Investigating the synthesis and thermal stability of barium tetrafluorobromate (III)

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Abstract

The barium fluorobromate (III) has been obtained as the product of interaction between barium fluoride and bromine (III) trifluoride. The heat of formation of Ba(BrF₄)₂ has been found by the isothermal calorimetry method. By the TG/DT analysis the thermal stability of Ba(BrF₄)₂ has been researched. It has been found that this compound was mostly stable in the atmosphere or argon up to 250°C.

Keywords: Synthesis ; bromine trifluoride ; fluorohalogenates ; TG/DT ; calorimetry ; fluorine

1. Introduction

Nowadays the chemistry of bromine trifluoride (III) attracts more and more attention, but because of its strong corrosive and oxidizing activity, the usage of this reagent is still limited. It is quite interesting to consider alkali and alkali-earth metals fluorobromates as solid state analogues of BrF₃. The common formulae of these compounds looks like MeBrF₄ for alkali metals fluorobromates and Me(BrF₄)₂ for alkali-earth metals fluorobromates. Me is the corresponding alkali or alkali-earth metal. These compounds are much milder and much more selective reagents in the field of inorganic and organic chemistry in comparison with BrF₃. Products of interaction of BrF₃ and alkali metals fluorides are well known, but there is not enough data regarding such compounds of BrF₃ and alkali-earth metals fluorides. It is only known that it is possible to synthesize Ba(BrF₄)₂ using barium chloride and bromine (III) trifluoride. It is also known that Ba(BrF₄)₂ is the only stable compound for all alkali-earth metals in this case.

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That’s why the research of synthesis, properties, and reactivity of this compound is very important for general chemistry.

2. Experimental

2.1. Equipment and methods

To prepare 1g of Ba(BrF₄)₂ 0.39 g (2.22 mmol, 1 eq) of BaF₂ have been placed into a PTFE vessel and layered with 5 g of Freon-113. Then 0.61 g (4.46 mmol, 2.01 eq) of liquid BrF₃ have been added via a dropping funnel under vigorous stirring. Freon-113 has been replaced as needed. The total yield of dry Ba(BrF₄)₂ was 0.99 g which corresponded to 99% yield (based on BaF₂).

The solid precipitate’s energy dispersive X-ray fluorescence analysis (EDXRF) has been carried out with an ARL QUANT’X EDXRF spectrometer (Thermo Scientific, USA) equipped with a Peltier cooled Si (Li) detector. The measurements have been done in two steps with different experimental conditions in order to get the primary lines for both barium and bromine. In the case of the barium line measurement a Cu thick filter together with 50 kV voltage on the X-ray tube have been used. Whereas for the bromine determination we have employed a Pd thick filter and 28 kV on the tube. Durations of the measurement in both cases were the same and equal to 120 seconds of lifetime. All measurements have been done in air atmosphere. The sample of solid precipitate has been introduced into the device in a solid form. The sample holders have been covered with thin layers of Prolene® Film (Chemplex Industries, USA).

The TG/DT-analyzer SDTQ-600 (TA Instruments, USA) has been used to determine the area of thermal stability of Ba(BrF₄)₂. The sample has been held in graphite crucibles under argon flow. The heating rate was 10 °C/min and the sample mass was ~20 mg. The mass loss has been measured with the precision of 0.1 μg, the DTA sensitivity was up to 0.001 °C.

2.2. Reagents and sample preparation procedure

All reagents involved into the synthesis were of commercial grade and were not additionally purified. To determine the quantitative composition of obtained product of BaF₂ and BrF₃ interaction, the compound was hydrolyzed with diluted ammonia solution to dissolve it completely. Barium has been determined gravimetrically as barium sulphate, bromine has been determined by the potentiometric titration with silver nitrate using eosin as an indicator and fluorine has been determined by the volumetric titration with zirconyl nitrate in the presence of sodium alizarin-sulfonate.

For the TG/DT analysis sample has been simply placed to the crucible in inert atmosphere of argon to prevent the decomposition of the sample.

3. Results and discussion

The reaction of Ba(BrF₄)₂ synthesis using barium fluoride and bromine (III) trifluoride is shown below:

\[ \text{BaF}_2 + 2\text{BrF}_3 \rightarrow \text{Ba(BrF}_4\text{)}_2 \] (1)

The chemical analysis has shown that the composition of obtained solid product of the interaction between BaF₂ and BrF₃ was fully constituent with Ba(BrF₄)₂. The found Ba:Br:F=1:2:8 ratio is completely correct.

