Combustion inhibition of cup-burner flame with C2HF3Cl2 and its kinetics mechanism investigation

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Abstract

In order to explore the possibility of C2HF3Cl2 (R123) for the fire extinguishing agent of aircraft cargo compartment, this paper conducted experimental and theoretical research on the fire extinguishing performance and mechanism of R123, furthermore, the analogous C2HF5 (R125) was compared to explore the in-depth fire extinguishing mechanism. The minimum extinguishing concentration (MEC) of R123 in methane/air flames is 7.31 %, which is lower than 8.91 % of R125. And the experimental results reveal interesting examples of flame height and temperature changed with the addition of R123. The flame height had a phenomenon to increase first and then decrease, in comparison, the flame height kept rising with R125 adding. And the change in height reflected the addition of R123 to affect the movement of the reaction kernel, so that the temperature at different heights changed, but the temperature as a whole showed the tendence of decreasing. In addition, theoretical calculations indicated that R123 and pyrolysis products could affect the combustion reaction, such as CF3CHCl2+H=CF3CHCl+HCl, HCl + OH = Cl + H2O, CF3CH2Cl=CF3+CH2Cl, these fluorine-containing or chlorine-containing groups generated had an excellent effect on the suppression of combustion chain reactions. The in-depth experimental and theoretical study of R123 boost the development of ideal halon replacement in aircraft cargo compartment.

Combustion inhibition of cup-burner flame with $C_2HF_3Cl_2$ and its kinetics mechanism investigation

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Abstract

In order to explore the possibility of $C_2HF_3Cl_2$(R123) for the fire extinguishing agent of aircraft cargo compartment, this paper conducted experimental and theoretical research on the fire extinguishing performance and mechanism of R123, furthermore, the analogous C_2HF_5 (R125) was compared to explore the in-depth fire extinguishing mechanism. The minimum extinguishing concentration (MEC) of R123 in methane/air flames is 7.31 %, which is lower than 8.91 % of R125. And the experimental results reveal interesting examples of flame height and temperature changed with the addition of R123. The flame height had a phenomenon to increase first and then decrease, in comparison, the flame height kept rising with R125 adding. And the change in height reflected the addition of R123 to affect the movement of the reaction kernel, so that the temperature at different heights changed, but the temperature as a whole showed the tendence of decreasing. In addition, theoretical calculations indicated that R123 and pyrolysis products could affect the combustion reaction, such as CF_3CHCl_2+H=CF_3CHCl+HCl, HCl + OH = Cl + H_2O, CF_3CH_2Cl=CF_3+CH_2Cl, these fluorine-containing or chlorine-containing groups generated had an excellent effect on the suppression of combustion chain reactions. The in-depth experimental and theoretical study of R123 boost the development of ideal halon replacement in aircraft cargo compartment.

Key words

Fire suppression; $C_2HF_3Cl_2$; extinguishing performance; kinetics mechanism; aircraft cargo compartment

1. Introduction

Even though halon fire extinguishing agents owned excellent fire extinguishing performance, they were prohibited due to the severe ozone damage[1, 2]. Aircraft cargo compartment was granted an exemption to keep using halon fire extinguishing agents in the short-run, mainly due to that the flight safety could not be ensured owing to complex operating environment and the unachievable fire extinguishing replacements for the alternatives. Nevertheless, the International Civil Aviation Organization (ICAO) had still proposed that newly produced aircraft after 2024 cannot be equipped with halon extinguishing agents, and halon fire extinguishing systems cannot be used on all aircraft after 2040[3, 4]. To develop the alternative agents with excellent fire extinguishing performance, FAA has issued Minimum Performance Standard (MPS) for halon replacements in aircraft cargo compartment[5-7]. It detailed that the replacement agents must pass the four fire test scenarios: bulk-load fire, containerized-load fire, surface-burning fire and aerosol can explosion simulation[6].

