The Reaction Pathway Analysis of 2-Bromo-3,3,3-trifluoropropene with the Active Radicals and Pyrolysis of 2-Bromo-3,3,3-trifluoropropene

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ABSTRACT

As a new kind of Halon replacement, 2-bromo-3,3,3-trifluoropropene (2-BTP) has been paid broad attention due to its superior fire suppression performance and properties. Although the fire suppression performance and extinguishing mechanism of 2-BTP have been widely reported so far, there is few theoretical and experimental research about the reaction mechanism of 2-BTP with the active radicals and pyrolysis of 2-BTP. In this study, 2-BTP was pyrolyzed with a flow of nitrogen carrier gas in a tubular pyrolysis reactor over the temperature range of 25-800 °C. Its decomposition products were analyzed by GC and GC-MS. The major decomposition products were verified to be CF3CCH and CF3Br. It can be speculated that only when flame temperature was above 600 °C, decomposition products were generated rapidly by pyrolysis of 2-BTP and reacted with reactive radicals to stop the combustion reaction. Based on the above experiment results, Gaussian 03 was applied to calculate the possible pathways of fire-extinguishing using the Density function theory (DFT) method with the 6-311++G(d, p) basis set. There are five possible pathways in the reaction of 2-BTP with OH radical and three possible pathways of 2-BTP pyrolysis. Combining the experimental results and theoretical calculations, the fire-extinguishing mechanism of 2-BTP was proposed.

KEYWORDS: 2-Bromo-3,3,3-trifluoropropene, fire-extinguishing mechanism, Gaussian 03, halon replacement.

INTRODUCTION

With the growing awareness of green chemistry, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are phased out gradually due to high ozone depletion potential (ODP) or global warming potential (GWP) [1, 2]. Searching for the Halon replacement agents that have low ODP and GWP has been the tendency, especially in the field of fire-extinguishing agents.

2-Bromo-3,3,3-trifluoropropene (CF3CBr = CH2, 2-BTP) has been selected as an excellent Halon replacement due to the superior fire suppression performance and acceptable environmental, physical and toxicological properties. Numerous studies on the physical properties and extinguishing characteristics of 2-BTP have been widely reported. The average cup burner extinguishment concentration of 2-BTP is 2.6% by volume which is lower than that of Halon 1301 [3]. Since a carbon-carbon double bond exists in the 2-BTP molecule which can promote tropospheric degradation, the ODP and GWP of 2-BTP are only 0.0028-0.0052 and 0.0028-0.0050, respectively [4]. 2-BTP is also a substance of low toxicity with the NOAEL and LOAEL values of 0.5% and 1.0% (vol.%) respectively, as low as the toxicity testing data of Halon 1211 [5]. Nonetheless, the extinguishing mechanism of 2-BTP is still unclear due to the complex reaction process. Therefore, deeper insight into the fire-extinguishing mechanism of 2-BTP should be required.
Just like the fire-extinguishing mechanism of fluorinated hydrocarbons, 2-BTP suppresses flames by both chemical and physical mechanisms. 2-BTP is able to extinguish flames physically by removing thermal energy from the flame. As for chemical mechanism, flames are surpressed by the reactions of 2-BTP and its pyrolysis products with the active ones, e.g., O, H and OH, that are necessary for the flame propagation. Therefore, in order to study its fire extinguishing mechanisms, it is significant to investigate its pyrolysis decomposition products.

In this study, 2-BTP was pyrolyzed with a flow of nitrogen carrier gas in a tubular pyrolysis reactor over the temperature range of 25-800 °C. Its decomposition products were also analyzed by GC and GC-MS. Based on the above experiment results, Gaussian 03 was applied to calculate the possible pathways of fire-extinguishing using the Density function theory (DFT) method with the 6-311++G(d, p) basis set. Combining the experimental data and theoretical calculations, the fire-extinguishing mechanism of 2-BTP was proposed.

EXPERIMENTAL

The schematic diagram of the thermal degradation device is shown in Fig. 1. This device consists of a tubular pyrolysis nickel-copper alloy reactor (40.0 cm long and 1.0 cm in internal diameter), a programmable temperature control device, a sampling system, a products analysis system and exhaust gas treatment system. All experiments were carried out at atmospheric pressure. 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.