EDXRF shows characteristic lines of barium (Lα=4.51 keV, Lβ=4.91 keV, Lg1=5.61 keV, Lg3=5.81 keV), characteristic lines of rhodium (Kα=20.15 keV, Kβ1=22.69 keV, Kβ2=23.31 keV) which is explained by using rhodium cathode in the X-ray tube and characteristic lines of bromine (Kα=11.92 keV, Kβ=13.29 keV). Fluorine cannot be detected due to some limitations of this method. The EDXRF spectra of Ba(BrF₄)₂ is shown in Fig. 1. The quantitative analysis of ammonia hydrolizate of Ba(BrF₄)₂ has also shown that the Ba:Br ratio was equal to 1:2 which also proves the quantitative composition of obtained compound. Also, this technique could be easily used for the determination of alkali and alkali-earth metals and bromine in hydrolizates of alkali and alkali-earth metals tetrafluorobromates. We should mention the limits of EDXRF in the mean on some light elements like lithium and
sodium. The precision of determination of such elements is not as high as needed for such kind of analysis. The EDXRF spectra of Ba(BrF₄)₂ is shown in Fig. 1.

![EDXRF spectra of Ba(BrF₄)₂](image1)

Fig. 1. EDXRF spectra of Ba(BrF₄)₂

To determine the area of thermal stability of Ba(BrF₄)₂ we’ve used a TG/DT analysis. The thermogram of the Ba(BrF₄)₂ decomposition is shown in Fig. 2.

![TG/DT graph of the Ba(BrF₄)₂ decomposition](image2)

Fig. 2. TG/DT graph of the Ba(BrF₄)₂ decomposition

We can observe two endothermic peaks and two exothermic peaks at the curve of heat effect. The first endothermic peak corresponds to the temperature of 47.6°C. This peak could be explained by the Freon R113 evaporation process. The boiling temperature is 47.6°C that’s why it could be easily explained. The second endothermic peak at 315.5°C corresponds to the melting of the Ba(BrF₄)₂ and intensive mass loss at the mass-change curve. This phenomena could be explained by the incongruent melting of Ba(BrF₄)₂ and is it constituent with literature data. The next peak at the heat flow curve at a temperature of 406.8°C is also exothermic. It could be explained by the interaction of BrF₃ released at the Ba(BrF₄)₂ decomposition stage with materials of crucible. Crucibles are made from carbon and carbon is not so resistive to BrF₃ and such temperatures. Interaction of BrF₃ with crucibles leads to the formation of intercalated graphite compounds with the CₓFₗyBrF₃ general formula. These compounds are usually decomposed at ~500 °C. The last exothermic peak at 538.8°C is explained by the
decomposition process of intercalated graphite compounds on the crucible surface. It is known that such kind of processes is an exothermic one.

At the ABCDEFG mass-change curve we can see clear zones (AB, BC, CD, DE etc.) and each of it corresponds to the partial Ba(BrF₄)₂ decomposition stage. AB zone corresponds to the first endothermic peak and it is explained by the evaporation of Freon R113. At the BC zone, the main process is the removal of BrF₃ to the gaseous phase. At the point C, the process of Ba(BrF₄)₂ melting is starting at a temperature of 232.3°C, and the process of the BrF₃ interaction with a crucible material is also starting to appear. The CD zone illustrates the Ba(BrF₄)₂ decomposition process. At the DE, stage the process of Ba(BrF₄)₂ decomposition is going to be over and the process of BrF₃ interaction with crucible material becomes a dominant one; this process corresponds to the first exothermic peak at the curve of heat flow. At the point E, the process of fluoropolymer decomposition is starting and turns into the equilibrium between processes of formation and decomposition of this intercalated compound at a temperature of 530°C. At the point F, all the processes are over and the sample becomes regular BaF₂. At the FG stage, sample mass is constant.

The determined heat of formation of Ba(BrF₄)₂ amounted to 2280±5 kJ/mole. This shows that the process of the BaF₂ and BrF₃ interaction is quite exothermic and it should be held with the presence of some thermal interface.

References