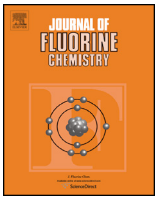
Journal of Fluorine Chemistry 185 (2016) 91–95

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor



Theoretical and experimental studies for preparing 1, 1-dibromo-1,2,2,2-tetrafluoroethane on gas-phase bromination of 1,1,1,2-tetrafluoroethane

Ruzhu Hu[a], Chengping Zhang[a], Feiyao Qing[a], Hengdao Quan[b,*]

[a] Beijing Institute of Technology, Beijing 100081, China
[b] National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba 305-8565, Ibaraki, Japan

ARTICLE INFO

Article history:
Received 6 January 2016
Received in revised form 11 March 2016
Accepted 16 March 2016
Available online 17 March 2016

Keywords:
1, 1, 1, 2-Tetrafluoroethane
Gas-phase bromination
1, 1-Dibromo-1, 2, 2, 2-Tetrafluoroethane
Density functional theory

ABSTRACT

Efficient gas-phase bromination of 1, 1, 1, 2-tetrafluoroethane (HFC-134a) for the preparation of 1, 1-dibromo-1, 2, 2, 2-tetrafluoroethane (CF_3CFBr_2) has been described for the first time. A wide-ranging experimental investigation on the influence of some relevant process parameters was performed with the use of optimized parameters, resulting in the HFC-134a conversion yield and the selectivity to CF_3CFBr_2 of higher than 98% and 60%, respectively. Furthermore, the possible reaction pathways and products were identified with state-of-the-art density functional theory calculations. The gas-phase bromination of HFC-134a provided a potential method to produce CF_3CFBr_2 in currently related industry field.

1. Introduction

Bromine industry plays an important role in the broader chemical industry. Organic bromine compounds have a number of applications in a variety of fields. Bromine compounds are used primarily in applications such as flame retardants [1–3], oil drilling [4], chemical synthesis [5], medicines [6], agriculture [7] and water disinfection [8]. The breakdown of bromine consumption in the world during 2013 by use is presented in Table 1 [9], showing that bromine compounds play a role in almost every aspect of our life.

Bromination processes are important not only for the preparation of the specific desired end compounds but also for the preparation of reactive intermediates. There has been considerable development of the brominating agents in organic synthesis over the past few decades, and organic bromine salts generating bromide ions play an central roles in the synthetic method for the synthesis of bromide compounds. 2,4,4,6-tetrabromo-2,5-cyclohexa-dienone (TBCO) [10–15], benzyltrimethylammonium tribromide [16–18], tetrabutylammonium tribromide [16–18], pyridinium hydrobromide perbromide [10,11] and *N*-bromosuccinimide (NBS) [21–24] were considered as efficient bromination reagents. For instance, TBCO was applied in the bromination of phenols [12], aromatic amines [13], alkenes [14,15], polyenes [15], unsaturated alcohols [16] and ketones [17]; although NBS was applied in the highly selective preparation of allylic bromide by the bromination of olefins [18–20], NBS is difficult to obtain due to its relatively complex preparation process. The above-mentioned brominating reagents are expensive and were always applied the liquid-phase bromination reactions, which led to intermittent operation and the large amount of solvent wasted. Therefore, the above technologies were not suitable for continuous industrial production of organic bromine compounds in many cases. Compared to the above-mentioned brominating reagents, bromine was a cheaper brominating agent and was applied mostly in liquid-phase bromination of olefins [21,22]; however, this technology produces much waste liquid. Especially, the explosive polymerization of the starting material, such as tetrafluoroethene [21] and hexafluoropropene [22], occurred easily as well as in gas-phase bromination [23]. Therefore, the bromination of olefin with bromine is not always a good method for the synthesis of organic bromine compounds in liquid phase as well as in gas phase. CF_3CFBr_2, an important raw material for the synthesis of hexafluorobutadiene [24]; it was obtained by the bromination of tetrafluoroethene [21] followed by the isomerization of 1,2-dibromo-1, 1, 2, 2-tetrafluoroethane($CF_2BrCFBr$) [25]. Thus, the above method was not suitable for industrial applications due to the explosive polymerization of tetrafluoroethene.

---

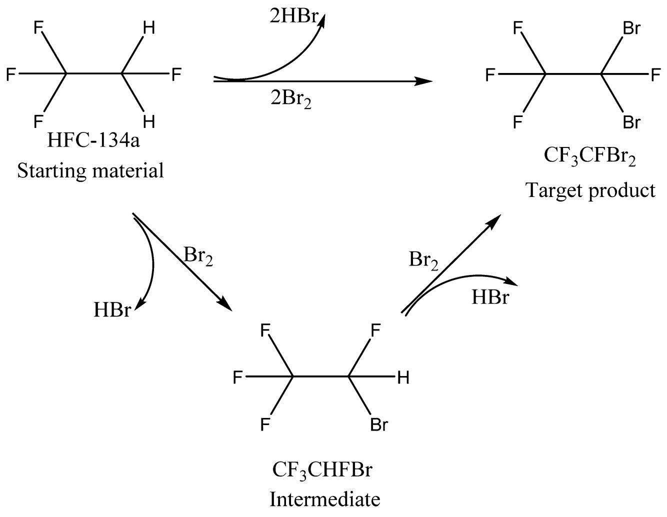
[*] Corresponding author at: National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba 305-8565, Ibaraki, Japan.
E-mail address: Hengdao-quan@aist.go.jp (H. Quan).

http://dx.doi.org/10.1016/j.jfluchem.2016.03.008
0022-1139/

Table 1
World bromine and bromine compounds consumption in 2013.[a]

Consumer segment	Consumption [Tons/year]
Flame retardants	483,000
Drilling fluids	103,500
Organic synthesis	86,300
Pharmaceuticals	77,600
Water treatment	69,000
Agriculture	43,100

[a] The data are derived from [9].