The 2-BTP purity was more than 99.75%. Prior to the experiment, the tubular pyrolysis reactor was immersed in acetone for 2 h to get rid of impurities firstly. Then the reactor was heated to 700 °C for 2 h with N₂ flow to remove contaminants. After cooling to room temperature, 2-BTP from the mixing chamber was injected into the tubular reactor and heated to 800 °C at a heating rate of 2 °C/min. The flow rate of nitrogen carrier gas was controlled as 6.4 ml/s and the mole fraction of 2-BTP was adjusted as 40%. After removal of particulates and acid gases by passing through a filter and a warm water scrubber, the gaseous degradation products were collected and then analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

Figure 1. Schematic diagram of the thermal degradation experiment system.
RESULTS AND DISCUSSION

The process of flame inhibition is extremely complex, including numerous chemical reactions. Flame inhibition in 2-BTP systems is a result of the chemical reactions of 2-BTP with the active radicals, the pyrolysis of the agent and the subsequent chemical reactions of its decomposition products. Therefore, reaction path analysis of 2-BTP with the active radicals and pyrolysis of 2-BTP were performed.

Fig. 2 shows the decomposition ratios of 2-BTP at various temperatures with a flow of nitrogen carrier gas. It can be seen that 2-BTP exhibited excellent thermostability below 600 °C. It implies that 2-BTP molecules primarily reacted with the active radicals to interrupt or terminate some key chain reactions when temperature was lower than 600 °C. When the temperature rose above 600 °C, the decomposition ratio of 2-BTP began to increase greatly. Then, it can be speculated that when flame temperature was above 600 °C, 2-BTP and decomposition products reacted with the active radicals to stop the combustion reaction.

Figure 2. The decomposition ratios of 2-BTP at various temperatures with a flow of nitrogen carrier gas.

The pyrolysis decomposition products were detected by GC-MS. The mass spectrum revealed two major decomposition products which were CF₃CCH and CF₃Br, respectively. CF₃CCH was detected to be the main product in a temperature range of 600-700 °C while the major product turned out to be CF₃Br at above 700 °C. To reveal the possible reaction pathways of 2-BTP pyrolysis, theoretical analysis by Gaussian 03 program package are performed. There are three pathways based upon density function theory (DFT) method accompanied with 6-311++G(d,p) basis set. One pathway that produces CF₃CCH+HBr has the lowest energy barrier of 300.1 kJ·mol⁻¹. Another pathway that leads to CF₂+BrCH₂ has an energy barrier of 437.1 kJ·mol⁻¹. The pathway that produces CF₃Br+CCH₂ has the highest energy barrier of 502.0 kJ·mol⁻¹. It seems that the formation of CF₃CCH is easier than that of CF₃Br, which is consist with experiment results. However, there is no evidence to prove the formation of CFBrCH₂. This is probably because that the CF₃Br is mainly formed by CF₃ and Br radicals dissociated from different 2-BTP molecules rather than formed by monomolecular cracking reaction. The dissociation energy of C-Br bond (308.2 kJ·mol⁻¹) is the lowest among all the bonds in the 2-BTP molecule, indicating that Br radical can be easily formed at a relatively lower energy. Besides, bond dissociation energy of C-C bond (386.3 kJ·mol⁻¹) is much lower than bond dissociation energy of C-F, C-H and C=C bonds. So, 2-BTP molecule may provide CF₃⁺ and Br radicals at high temperature more easily than generate CF₂+BrCH₂. In other word, CF₃Br can be generated with much less energy than FBrCH₂. Subsequently, these pyrolysis decomposition products
take part in the flame inhibition. The fire-extinguishing mechanism of these products was analyzed in early works [6-8].

\[
\begin{align*}
\text{CF}_3\text{CBr} + \text{CH}_2 & \rightarrow \text{TS}_1 \rightarrow \text{CF}_3\text{CCH} + \text{HBr} \\
\text{TS}_2 & \rightarrow \text{CH}_2\text{CFBr} + \text{CF}_2 \\
\text{TS}_3 & \rightarrow \text{CF}_3\text{Br} + \text{CCH}_2
\end{align*}
\]

As for the chemical reactions of 2-BTP with the active radicals, many literatures have studied. It is well known that active radicals present in combusting systems notably are H and OH. Burgess Jr. et al. reported that radicals added into the double bond of 2-BTP rapidly, particularly H and OH, and formed unstable intermediates that would rapidly fragmented, producing Br, CF₃, and other intermediates [6]. Babushok et.al also proposed the reaction path of 2-BTP with the active radicals, e.g. H, OH and CF₃ [8]. Nonetheless, these reactions still needs further investigation. The reaction types of 2-BTP with H radical have addition/beta-scission and abstraction, but the reaction mechanism between 2-BTP and OH is inadequacy.

