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n-Hexane bromination using barium fluorobromate $\text{Ba}(\text{BrF}_4)_2$

Vasily Sobolev^{a,*}, Vyacheslav Radchenko^a, Roman Ostvald^a,
Viktor Filimonov^a, Ivan Zherin^a

^aNational Research Tomsk Polytechnic University, Tomsk, 634050, Russia

Abstract

It was observed that $\text{Ba}(\text{BrF}_4)_2$ demonstrates a high reactivity towards n-hexane. It was found that the heating the reaction mass proceed with intensive self-heating up to 40 °C and release of elemental bromine. The GC-MS analysis showed that the main product of $\text{Ba}(\text{BrF}_4)_2$ interaction with n-hexane is 3-bromohexane. The optimal interaction parameters were found. The heat effect of the reaction was determined by isothermal calorimetric method, it was –1451 kJ/mole. The qualitative composition of solid precipitate was determined by EDXRF and XRD analyses. BaF_2 is formed as only solid product of the reaction between $\text{Ba}(\text{BrF}_4)_2$ and n-hexane. It was found that conditions of researched reaction are quite unusual for known free-radical hydrogen substitution processes in case of alkanes. Also we can conclude that $\text{Ba}(\text{BrF}_4)_2$ is much more soft reagent is case of interaction with alkanes in comparison with BrF_3 and it can provide more or less selective bromination of alkane unlikely to BrF_3 .

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1. Introduction

Bromination of alkanes is the typical free-radical process which is held at high temperatures like 450 °C and under UV beams or with various free-radical initiators like HgO^{1-4} . The main disadvantages of mentioned processes are low selectivity and hard conditions that's why the development of new, soft and selective reagents of direct alkane's bromination is very promising and interesting for organic synthesis purposes.

* Vasily Sobolev. Tel.: +7-913-846-2548
E-mail address: vsobolev1989@tpu.ru

Application of various halogen fluorides like BrF_3 ⁵⁻⁷ was well-researched in such kind of reactions – the process occurs without any catalysts or lightning with good yields but with extremely high exothermic effect⁸.

So the application of such analogues of BrF_3 as fluorobromates of alkali and alkali-earth metals is very proposing in the goal of reducing the mentioned disadvantages. Not so long ago we've found that barium fluorobromate $\text{Ba}(\text{BrF}_4)_2$ demonstrates a high reactivity towards arenes and different unsaturated hydrocarbons. This paper is aimed to research the interaction process of barium fluorobromate with n-hexane, to determine the interaction products and find out the value of heat effect of the reaction.

2. Experimental

2.1. Equipment and methods

GC-MS data were obtained by a gas chromatograph Agilent 7890A (Agilent Technologies, USA) connected with a mass-spectrometer Agilent 5975C (Agilent Technologies, USA) under the following conditions– the temperature of the liner was 280 °C; the temperature of thermostat was changing from 50 to 250 °C; heating rate was 10 °C/min; mass scan area was from 33 to 350.

The solid precipitate's energy dispersive X-ray fluorescence analysis (EDXRF) was carried out with an ARL QUANT'X EDXRF spectrometer (Thermo Scientific, USA) equipped with a Peltier cooled Si(Li) detector. The measurements were 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 were used, while for the bromine determination we employed a Pd thick filter and 28 kV on the tube. The durations of the measurement in both cases were the same and equal to 120 seconds of lifetime. All measurements were done in air atmosphere. The sample of solid precipitate was introduced into the device in a solid form. The sample holders were covered with thin layers of Prolene® Film (Chemplex Industries, USA)⁹.

Powder X-ray diffraction (XRD) patterns were obtained with a Stadi-P-Diffractometer (Stoe, Germany) using Cu-K α radiation, a germanium monochromator, and a Mythen1K detector⁹. The data were handled using the WINXPow software¹⁰. The compounds were filled into Lindemann capillaries and flame-sealed. Le Bail profile fitting and Rietveld refinement was done in the Jana2006 software¹¹.

2.2. Reagents and sample preparation procedure

Organic compounds and solvents were of commercially grade and were not additionally purified. Barium fluorobromate $\text{Ba}(\text{BrF}_4)_2$ was obtained by a method described in⁶ and held a Teflon container. For the reaction intensity decreasing the solution of n-hexane and Freon R113 was used. The Freon R113 reacts with neither BrF_3 nor $\text{Ba}(\text{BrF}_4)_2$ that's why it is very useful in such kind of processes⁷.

A flask with a mixture of p-nitrotoluene and Freon-113 was cooled down to -25 °C. Then the $\text{Ba}(\text{BrF}_4)_2$ was added to a flask and the mixture of reagents was held for 30 minutes with vigorous stirring. Then the crude reaction mass was heated up to the room temperature for further sample preparation. The crude product mass was treated with water to remove the possible excess of unreacted $\text{Ba}(\text{BrF}_4)_2$ and filtered from BaF_2 solid precipitate. Then the separated organic phase was treated with 10% sodium nitrite solution and 20% calcium chloride water solution to remove the possible presence excess of bromine and fluorine anions. After that the organic phase was analyzed by a GC-MS method to determine the qualitative and quantitative composition of the sample. The reagent's amounts are shown at table 1. Heat effect determination procedure was held by an isothermal calorimetric method.

