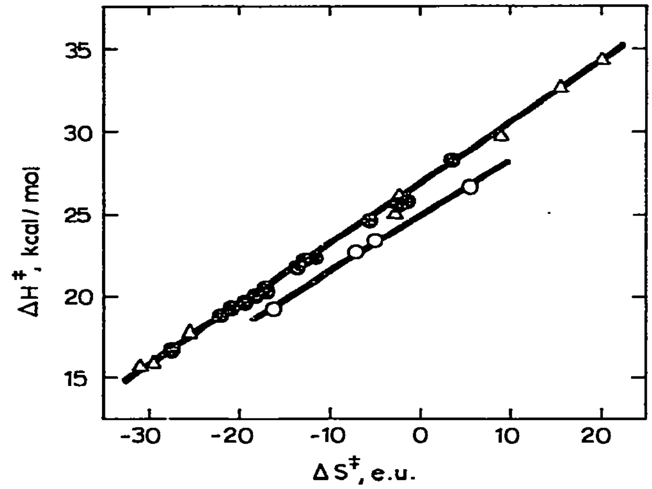

Fig. 1. Isokinetic plots for the deaquation—anation of compounds of the type $[M(NH_3)_5(H_2O)]X_3$, where M = Cr (△), Co (●), or Ru (◎) and $X^- = Cl^-, Br^-, I^-$, or NO_3^-. All data are from isothermal studies.

those obtained by Wendlandt and Bear [4] fit a linear isokinetic plot, Fig. 1 *. The slope of this plot is $T_i = 362 \pm 7$ K and the intercept is 26.6 ± 0.1 kcal $mole^{-1}$ (where the error limits are standard deviations); the correlation coefficient is $R = 0.9980$. These results for $[Co(NH_3)_5(H_2O)]X_3$ are statistically indistinguishable from those of the corresponding chromium complexes (Fig. 1) [17]. However, the isokinetic plot for $[Ru(NH_3)_5(H_2O)]X_3$ complexes differs slightly (Fig. 1) [18].

The isokinetic relationship can arise from random errors in $\Delta H^{\ddagger}$ that are correlated with errors in $\Delta S^{\ddagger}$ (compensating errors); it can also arise when differences in activation parameters in a series are due to either substituent effects ("structural" or "chemical" factors) or to differences in reaction conditions (procedural factors). The fact that the same isokinetic plot is obtained for both $[Co(NH_3)_5(H_2O)]X_3$ and $[Cr(NH_3)_5(H_2O)]X_3$ complexes, regardless of entering anion, X^-, suggests to us that the isokinetic relationship is not due merely to chemical factors. Exner [21] has pointed out that if an isokinetic relationship arises from chemical causation, a linear correlation should occur between rate constants at two different temperatures through the series. Such a correlation of rate constants should provide a statistically more rigorous test for chemical causation than the $\Delta H^{\ddagger} - \Delta S^{\ddagger}$ correlation itself. In the present studies, no correlation was observed between k_{60° and k_{90° values.

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* The activation parameters in ref. 4 were redetermined by least-squares analysis of a plot of $\log(k/T)$ vs. $1/T$ to give $\Delta H^{\ddagger} = 16.8$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = -27.6$ e.u. for Cl^-, $\Delta H^{\ddagger} = 26.0$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = 1.6$ e.u. for Br^-, and $\Delta H^{\ddagger} = 28.3$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = 3.7$ e.u. for NO_3^-.

TABLE 2

Effect of pressure on the deaquation—anation of $[Co(NH_3)_5(H_2O)](NO_3)_3$ [a]

Pressure (Torr)	$\Delta H^{\ddagger}$ (kcal $mole^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)
0.5	21.7	—13.8
65	28.3	3.0
227	26.7	—1.2
491	30.4	9.1

[a] All results at a heating rate of 5° min^{-1}.

Non-isothermal studies

To further test the effects of procedural variables on activation parameters, a series of 22 non-isothermal kinetic studies were performed. In these studies, the effects of particle size, sample mass, sample packing, heating rate, and pressure were investigated. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were evaluated from TG curves using the procedure of McCallum and Tanner [22,23]. The "first-order" rate law gave a better linear fit to the Arrhenius equation than the contracting cube rate law, and the activation parameters based on the first-order rate expression are the ones cited in this article. Although the choice of rate law influences the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, it does not alter the effect that changes in procedural variables have on activation parameters.

It was found that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ increased with an increase in the pressure of the atmosphere surrounding the sample, Table 2. Consistent with these results, kinetic evaluation of DSC curves obtained at 670 Torr under flowing N_2 generally gave activation energies above 30 kcal $mole^{-1}$. Values reported elsewhere from TG experiments under a dynamic nitrogen atmosphere range from 31 to 37 kcal $mole^{-1}$ [10].