Among early studies, V. L. Orkin et al. have disclosed that the major reaction product of 2-BTP with OH radical was CF₃CBrCH₂OH [9]. Similarly, to reveal the possible reaction pathways between 2-BTP and OH radicals, theoretical analysis by Gaussian 03 program package is also performed. There are five possible pathways for the reaction of 2-BTP with highly nucleophilic OH radicals based upon the CCSD/aug-cc-pvdz relative energies. The potential energy diagram for the reaction of 2-BTP with OH is plotted in Fig. 3. \(\Delta E\) and \(\Delta H\) in the following paragraphs represent the energy barrier and thermal effect of each reaction channel respectively. The accurate structures of 2-BTP, the intermediates and products, as well as the optimized geometrical parameters associated with the critical points are depicted in Appendix A.

**Figure 3.** Potential energy diagram for the reaction between 2-BTP and OH radicals. The relative energies (kJ/mol) are obtained at the CCSD/aug-cc-pvdz//B3LYP/6-311++G (d, p) level of theory.

Pathway A:

\[
\begin{align*}
\text{CF}_3\text{CBr} = \text{CH}_2 + \cdot \text{OH} & \rightarrow \text{CF}_3\text{CBrCH}_2\text{OH}(P_{1,1}) \: \Delta H = -125.5 \text{ kJ/mol} \: (R_{1,1}) \\
\text{CF}_3\text{CBr} = \text{CH}_2 + \cdot \text{OH} & \rightarrow \text{CF}_3\text{CBrCH}_2\text{OH}(P_{1,2}) \: \Delta H = -123.9 \text{ kJ/mol} \: (R_{1,2}) \\
\text{CF}_3\text{CBr} = \text{CH}_2 + \cdot \text{OH} & \rightarrow \text{CF}_3\text{CBrCH}_2\text{OH}(P_{1,3}) \: \Delta H = -120.8 \text{ kJ/mol} \: (R_{1,3})
\end{align*}
\]
In this pathway, $P_{1-1}$, $P_{1-2}$ and $P_{1-3}$ are isomers and can be inter-converted to each other. By comparing of above three reaction, it is worth to note that product $P_{1-1}$ is more stable and easier to form than $P_{1-2}$ and $P_{1-3}$. As this reaction is an intense exothermic reaction, $\text{CF}_3\text{CBrCH}_2\text{OH}$ ($P_{1-1}$) is formed without any obstacle when OH radical attacks the terminal carbon atom of 2-BTP.

Pathway B:

$$\text{CF}_3\text{CBr=CH}_2 + \cdot \text{OH} \rightarrow \text{TS}_4 \rightarrow \text{CF}_3\text{C(OH)CH}_2(P_2) + \cdot \text{Br},$$

$$\Delta E = 13.3 \text{ kJ/mol, } \Delta H = -103.2 \text{ kJ/mol } (R_2);$$

$\text{CF}_3\text{C(OH)CH}_2(P_2)$ and Br radical can also be generated by going over a relatively low energy barrier of 13.3 kJ/mol. According to $-103.2$ kJ/mol, the Br-substituted reaction $R_2$ is a highly exothermic process. This reaction can also be recognized as one of the possible pathways for the reaction of 2-BTP with OH radicals.

Pathway C:

$$\text{CF}_3\text{CBr=CH}_2 + \cdot \text{OH} \rightarrow \text{TS}_5 \rightarrow \text{CF}_3\text{CBr=CH}(P_3) + \cdot \text{H}_2\text{O},$$

$$\Delta E = 28.6 \text{ kJ/mol, } \Delta H = -14.8 \text{ kJ/mol } (R_{3,1});$$

$$\text{CF}_3\text{CBr=CH}_2 + \cdot \text{OH} \rightarrow \text{TS}_6 \rightarrow \text{CF}_3\text{CBr=CH}(P_3) + \cdot \text{H}_2\text{O},$$

$$\Delta E = 31.7 \text{ kJ/mol, } \Delta H = -9.1 \text{ kJ/mol } (R_{3,2});$$

When OH radicals attack one of H atoms in the molecule of 2-BTP, $P_{3-1}$ and $P_{3-2}$ are generated and they are also isomers. According to the calculated results, the O atom of OH radical may directly take away the H atom to form $P_{3-1}+\cdot \text{H}_2\text{O}$ via $\text{TS}_5$ with an energy barrier of 28.6 kJ/mol. It is another direct H abstraction that OH radical attack the other H atom located on the same side of C=C band with Br atom. In this way, $P_{3-2}+\cdot \text{H}_2\text{O}$ can be formed via $\text{TS}_6$ by overcoming a slightly higher barrier height of 31.7 kJ/mol. They are also exothermic reactions.

