Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

DIFFERENTIAL THERMAL ANALYSIS OF AMMONIUM TETRAFLUOROBORATE AND HEXAMMINONICKEL- AND TETRAMMINOZINC-TETRAFLUOROBORATE*

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(Received March 15th, 1972)

ABSTRACT

Differential thermal analysis (DTA) has been used to investigate the thermal decomposition of NH_4BF_4, $Ni(NH_3)_6(BF_4)_2$ and $Zn(NH_3)_4(BF_4)_2$ over a temperature range of 25–500 °C and heating rates of 5, 10 and 25 °C min^{-1}. The DTA patterns show the effects of dehydration, desorption, dissociation, vaporization, and in one case, NH_4BF_4, solid-solid transition. An evaluation of change in furnace atmosphere and heating rate are also reported.

INTRODUCTION

This work is part of a continuing study of tetrafluoroborates[1–4]. It was shown previously that sharp, reversable endothermic peaks were observed at the rhombic-to-cubic transition temperature of the alkali metal tetrafluoroborates, while later it was found that calcium, cobalt, copper and nickel tetrafluoroborate do not undergo such solid–solid transition in the temperature range of 25–500 °C.

EXPERIMENTAL PROCEDURE

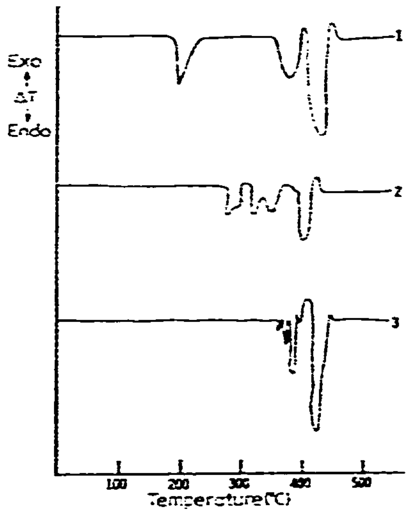
This study was performed using a commercial differential thermal analysis system manufactured by Fisher Scientific Company. The instrumental layout and the general analytical method have been given previously[1–4]. Materials used for this investigation were purchased from Alfa Inorganics and were 99%+ pure based on boron analysis. The compounds were ground to 100–200 mesh just prior to use and were used without any prior drying.

RESULTS

In the DTA scans, made at 5 °C min^{-1} and under a flowing argon atmosphere, shown in Fig. 1, the rhombic to cubic transition ($S_1 \rightarrow S_2$) for NH_4BF_4 occurred at

*Presented before the Third Annual Meeting of the North American Thermal Analysis Society in Waco, Texas, on February 7–8, 1972.

189°C and the BF_3 liberation appeared at 400°C. For the $Ni(NH_3)_6(BF_4)_2$ and $Zn(NH_3)_4(BF_4)_2$ there were no $S_1 \rightarrow S_2$ transitions noted. The peaks between 286°C and 362°C for $Ni(NH_3)_6(BF_4)_2$ and 370°C and 393°C for $Zn(NH_3)_4(BF_4)_2$ were believed due to the dissociation and liberation of NH_3. Finally for $Ni(NH_3)_6(BF_4)_2$ the BF_3 was liberated at 398°C and for $Zn(NH_3)_4(BF_4)_2$ the BF_3 was liberated at 403°C.