According to the Federal Aviation Administration-mandated test for cargo-bay fire suppression (abbreviated herein as the FAA-ACT), the fire extinguishing agents, when added at sub-suppressing concentration, cannot induce the overpressure phenomenon compared with the uninhibited case. Several potential halon replacement agents, like C_3HF_7, $C_6F_{12}O$, $C_3H_2F_3Br$ (2-BTP), had failed in the FAA-ACT[3, 4]. Relevant research analyzing the FAA-ACT reported that the overpressure in the fire extinguishing tests might be due to the higher heat releasing from the reactions of fire extinguishing agents[8-11]. It is surprised that the agent $C_2HF_3Cl_2$ (R123) overcame the overpressure in the FAA-ACT[12, 13], hence, R123 is considered as the potential halon fire extinguishing agents.

The main advantage for R123 in the progress of fire extinguishing is that the heat release is lower after addition. Holmstedt et al.[14] conducted co-flow diffusion flame experiments using propane as fuel and HFCs, HCFCs and halon 1301 as inhibitors, and found that R123 was the only inhibitor other than halon 1301 that had not increased heat release rate. Takahashi et al.[13, 15-17] found that C_2HF_5 increased the total heat release in the flame by 158% and $C_2HF_3Cl_2$ increased by only 37%. However, it is unfortunate that the R123 was classified as a controlled replacement by Montreal Treaty due to its low ozone destruction potential[18]. Herein, even though R123 may be used as the fire extinguishing agent of aircraft cargo compartment in the short term, it will eventually be banned in a long-term halon replacement. Even so, in depth exploration of molecular-structural advantages of R123 for fire extinguishing performance at the molecular level are extremely useful for further screening the fire extinguishing agents with excellent environmental performance and conforming to the requirements of fire extinguishing performance of aircraft cargo. However, the fire extinguishing performance and mechanism analysis of R123 are still unclear, dramatically hindering the development of halon replacement.

This study provides the fire extinguishing performance and mechanism analysis of R123. For comparison, the similar analysis is also performed for the analogous HFC compound C_2HF_5(R125). The fire suppression effectiveness is evaluated by the cup burner apparatus, and the mechanism is simulated with high precision quantum mechanics based on density functional theory (DFT). Moreover, theoretical study of the reactions of OH· and H. with R123 and R125 can unravel the fire extinguishing mechanism associated with Cl· and F·. In-depth research on R123 can provide a basis for exploring environment friendly and highly efficient halon replacement agents for aircraft cargo compartment.

2. Experimental methods

2.1 Fire extinguishing experiment

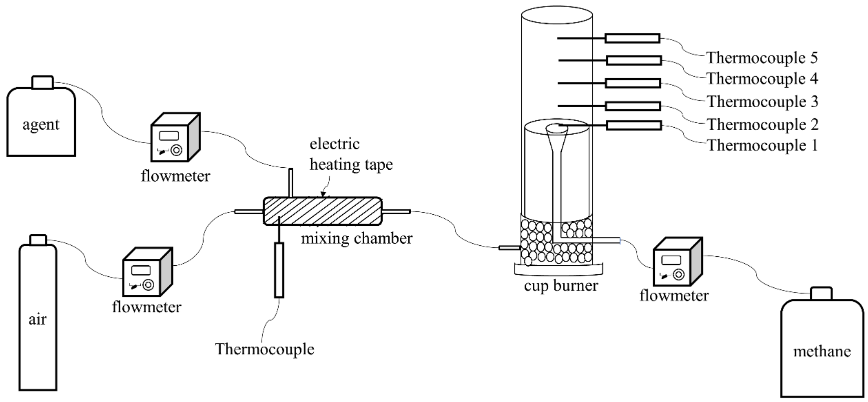

Figure 1 Schematic diagram of the cup burner system.