Pathway D:

$$\text{CF}_3\text{CBr=CH}_2 + \cdot \text{OH} \rightarrow \text{TS}_7 \rightarrow \text{CF}_2\text{CBr=CH}(P_4) + \cdot \text{FOH},$$

$$\Delta E = 315.9 \text{ kJ/mol, } \Delta H = 307.2 \text{ kJ/mol } (R_4);$$

Since F atom has strong electronegativity, the C-F band in 2-BTP is much more stable and stronger than C-H band. When OH radicals attack the F atoms from different directions, only one direct F abstraction reaction channel is found and a far larger energy of 315.9 kJ/mol is needed. Due to the very high barrier height, $R_4$ is almost impossible unless the energy is high enough to surmount the huge energy barrier.

Pathway E:

$$\begin{align*}
\text{TS}_8 \rightarrow & \text{IM}_1 \rightarrow \text{TS}_9 \rightarrow \text{CF}_2(\text{OF})\text{CBrCH}_2(P_{5,1}) + \cdot \text{H} (R_{5,1}) \\
\text{TS}_{10} \rightarrow & \text{IM}_2 \rightarrow \text{TS}_{11} \rightarrow \text{CF}_2(\text{OF})\text{CBrCH}_2(P_{5,2}) + \cdot \text{HF} (R_{5,2}) \\
\text{TS}_{12} \rightarrow & \text{IM}_3 \rightarrow \text{TS}_{13} \rightarrow \text{CF}_2(\text{OF})\text{CBrCH}_2(P_{5,3}) + \cdot \text{H} (R_{5,3}) \\
\text{TS}_{14} \rightarrow & \text{IM}_4 \rightarrow \text{TS}_{16} \rightarrow \text{CF}_2(\text{OF})\text{CBrCH}_2(P_{5,4}) + \cdot \text{H} (R_{5,4}) \\
\text{TS}_{15} \rightarrow & \text{IM}_5
\end{align*}$$

Based on the calculated results, $\text{CF}_2(\text{OF})\text{CBrCH}_2(P_{5,1})+\cdot \text{H}$ will be produced via an intermediate of IM$_1$ and two transition states of TS$_8$ and TS$_9$ with the very high energy barriers of 320.2 kJ/mol and 530.1 kJ/mol, respectively, just like the three other reaction channels that can generate $P_{5-3}$ and $P_{5-4}$. For the reaction that leads to $\text{CF}_2(\text{O})\text{CBrCH}_2(P_{5,2})+\cdot \text{HF}$, even though it is exothermic, it is extremely
difficult to occur because formation of IM₄ needs to overcome a high energy barrier of 326.2 kJ/mol. Therefore, these four reaction channels cannot be practical because of the high energies.

By comparing the energy barriers and thermal effect of each reaction channel, it is found that pathway A is the main reaction channel in the reaction of 2-BTP with OH radical; pathway B and C also occur at relatively low temperature; pathway D and E need high temperature.

Based on above experimental results and theoretical analysis, the concise fire-extinguishing process of 2-BTP is proposed as follows: when temperature is lower than 600°C, 2-BTP molecules react with the active radicals e.g., OH, to produce CF₃CBrCH₂OH. With the increase of temperature, CF₃C(OH)CH₂, Br radical, CF₃CBr=CH and H₂O are generated by the pathway B and C. When the temperature reaches to 600°C, 2-BTP begins to decompose. CF₃CCH and HBr are produced and pathway D begins to proceed. As the temperature rises, CF₃ and Br radicals will be dissociated from 2-BTP molecules and contribute to the generation of CF₃Br. Immediately, these products and radicals also take part in extinguishing a fire.

There have been many studies on fire-extinguishing mechanism of the reactions of these products with radicals [10]. It is well known that Br radical can remove hydrogen atoms and hydroxyl radicals by catalytic cycles: H· + Br· + M → HBr + M; Br· + Br· + M → Br₂ + M; H· + Br₂ → HBr + Br·[11]. The concise extinguishing mechanism of 2-BTP at high temperature is shown in Fig. 4.

![Figure 4. The concise extinguishing mechanism of 2-BTP at high temperature.](image-url)
APPENDIX A

OH
FOH
H₂O

CF₃CBrCH₂OH (P₁,1)

CF₃CBrCH₂OH (P₁,2)

CF₃CBrCH₂OH (P₁,3)

CF₃C(OH)CH₂ (P₂)

CF₃CBrCH (P₃,1)

CF₃CBrCH (P₃,2)

CF₂CBrCH₂ (P₄)

CF₂(OF)CBrCH₂ (P₅,1)

CF₂(O)CBrCH₂ (P₅,2)
REFERENCES


