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THE TG, DTG, DTA, AND EC OF SOME $[Co(NH_3)_5H_2O]X_3$ AND $[Co(NH_3)_5X]X_2$ COMPLEXES

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ABSTRACT

The EC, DTA, TG, and DTG curves of the $[Co(NH_3)_5H_2O]X_3$ and $[Co(NH_3)_5X]X_2$ ($X^- = Cl$, Br, I, and NO_3) complexes were determined. The EC data reveal the deaquation and partial fusion and dissociation reactions. High resolution DTA data clearly indicated a multi-step deaquation reaction in which a liquid water phase is present. This behavior is similar to the deaquation of certain metal salt hydrates previously described. The TG and DTG curves show the deaquation and dissociation reactions. In the case of the latter technique, the decrease in thermal dissociation temperatures follows the order: chloride > nitrate > bromide > iodide.

INTRODUCTION

The deaquation and anation reactions of $[Co(NH_3)_5H_2O]X_3$ (X^- is Cl, Br, I, and NO_3), as represented by the equation

$$[Co(NH_3)_5H_2O]X_3\ (c) \xrightarrow{\Delta} [Co(NH_3)_5X]X_2\ (c) + H_2O\ (g) \qquad (1)$$

have been investigated by a number of workers[1]. More recent investigations include high temperature reflectance spectroscopy[2,3] kinetics[4], and thermochemical[5,6] studies.

The thermochemistry of these complexes is extremely interesting because it indicates that at least two reactions are involved. At atmospheric pressure, the deaquation reaction generally consists of a single DTA endothermic peak, in the temperature range from 75 to 150 °C[5,7]. Using sealed capillary sample tubes, however, the DTA curve for this same reaction consists of an exothermic peak[5]. This rather unexpected result was explained on the basis of two reactions taking place in the sealed tube: (*a*) A $Co^{3+}\cdots OH_2$ bond-breaking (deaquation) reaction, which is endothermic; and (*b*) a $Co^{3+}\cdots X$ bond-making (anation), reaction, which is exothermic. It is obvious that reaction (*b*) is larger than reaction (*a*) in the sealed tube, but at atmospheric pressure, the large endothermic ΔH_v of water masks these effects so that only an endothermic peak is observed. It should be noted that the experimental ΔH values[5] for the deaquation and anation reactions agreed well with calculated values[6].

In order to obtain additional information on the $[Co(NH_3)_5H_2O]X_3$ and

$[Co(NH_3)X]X_2$ complexes, the compounds were investigated by electrical conductivity (EC), high resolution differential thermal analysis (DTA), thermogravimetry (TG), and differential thermogravimetry (DTG).

EXPERIMENTAL

$[Co(NH_3)_5H_2O]X_3$ complexes — The compounds, $[Co(NH_3)_5H_2O]X_3$ (X^- is Cl, Br, I, and NO_3), were prepared as previously described[8]. The corresponding $[Co(NH_3)_5\ X]X_2$ complexes were prepared from the above by thermal deaquation of a slurry at 60 or 100°C. The compounds were analyzed for halide content by argentometric titration using potentiometric end-point detection. Coordinated water was obtained by mass-loss on the thermobalance or by drying in an oven (120°C) to constant weight. The cobalt contents of the complexes were determined by residue analysis (as Co_3O_4) using the thermobalance. All of the compounds were of a purity of better than 99%, as determined by the above analysis.

Thermobalance — The thermobalance consisted of a Cahn Model RG Electrobalance converted to a thermobalance by the addition of a small furnace and sample holder. The outputs from the balance and a chromel–alumel thermocouple located in the furnace chamber were recorded on a Sargent two-pen strip-chart potentiometric recorder. The mass-curve was recorded as percent mass-change using the variable span control[9]. The DTG curve was obtained by differentiation of the balance signal by means of a Harrop analog computer, and recorded on another Sargent recorder. In each case, the sample mass was 10 mg and a furnace heating rate of 5°C/min was employed. For the nitrate complex, a sample size of 5 mg was used because of the explosive dissociation of this compound. All thermal decomposition reactions were carried out in a dynamic nitrogen gas atmosphere at a flow-rate of 50 ml/min.

DTA apparatus — The high resolution DTA apparatus consisted of a DuPont Thermograph block-type furnace and sample holder. The ΔT signal was amplified by a Leeds and Northrup low-level microvolt d.c. amplifier and recorded on a Hewlett–Packard X–Y recorder. Sample sizes ranged in mass from 5 to 10 mg, while a heating rate of 5°C/min was employed.