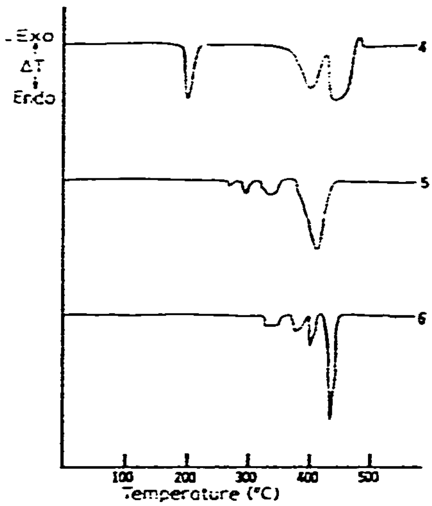
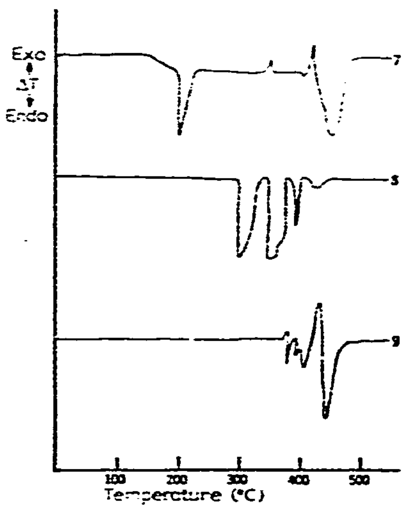


Fig. 1. DTA curves recorded at a heating rate of 5°C min^{-1} in argon.

Fig. 2. DTA curves recorded at a heating rate of 5°C min^{-1} in static air.

With static air (Fig. 2) there was an increase in the $S_1 \rightarrow S_2$ transition temperature of NH_4BF_4 to 194°C, while the BF_3 liberation was at 403°C. The $Ni(NH_3)_6(BF_4)_2$



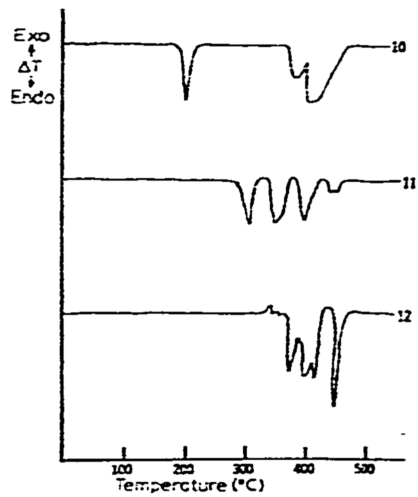


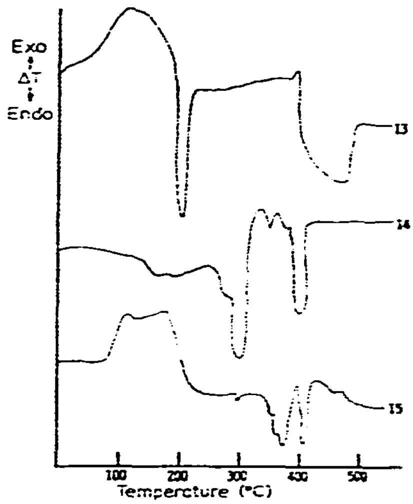
Fig. 3. DTA curves recorded at a heating rate of 10°C min^{-1} in argon.

Fig. 4. DTA curves recorded at a heating rate of 10°C min^{-1} in static air.

and the $Zn(NH_3)_4(BF_4)_2$ gave no $S_1 \rightarrow S_2$ transitions under these conditions. The peaks between 225°C and 320°C for $Ni(NH_3)_6(BF_4)_2$ and between 330°C and 372°C were believed due to the liberation of NH_3 while the peaks at 385°C and 396°C, respectively, were due to the liberation of BF_3.

The DTA curves made at 10°C min^{-1} (Figs. 3 and 4) showed little if any change in the general shape and position of the peaks. The runs made with flowing argon on NH_4BF_4 had the $S_1 \rightarrow S_2$ transition at 190°C and the liberation of BF_3 at 414°C and 420°C. Again there was no $S_1 \rightarrow S_2$ transition for either $Ni(NH_3)_6(BF_4)_2$ or $Zn(NH_3)_4(BF_4)_2$. The liberation of NH_3 for $Ni(NH_3)_6(BF_4)_2$ appeared as a series of peaks starting at 285°C and ending at 360°C, while the $Zn(NH_3)_4(BF_4)_2$ liberated its NH_3 as a series of peaks beginning at 365°C and ending at 394°C. The BF_3 was evolved at 390°C for $Ni(NH_3)_6(BF_4)_2$ and at 405°C for the $Zn(NH_3)_4(BF_4)_2$.