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were found to decrease with increasing heating rate (1° min^{-1} to 10° min^{-1}), and with increasing sample mass (5 mg to 20 mg). For example, at 1° min^{-1}, 10 mg of a sample gave $\Delta H^{\ddagger} = 34.3$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = 23.1$ e.u., while at 5° min^{-1}, the same sample gave $\Delta H^{\ddagger} = 26.1$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = -3.5$ e.u. At 5° min^{-1}, 5 mg of another sample gave $\Delta H^{\ddagger} = 28.0$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = 1.2$ e.u., while 20 mg of that sample gave $\Delta H^{\ddagger} = 24.1$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = -9.5$ e.u. Heating rate and sample mass have been reported recently to have the same effects on the dehydration of $CaC_2O_4 \cdot H_2O$ [24] *. The rate of dehydration of $Sr(OH)_2 \cdot 8\,H_2O$ has also been found to decrease with increasing sample mass [25].

Compaction of the sample also causes an increase in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. For example, at 5° min^{-1}, 10 mg of a compacted sample gave $\Delta H^{\ddagger} = 30.9$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = 10.1$ e.u. Loosely packed samples consistently gave lower activation parameters. Non-isothermal results also agreed with isothermal results in indicating that activation parameters increased in magnitude with increasing particle size.

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* From the data in the $CaC_2O_4 \cdot H_2O$ study, isokinetic behavior is also found. In this study, only procedural parameters are varied.

The effects of atmosphere, heating rate, sample mass, and compaction could arise from the same cause. For example, the temperature variation in rate could be strongly dependent on the pressure of water vapor near the particles. Water vapor could affect the rate of the back-reaction in the reaction interface by a mass-action effect. However, some self-cooling could be involved in the reactions, which are slightly endothermic. The water vapor will then affect the thermal conductivity of the surrounding gases, causing variations in the extent of self-cooling.

In any regard, the present experiments indicate that the activation parameters for the deaquation—anation of $[Co(NH_3)_5(H_2O)]X_3$ salts are highly dependent on reaction conditions. Indeed, $\Delta H^\ddagger$ values ranging from 20 to 35 kcal were obtained, depending on experimental conditions. Nevertheless, the activation parameters gave a linear isokinetic plot (Fig. 2). The slope of this plot is $T_i = 375 \pm 12°$, and the intercept is 26.9 ± 0.3 kcal mole^{-1}. This result seems to substantiate the idea that the isokinetic relationship can arise from variations in procedural variables. The slopes and intercepts for the isokinetic plots obtained from isothermal and from non-isothermal kinetics agree within experimental error (one standard deviation).

General conclusions

Differences reported in the literature for activation parameters for the deaquation—anation of $[Co(NH_3)_5(H_2O)]X_3$ salts cannot be ascribed either to differences in the entering groups, X^-, or to differences in crystal structures. The effects of procedural variables obscure effects due to these structural variables. When procedural variables are held constant, activation parameters for different salts agree within experimental error. This could mean that an S_N1 (dissociative) mechanism is involved in the ligand exchange process. However, this interpretation leaves unexplained the fact that the ClO_4^- salt does not undergo anation. In general, we agree with the notion

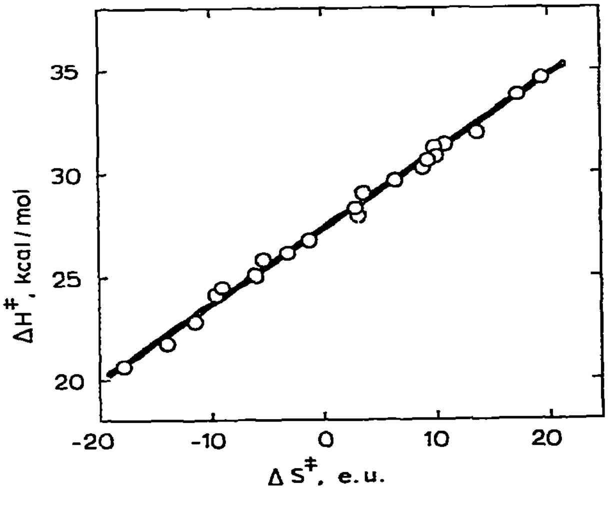

Fig. 2. Isokinetic plot for the non-isothermal deaquation—anation of $[Co(NH_3)_5(H_2O)]X_3$, where $X^- = Cl^-$, Br^-, or NO_3^-.

that lattice defects may control the rates of these reactions [16]. However, the generation of such defects may be strongly influenced by the partial pressure of water vapor near the sample. Thus, while the present data indicates that assignment of an S_N2 mechanism based on variations in activation parameters is unwarranted, it does not allow us to assign any other mechanism unambiguously.

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