EC apparatus — The EC apparatus has been previously described[10].

RESULTS AND DISCUSSION

The electrical conductivity curves of the $[Co(NH_3)_5H_2O]X_3$ and $[Co(NH_3)_5X]X_2$ complexes are shown in Fig. 1.

For the $[Co(NH_3)_5H_2O]X_3$ complexes, curve peaks were observed for the deaquation reactions in the temperature range 75–135°C, and also in the temperature region at which decomposition of the complexes began. In the case of the $[Co(NH_3)_5X]X_2$ complexes, only the latter-type curve deviations were observed. The EC curve peaks during the deaquation reactions indicate the presence of a liquid water phase which caused the increase in electrical conductivity of the compounds. Such an increase in conductivity has previously been observed for the metal salt hydrates, $CuSO_4 \cdot 5H_2O$[10,11], $BaX_2 \cdot 2H_2O$[10,12], and $CoX_2 \cdot 6H_2O$[13]. The increase in electrical conductivity at the higher temperatures is due to the fusion and decomposition of the $[Co(NH_3)_5X]X_2$. Because of the large increase in conductivity, the curves went off the scale of the recorder chart and are not reproduced here.

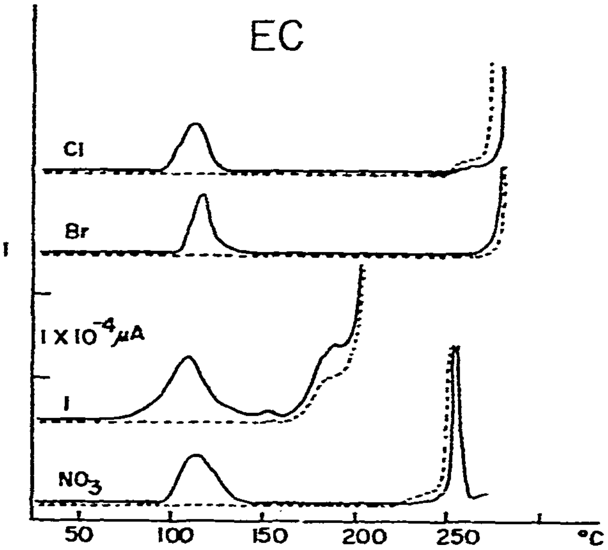

Fig. 1. Electrical conductivity curves of $[Co(NH_3)_5H_2O]X_3$ and $[Co(NH_3)_5X]X_2$ complexes; (————) $[Co(NH_3)_5H_2O]X_3$; (– – – – – –) $[Co(NH_3)_5X]X_2$ complexes; anions indicated.

There was little anion effect shown in the deaquation reaction of the $[Co(NH_3)_5H_2O]X_3$ complexes. The iodide complex deaquated at a lower temperature and over a larger temperature range than the other complexes. However, there was a much greater anion effect exhibited during the decomposition reactions, in which the iodide complex was the least stable. It is to be expected that the chloride and bromide complexes decompose by similar mechanisms while the iodide and nitrate decompose in a different manner. The nitrate complex, because of the presence of oxidizing and reducing groups, decomposes quite rapidly but in a different manner from that of the iodide complex. In the latter, the iodide ion probably competes with the ammonia molecule for the reduction of the cobalt(III) ion to cobalt(II)[14]. There was no evidence from the EC curves of the presence of the anation reaction which occurs simultaneously with the deaquation reaction[5].

The high-resolution DTA curves are shown in Fig. 2. For the chloride, bromide and iodide complexes, two endothermic peaks were observed in each curve. The first peak, in the temperature range 80–120 °C, was due to the deaquation reaction, while the second endothermic peak, in the temperature range 200–300 °C was caused by the decomposition reaction. As expected, the second peak in the nitrate complex was exothermic. The deaquation peaks for the chloride, bromide, and nitrate complexes indicate a multi-step reaction. Shoulder peaks were observed in all of the

