



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

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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.

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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 a 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.

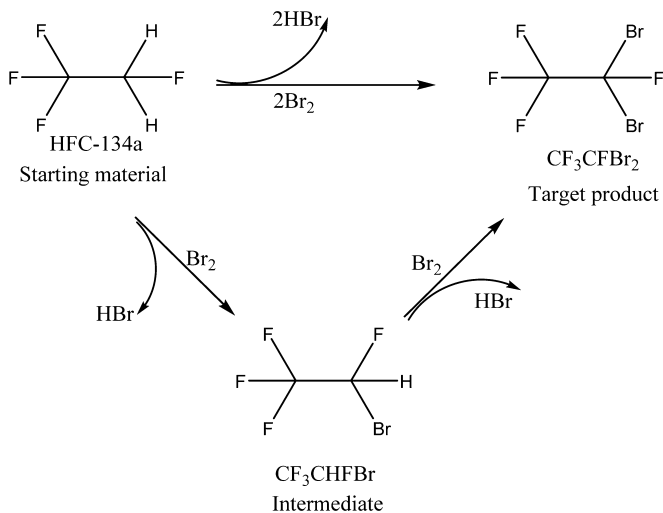
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Table 1
World bromine and bromine compounds consumption in 2013.^a

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 ($\text{CF}_2=\text{CHF}$), 1,2-dibromo-1,1,2-trifluoroethane ($\text{CF}_2\text{BrCHFBr}$), 1-bromo-1,1,2-trifluoroethane ($\text{CF}_2\text{BrCH}_2\text{F}$) 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

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: $\text{Br}_2/\text{HFC-134a}=2/1$, $P=0.1$ MPa and contact time = 15 s.

^b Conversion and selectivity were determined by GC area percent.

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 $\text{Br}_2/\text{HFC-134a}$ molar ratio. Therefore, 550 °C was chosen as the optimal temperature.

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 $\text{Br}_2/\text{HFC-134a}$ 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 $\text{Br}_2/\text{HFC-134a}$ in the 0.5–2 range, but it only increased slowly with the increasing $\text{Br}_2/\text{HFC-134a}$ feed molar ratio in the 2–2.5 range. By contrast, the selectivity to CF_3CHFBr decreased sharply with the increasing $\text{Br}_2/\text{HFC-134a}$ feed molar ratio in the 0.5–2 range, but decreased only slowly with the increasing $\text{Br}_2/\text{HFC-134a}$ 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 $\text{Br}_2/\text{HFC-134a}$ feed molar ratio in the 0.5–2.5 range, indicating that the byproducts other than CF_3CHFBr were independent of the $\text{Br}_2/\text{HFC-134a}$ 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

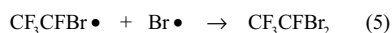
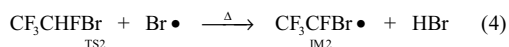
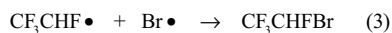
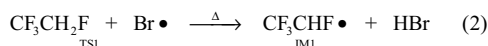
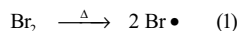
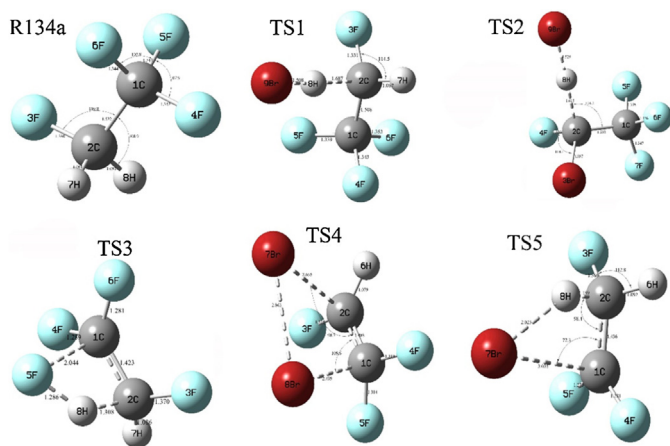
It is well known that the exchange reaction between bromine and saturated hydrocarbons is based on atomic radicals [26–28]. Based on the above experimental results and theoretical analysis, the gas-phase bromination of HFC-134a mechanisms were summarized in Fig. 1, with the structures and optimized geometrical 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

Table 3
Impact of feed ratio on the bromination of HFC-134a.^a

Br ₂ /HFC-134a feed molar ratio [mol/mol]	Conversion of HFC-134a [%] ^b	Selectivity [%] ^b	
		CF ₃ CHFBr	CF ₃ CFBr ₂
1:2	42.8	61.2	35.0
1:1	67.6	54.4	43.2
1.5:1	80.1	46.1	53.3
2:1	98.5	37.1	61.1
2.5:1	99.5	35.1	63.9

^a Reaction conditions: temperature = 550 °C, P = 0.1 MPa and contact time = 15 s.^b Conversion and selectivity were determined by GC area percent.**Table 4**
Impact of contact time on the bromination of HFC-134a.^a