Scheme 1. Gas-phase bromination of HFC-134a with bromine.

In this paper, we reported for the first time the synthesis of CF_3CFBr_2 from gas-phase bromination of HFC-134a with bromine (Scheme 1.). The effects of the relevant process parameters with potential industrial values of the reaction systems were studied and analyzed. To understand the gas-phase bromination of HFC-134a well, we investigated for the first time the bromination reaction of HFC-134a with bromine by using the B3LYP density functional method (DFT) with the 6–311 + G(d,p) triple-ζ basis set. We demonstrated a safer and more inexpensive method for production of CF_3CFBr_2 by gas-phase bromination that can be potentially applied in continuous industrial production of CF_3CFBr_2.

2. Results and discussion

2.1. Gas-phase bromination of HFC-134a

HFC-134a can react with bromine to produce CF_3CFBr_2, CF_3CHFBr and HBr (Scheme 1) following the Br/H exchange reaction between Br_2 and HFC-134a. Under this reaction, high conversion of HFC-134a (approximately 98%) was obtained with almost 66% selectivity for the CF_3CFBr_2 target product. Additionally, intermediate CF_3CHFBr and trifluoroethylene($CF_2=CHF$), 1,2-dibromo-1,1,2-trifluoroethane($CF_2BrCHFBr$), 1-bromo-1,1,2-trifluoroethane(CF_2BrCH_2F) were produced as the by-products in the reaction system.

The conversion of HFC-134a and the selectivity to CF_3CHFBr and CF_3CFBr_2 at different temperature with the constant contact time under the same feed ratio were listed in Table 2. The results presented Table 2 indicated that the reaction depends on the reaction temperature. The conversion of HFC-134a increased with the increasing temperature in the 400–600 °C range, while the selectivity to CF_3CHFBr and CF_3CFBr_2 first increased and then decreased with the increasing temperature. On the other hand, the cleavage reaction of HFC-134a occurred easily at high temperature over 550 °C, leading to the formation of a large number of by-products. Additionally, the total selectivity to CF_3CHFBr and CF_3CFBr_2 first increased and then decreased with the increasing temperature in the 400–600 °C range, indicating that both the main products and by-products were dependent on the feed Br_2/HFC-134a molar ratio. Therefore, 550 °C was chosen as the optimal temperature.

Table 2
Impact of Temperature on the bromination of HFC-134a.[a]

T [°C]	400	450	500	550	600
Conversion of HFC-134a [%][b]	21.7	52.3	54.9	98.5	99.5
Selectivity to CF_3CHFBr [%][b]	50.0	55.7	61.0	37.3	33.7
Selectivity to CF_3CFBr_2 [%][b]	12.1	34.0	35.1	60.1	58.6

[a] Reaction conditions: Br_2/HFC-134a = 2/1, P = 0.1 MPa and contact time = 15 s.
[b] Conversion and selectivity were determined by GC area percent.

Table 3 shows the influence of the feed ratio on the conversion of HFC-134a and product selectivity at 550 °C. The conversion of HFC-134a increased with increasing Br_2/HFC-134a feed molar ratio in the 0.5–2.5 range. Additionally, the selectivity to CF_3CFBr_2 increased rapidly with the increasing feed molar ratio of Br_2/HFC-134a in the 0.5–2 range, but it only increased slowly with the increasing Br_2/HFC-134a feed molar ratio in the 2–2.5 range. By contrast, the selectivity to CF_3CHFBr decreased sharply with the increasing Br_2/HFC-134a feed molar ratio in the 0.5–2 range, but decreased only slowly with the increasing Br_2/HFC-134a feed molar ratio in the 2–2.5 range, implying that further bromination of CF_3CHFBr could generate CF_3CFBr_2. However, the total selectivity to CF_3CHFBr and CF_3CFBr_2 was maintained at over 96% for the increasing Br_2/HFC-134a feed molar ratio in the 0.5–2.5 range, indicating that the byproducts other than CF_3CHFBr were independent of the Br_2/HFC-134a feed molar ratio. Hence, based on the high yield of CF_3CFBr_2 and the full utilization of materials, 2:1 was chosen as the optimal ratio.

The effects of the contact time of this reaction on the product distribution were investigated, with the results shown in Table 4. The conversion of HFC-134a increased rapidly at first and then increased slowly with the increasing contact time in the 5–25 s range. Additionally, the selectivity to CF_3CFBr_2 first increased and then decreased with the increasing contact time in the 5–25 s range, while the selectivity to CF_3CHFBr first decreased and then increased with the increasing contact time. However, the total selectivity to CF_3CHFBr and CF_3CFBr_2 was maintained at over 98% with the increasing contact time in the 5–25 s range, indicating that the yields of by-products other than CF_3CHFBr were independent of the contact time. Therefore, based on the high yield of CF_3CFBr_2, 15 s was chosen as the optimal contact time.

2.2. Gas-phase bromination mechanisms

It is well known that the exchange reaction between bromine and saturated hydrocarbons is based on atomic radicals [26–28]. Based on the above experimental results and theoretical analysis, the gas-phase bromination of HFC-134a mechanisms were summarized in Fig. 1, with the structures and optimized geometrical parameters associated with the critical points involved in the reaction depicted in Fig. 2. When the temperature reached the desired temperature, the lowest energy barrier (190.79 kJ mol^{-1}) was surmounted and Br_2 decomposition began, leading to the formation of the Br$^\bullet$ radical, which was probably sufficient for the chain-reaction initiation. The results of theoretical calculations indicated that the energy barrier for the formation