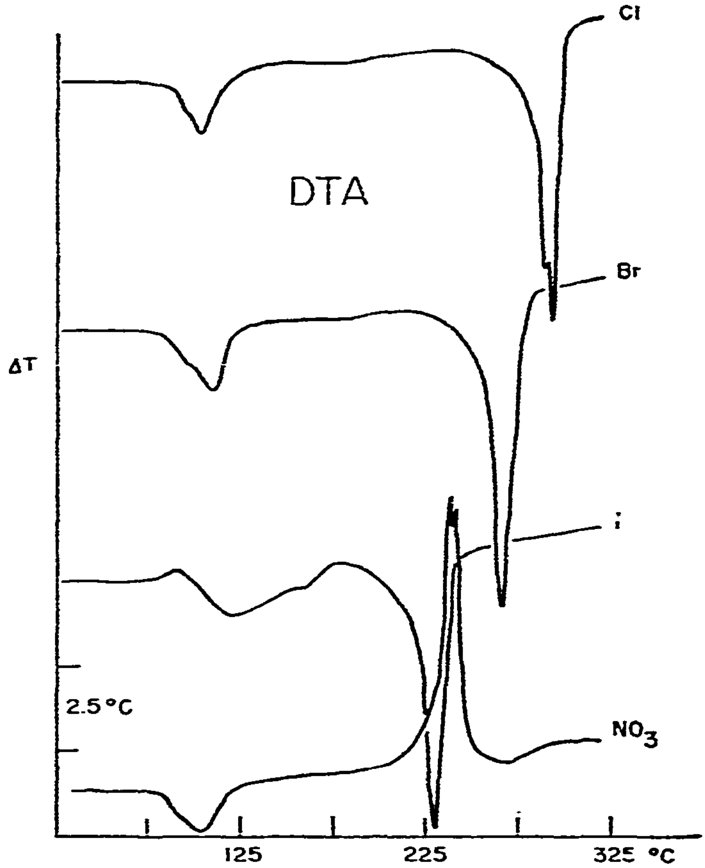

Fig. 2. DTA curves of $[Co(NH_3)_5H_2O]X_3$ complexes. Anions are indicated.

curves at about 100°C. The presence of these shoulder peaks indicate a deaquation reaction similar to that previously observed for other metal salt hydrates[10-13]; namely, the formation of a liquid water phase followed by the vaporization reaction. These reactions are probably of the type

$$[Co(NH_3)_5\,H_2O]X_3\,(c) \rightarrow [Co(NH_3)_5X]X_2\,(c) + H_2O\,(l) \qquad (2)$$

$$H_2O\,(l) \rightarrow H_2O\,(g) \qquad (3)$$

The shoulder peaks have not been observed on lower-resolution DTA instruments[5]. It is most likely that the anation reactions take place simultaneously with the bond-breaking deaquation reactions. As was previously observed by the sealed-tube DTA data[5], the anation reaction is exothermic and can easily be masked by the highly endothermic vaporization reaction (3) indicated above.

The deaquation of the iodide complex appears to be more complicated than the other compounds. An initial exothermic reaction is indicated followed by a larger, endothermic reaction. This is rather surprising because the ΔH of reaction[5] for the iodide complex was -1.7 kcal/mole compared to -4.6 kcal/mole for the chloride complex. The calculated[6] value for this reaction is -3.6 ± 2.5 kcal/mole for both compounds.

The TG and DTG curves of the $[Co(NH_3)_5H_2O]X_3$ and $[Co(NH_3)_5X]X_2$ complexes are given in Figs. 3 and 4, respectively.

The TG curves of the two series of complexes are similar except for the loss of water in the low-temperature region for the $[Co(NH_3)_5H_2O]X_3$ complexes. This water-loss takes place in one step, as seen from the decomposition curve. The decomposition of the $[Co(NH_3)_5X]X_2$ complexes proceeds *via* a multi-step process. The intermediate in the curve is the mixture, in the case of the chloride and bromide complexes, of $CoX_2 + (NH_4)_2CoX_4$. Dissociation of $(NH_4)_2CoX_4$ then yields the volatile NH_4X and the CoX_2 which reacts with air to give the oxide, Co_3O_4, or a mixture of the oxide plus CoX_2.

The nitrate complex dissociates explosively to yield Co_3O_4. If a small enough sample size is used, *e.g.* 5 mg, the amount of Co_3O_4 obtained is stoichiometric; too large a sample size results in loss of the oxide residue from the sample container.

There is a decided anion effect in the initial thermal decomposition temperares of the $[Co(NH_3)_5X]X_2$ complexes. The order appears to be chloride > nitrate > bromide > iodide.