With static air and 10°C min^{-1} for NH_4BF_4 the $S_1 \rightarrow S_2$ transition appeared at 190°C and the BF_3 evolved at 389–414°C. NH_3 was evolved at 293°C to 375°C and the BF_3 at 392°C for $Ni(NH_3)_6(BF_4)_2$ while for $Zn(NH_3)_4(BF_4)_2$ the NH_3 was evolved over a range from 347°C to 408°C with the BF_3 liberated at 414°C. As before, the metal salts did not exhibit a $S_1 \rightarrow S_2$ transition.



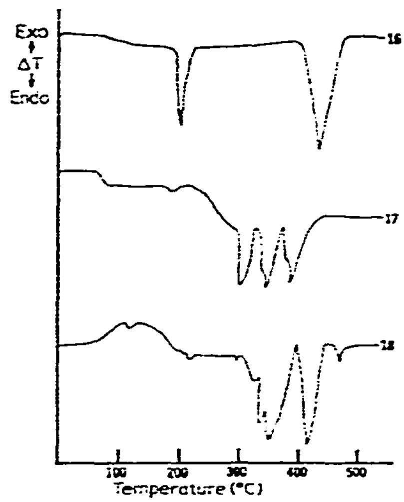


Fig. 5. DTA curves recorded at a heating rate of 25°C min^{-1} in argon.

Fig. 6. DTA curves recorded at in heating rate of 25°C min^{-1} in static air.

Finally the DTA curves shown in Figs. 5 and 6 were run at 25°C min^{-1} with static air and flowing argon respectively. With flowing argon, the $S_1 \rightarrow S_2$ transition of NH_4BF_4 appeared at a temperature of 185°C while the evolution of BF_3 appeared at range 387–390°C. As before no $S_1 \rightarrow S_2$ transition was seen for either the $Ni(NH_3)_6(BF_4)_2$ or $Zn(NH_3)_4(BF_4)_2$ but the liberation of NH_3 was clearly indicated at 270–365°C for the nickel salt and 295–395°C for the zinc salt. The BF_3 was evolved at a temperature of 390°C for the $Ni(NH_3)_6(BF_4)_2$ and 400°C for the $Zn(NH_3)_4(BF_4)_2$.

In the runs made in static air at 25 °C min^{-1}, the NH_4BF_4 $S_1 \rightarrow S_2$ transition appeared at 190 °C and the BF_3 was evolved at 397 °C. The $Ni(NH_3)_6(BF_4)_2$ evolved NH_3 between 295 °C and 375 °C, with BF_3 evolution at 400 °C. Lastly, the $Zn(NH_3)_4$-$(BF_4)_2$ evolved NH_3 between 295 °C and 395 °C with the BF_3 being liberated at 400 °C.

DISCUSSION

As has been noted that the NH_4BF_4 of this series has the rhombic to cubic $S_1 \rightarrow S_2$ transition and it was found to take place at 189 ± 5 °C. The liberation of the NH_3 from the $Ni(NH_3)_6(BF_4)_2$ and from the $Zn(NH_3)_4(BF_4)_2$ was found to take place over a range from 270 °C to 395 °C with not much variance in the onset peak or intermediate peaks with regard to the conditions of obtaining the DTA data.

The liberation of BF_3 in all three samples occurred over a range from 385 °C to 420 °C, and when a flowing-argon atmosphere was used, there was an exotherm before the endotherm which was not apparent in the static air runs.

As seen from the DTA curves, the type of atmosphere had little, if any, effect on the $S_1 \rightarrow S_2$ transition.

In all cases the nickel salt liberated NH_3 at a lower temperature than the zinc salt, and liberated BF_3 at a lower temperature. The exact cause for this is yet unknown but is most likely related to differences in bond strength and/or type of coordination that occurs between the metal and the BF_4 ion.

ACKNOWLEDGEMENT

The authors wish to acknowledge the financial support of the Robert A. Welch Foundation, Houston, Texas.

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