Contact time [s]	Conversion [%] ^b	Selectivity [%] ^b	
		CF ₃ CHFBr	CF ₃ CFBr ₂
5	88.1	63.5	36.0
10	93.6	48.6	51.3
15	98.2	35.5	63.4
20	98.9	53.1	43.1
25	99.1	65.5	31.5

^a Reaction conditions: temperature = 550 °C, P = 0.1 MPa, Br₂/HFC-134a = 2:1.^b Conversion and selectivity were determined by GC area percent.**Fig. 1.** Main reaction pathways of HFC-134a with Br₂.**Fig. 2.** Geometrical optimization of HFC-134a and five possible transition states.

of the Br• radical was the highest energy barrier of the bromination reaction (Table 5). Following the initial generation of the Br• radical, a rapid Br/H exchange occurs between Br₂ and HFC-134a

via the transition state TS1 by overcoming an energy barrier of 52.73 kJ mol⁻¹ to form HBr and the IM1 intermediate with an energy of 476.2 kJ mol⁻¹, slightly lower in energy than HFC-134a (476.8 kJ mol⁻¹). Equation 3 in Fig. 1 is a concerted radical reaction of IM1 and Br• that releases the energy (-255.68 kJ mol⁻¹) for the formation of CF₃CHFBr with the new C-Br bond. Similarly, Br• radical reacted with the newly formed CF₃CHFBr via the transition state TS2 by overcoming an energy barrier of 41.08 kJ mol⁻¹ to form HBr and intermediate IM2. All bromination reactions products could be simply related to the Br• radical. Therefore, it was obvious that the most important factor that affected the bromination reaction was the thermal pyrolysis of bromine molecule into radical Br• during the bromination of HFC-134a. The two termination steps (3) and (5) were clearly related to the formation of CF₃CHFBr and CF₃CFBr₂.

The formation mechanisms for the undesired side-products CF₂=CHF, CF₂BrCHFBr and CF₂BrCH₂F were different from that of the Br/H radical exchange reaction (Fig. 3). It was found that the release of the side-products was mostly caused by the pyrolysis of HFC-134a at high temperatures (>550 °C). According to the theoretical calculations (Table 5), the pyrolysis of HFC-134a to CF₂=CHF must overcome an energy barrier of 115.10 kJ mol⁻¹ which is lower in energy for thermal decomposition of Br₂ than

Table 5

Relative zero-point vibrational energies ((ΔZPVEs) (in kJ mol⁻¹) of each reaction and transition states involved in the bromination of HFC-134a. The ZPVEs are scaled by 0.96 [29] when calculating DE (DFT).

	Species	ΔZPVEs
Eq. (1)	Br ₂ → 2Br•	190.79
Eq. (2)	CF ₃ CH ₂ F + Br• → CF ₃ CHF• + HBr	41.89
Eq. (3)	CF ₃ CHF• + Br• → CF ₃ CHFBr	-255.68
Eq. (4)	CF ₃ CHFBr + Br• → CF ₃ CFBr• + HBr	30.11
Eq. (5)	CF ₃ CFBr• + Br• → CF ₃ CFBr ₂	-299.40
Eq. (6)	CF ₃ CH ₂ F → CF ₂ =CHF + HF	115.10
Eq. (7)	CF ₂ =CHF + Br ₂ → CF ₂ BrCHFBr	-101.90
Eq. (8)	CF ₂ =CHF + HBr → CF ₂ BrCH ₂ F	81.87
TS1		52.73
TS2		41.08
TS3		295.36
TS4		209.44
TS5		166.51

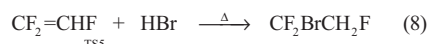
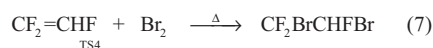
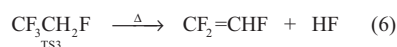
**Fig. 3.** Probable side reactions in bromination of HFC-134a.

Table 6
GC and GC–MS operation conditions.

Parameters	GC	GC–MS
Instrument	Shanghai Huaai GC-9560	Shimadzu GC–MS–QP2010 ultra
Column	DB–VRX (60.0 m × 0.32 mm × 1.8 μm)	Rxi–5Sil MS (30.0 m × 0.25 mm × 0.25 μm)
Carrier gas flow rate [mL·min ⁻¹]	6,N ₂	2,He
Column temperature [°C]	200	180
Injection volume [μL]	1	1
Split ratio	1:50	1:50
Injection temperature [°C]	250	250
Detector (FID) temperature [°C]	220	
Ion source temperature [°C]		200
Scan range		m/z 35.00–500.00

HFC-134a (190.79 kJ mol⁻¹); however, experimentally only a small amounts of side-products including CF₂=CHF were formed. The formation of CF₂=CHF required that the reaction be carried out at high temperatures in the presence of catalyst [30–32]. Theoretical calculations of transition state energies (Table 5) showed that formation of possible by-products such as CF₂CHF (295.36 kJ mol⁻¹), CF₂BrCHFBr (209.44 kJ mol⁻¹) and CF₂BrCH₂F (166.51 kJ mol⁻¹) required higher energies compared to the main products such as CF₃CHFBr (52.73 kJ mol⁻¹) and CF₃CFBr₂ (41.08 kJ mol⁻¹). Therefore, it was easy to avoid by-products at the relatively low reaction temperature in the gas-phase bromination of HFC-134a. In this paper, higher than 60% selectivity of CF₃CFBr₂ was achieved at temperatures lower than 600 °C.