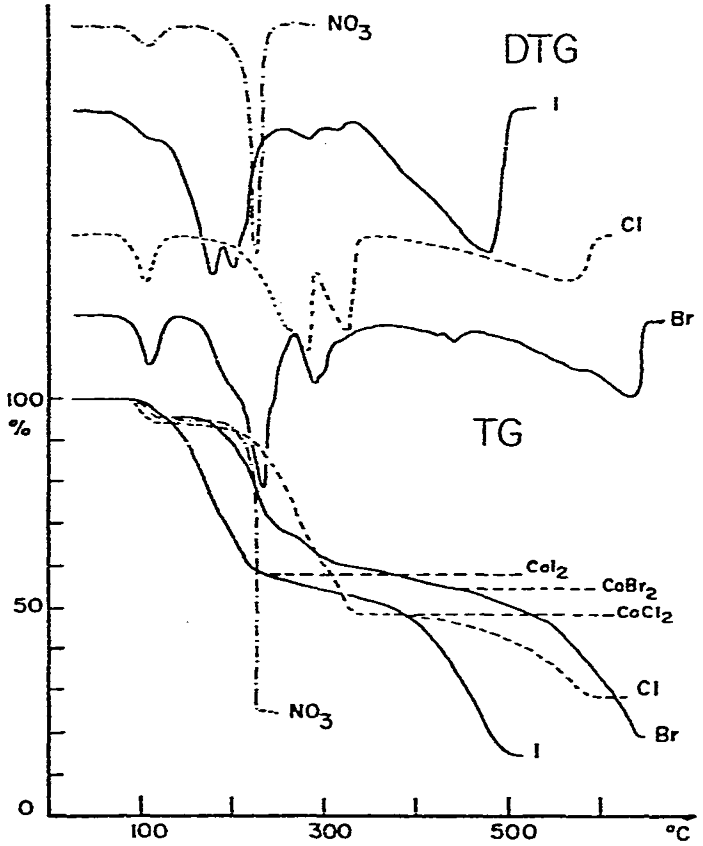

Fig. 3. TG and DTG curves of $[Co(NH_3)_5H_2O]X_3$ complexes. Anions are indicated.

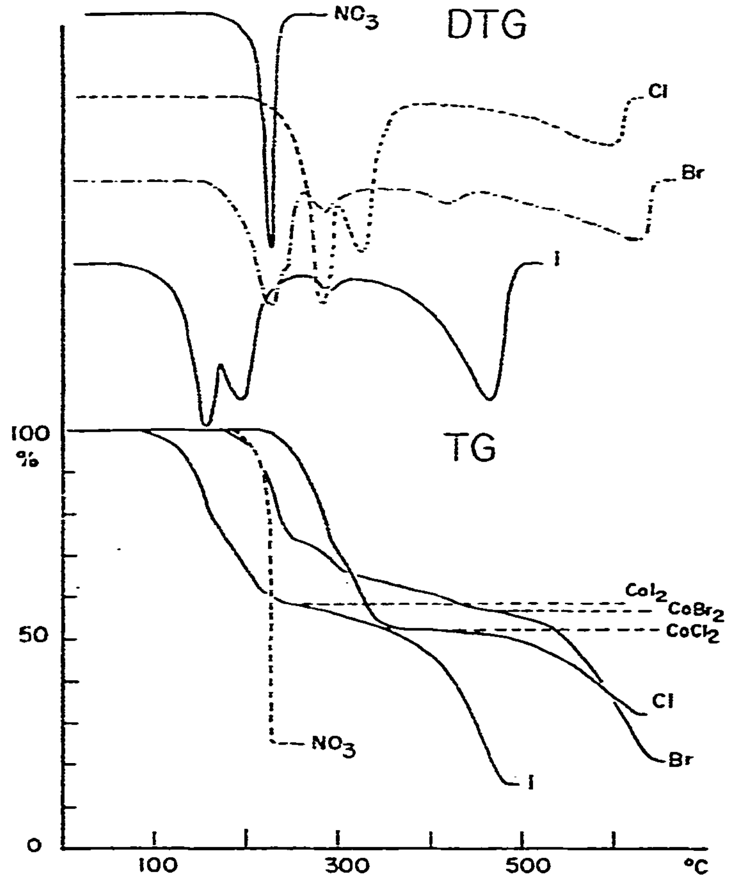

Fig. 4. TG and DTG curves of $[Co(NH_3)_5X]X_2$ complexes. Anions are indicated.

As discussed earlier, the decomposition mechanism is different from that of the other two halide complexes and this perhaps accounts for the lower decomposition tempera-tuture.

The DTG curves reveal features in the TG curves somewhat more clearly. Small inflections in the latter curves are seen as definite peaks in the DTG curves.

ACKNOWLEDGEMENT

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