3. Results and discussion

The information about $\text{Ba}(\text{BrF}_4)_2$ interaction with organic compounds is still very poor therefore it is known that halogen fluorides rapidly react with most of organic substances even with dissolution of organic substance and at very low temperatures about -120 °C. This process occurs with complete decomposition of hydrocarbon chain, bromine and hydrogen fluoride release⁸.

It was observed that $\text{Ba}(\text{BrF}_4)_2$ demonstrates a high reactivity towards n-hexane. It was found that the heating the

reaction mass proceed with intensive self-heating up to 40 °C and realizing of elemental bromine. The GC-MS analysis showed that the main product of Ba(BrF₄)₂ interaction with n-hexane is 3-bromohexane. It seems to be very unusual, because the BrF₃ (the most possible Ba(BrF₄)₂ decomposition product) should partially fluorinate⁵⁻⁷ the organic substance without any bromination. The possible reaction scheme with the formation of mono-brominated n-hexane is showed in Fig. 1.

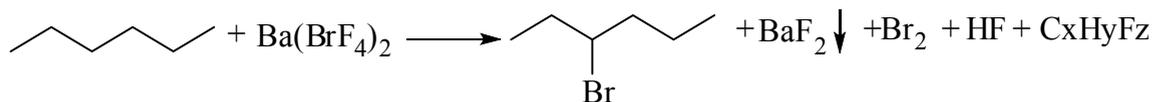


Fig. 1. Ba(BrF₄)₂ and n-hexane interaction scheme.

In order to optimize the process parameter's and total 3-bromohexane yield the most suitable reagent's ration was determined. The reagent's ratios and the total yields are shown at Table 1.

Table 1. Reagent's ratios and 3-bromohexane total peak area.

№	Molar ratio hexane/barium fluorobromate	n-hexane amount, mmol	Ba(BrF ₄) ₂ amount, mmol	Freon R113 amount, mmol	Relative value of 3-bromohexane total peak area
1	3/1	1.34	0.45	7	66.1
2	4/1	1.78	0.45	9.3	67.2
3	5/1	2.23	0.45	11.6	69.8
4	6/1	2.67	0.45	14	63.3
5	7/1	3.12	0.45	16.3	59.1

We can see that the most sufficient yield of 3-bromohexane demonstrates the sample №3 with the 5/1 molar ratio of the reactants. At Fig. 2 we can see that graph of dependence of 3-bromohexane yield on reactant's molar ratio.

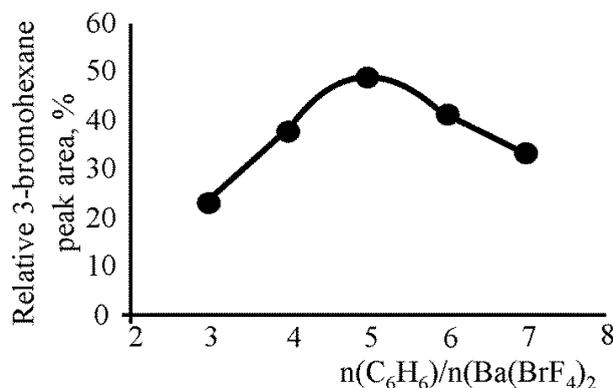


Fig. 2. Dependence of 3-bromohexane yield on reactant's molar ratio.

It was found that the heat effect of the interaction process between Ba(BrF₄)₂ and n-hexane was -1451 kJ/mole. The process is quite exothermic but possible and selective in case of providing the appropriate reaction mass cooling.

EDXRF and XRD analyses showed that solid precipitate of BaF₂ is formed during the reaction. X-ray powder diffraction found only the reflections of BaF₂ and the EDXRF showed characteristic lines of barium (Lα=4.51 keV, Lβ=4.91 keV, Lg1=5.61 keV, Lg3=5.81 keV) and characteristic lines of rhodium (Kα=20.15 keV, Kβ1=22.69 keV, Kβ2=23.31 keV), which is explained by using rhodium cathode in X-ray tube. Fluorine cannot be detected because

of method possibilities. So both analysis methods have shown that pure barium fluoride is formed as a solid precipitate.

The research of the reaction mechanism was not the aim of this work, but we should give some comments about this anyway. The bromination of n-hexane using barium fluorobromate is quite unusual by the following reasons. All known alkane bromination reactions a free-radical and because of this all these processes occur at high temperatures under hard conditions (except allylic and benzylic bromination [12]). The fact of n-hexane bromination at low temperatures without any free-radical external initiation indicates that mechanism of this reaction could not be a free-radical one which is very rare phenomena is chemistry of unsaturated hydrocarbons.

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