3. Conclusions

The gas-phase bromination of HFC-134a was investigated experimentally and theoretically in this study. In this reaction, HFC-134a started to react with Br• at approximately 400 °C, and the optimal reaction temperature for the CF₃CFBr₂ production was approximately 550 °C. The conversion yield of HFC-134a was greater than 98%, and the selectivity of CF₃CFBr₂ was greater than 60% under the following optimal reaction conditions: pressure of 0.1 MPa, T=550 °C, Br₂/HFC-134a=2:1, contact time=15 s. CF₃CFBr₂ and CF₃CHFBr were the main bromination products. A small amount of three by-products including CF₂=CHF, CF₂BrCHFBr and CF₂BrCH₂F was detected. The reaction intermediates, reaction path and products were theoretically analyzed using the Gaussian software package. The results of theoretical calculations were consistent with the experimental results, and experimental and theoretical analysis results were also in good agreement. In a sense, the gas-phase bromination of HFC-134a provided a potential method for continuous industrial production of CF₃CFBr₂.

4. Experimental and computational methods

4.1. Experimental

HFC-134a (purity > 99.9%) was purchased from Sinochem Lantian Co., Ltd. (Zhejiang, China), elemental bromine (99.85% pure) was purchased from China National Pharmaceutical Group Corporation (Beijing, China). The HFC-134a flow rate was controlled by a mass flowmeter (D07-7B/ZM, Beijing Seven-star Electronics Co., Ltd., China) and the flow rate of elemental bromine was controlled by a high pressure liquid metering pump (Leadfluid, TYD01) capable of feeding between 0.05 and 20.0 mL min⁻¹. The reaction system consists of an alumina ceramic tube (40.0 cm in length, 1.0 cm inner diameter), a programmable temperature control device (the temperature of the reactor was measured and controlled by the temperature control device with three

K-type sheathed thermocouples evenly distributed throughout the surface of the reactor, showing that the temperature deviation was controlled within ±5 °C), an exhaust gas treatment system and a test analysis system. A thermocouple placed in the center of the sorbent bed was used to measure the reaction temperature.

Experiments were carried out in the system described above. A mixture of HFC-134a and Br₂ in a certain molar ratio was added to the reaction tube at a preset temperature. The out gases passed through water and a KOH solution to neutralize the formed HBr. The exiting gas was then analyzed by gas chromatography-mass spectrometry (GC–MS). The operating conditions of the GC and GC–MS are shown in Table 6.

The MS data were as follows:

1. CF₃CH₂F, m/z: 83, CF₃CH₂⁺; 69, CF₃⁺; 63, CF₂C⁺; 51, CHF₂⁺.
2. CF₃CFBr₂, m/z: 260, ⁺CF₃CFBr₂; 191, ⁺CFBr₂; 180, CF₃C⁺FBr; 161, CF₃C⁺Br; 111, ⁺CFBr; 100, CF₃C⁺F; 91, ⁺CBr; 81, CF₃C⁺; 69, +CF₃; 50, CF₂⁺.
3. CF₃CHFBr, m/z: 181, CF₃C⁺HFB; 161, CF₃CBr; 111, ⁺CFBr; 100, CF₃C⁺F; 91, ⁺CBr; 81, CF₃C⁺; 69, ⁺CF₃; 51, CHF₂⁺.
4. CF₂=CFH, m/z: 82, CF₂=CF⁺; 63, CF₂=C⁺; 51, ⁺CHF₂.
5. CF₂BrCHFBr, m/z: 241, CF₂BrC⁺HFB; 221, CF₂BrC⁺Br; 161, CF₂BrC⁺HF; 140, CF₂BrC⁺; 130, ⁺CF₂Br; 110, ⁺CFBr; 31, ⁺CF.
6. CF₂BrCH₂F, m/z: 161, CF₂BrC⁺HF; 140, CF₂BrC⁺; 130, ⁺CF₂Br; 50, ⁺CF₂; 31, ⁺CF.

4.2. Computational methods

To elucidate the gas-phase bromination of HFC-134a, in this work, theoretical analysis was performed using the Gaussian 03 software packages. All possible reaction pathways for the reaction system were examined using density functional theory calculations, which provided a method for good understanding of the origin of the reaction products identified in experiments. The geometries of the major reactants, products, possible intermediates and transition structures were fully optimized using the B3LYP functional with the 6–311++G (d, p) basis set [33–35]. The vibrational frequencies of the reactants, products and the intermediates were all real, whereas the transition state structures exhibited only one imaginary frequency. The intrinsic reaction coordinate (IRC) calculations at the B3LYP/6–311++G (d, p) level confirmed the connections between reactants, intermediates, transition structures and products [34–37].

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