The schematic of the cup burner system is shown in Figure 1[1]. There are specific descriptions about the standard cup burner apparatus in ISO-14520. Hence, this study referred to the standard and gave a brief description here. The cup burner apparatus consists of the burner nozzle, the chimney, and the glass cover. The inner and outer diameters of the burner nozzle are 26 and 31 mm, respectively. The burner nozzle is located in the internal center of the chimney. The bottom of the burner is filled with 5mm and 7mm glass beads for uniform flow of air/agent. The outermost layer is a glass cover. The height of glass cover is 537 mm and the inside and outside of diameters are 83 mm and 89 mm, respectively. The fuel used in this study is methane (purity[?] 99.9 %) and the oxidizer is synthetic air (O_2 20.9 %; N_2 79.1 %). This study chose R123 as the main study object and R125 as the reference object. Temperature measurement is mainly achieved by K-type thermocouple and paperless recorder. There were five K-type thermocouples forming a 'thermocouple tree' and they are set at 0 cm (the bottom of the flame), 5 cm, 10 cm, 15 cm, and 20 cm respectively. The changes of temperature at different flame heights were measured in real time, and they were also displayed in real time by the paperless recorder, and the temperature data were collected every 1 second. Digital and high-speed cameras separately recorded the entire flame burning to extinguishing process.

Prior to the experiment, the mixing chamber and pipes were heated to 80 ˚C with heating bands to ensure that the R123 evaporated during delivery. In the experiment, the air flow rate was kept at 40 L/min and the flow rate of methane was adjusted to 240 mL/min, which were both controlled by the flow meters, consequently keeping the flame at 8 cm. After the stable burning of methane flame for at least 60 s, the agents were transported to the mixing chamber with air, then flowing into the cup burner. The amount in each increment of the flowmeter readings was 0.2 L/min, growing until flame extinguishment occurred. At the same time, in order to ensure that the agent and air reached the burner proportionally, the interval between each adjustment was at least 20 s. And finally, the experiment was repeated 3 times to ensure the reproducibility of the results. To investigate the extinguishing effect of R123, R125 was chosen to do the same experimental procedures as the reference object, and the experiments were also repeated for several times.

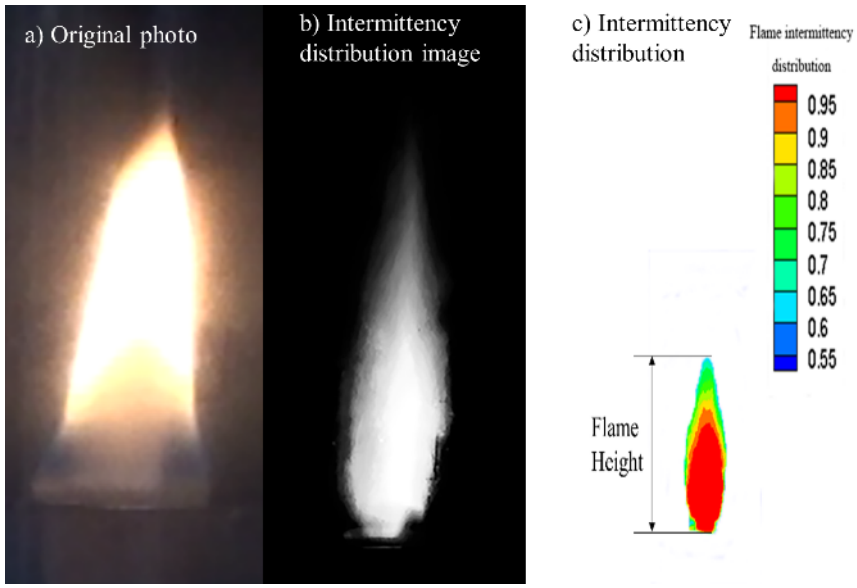

Figure 2 Flame processing images.

Flame morphology and flame height variations were recorded by digital and high-speed cameras. In each experiment, the two cameras were set at a certain distance from the cup burner, so the entire flame pattern could be recorded. In this study, Otsu's method was used to process flame images to obtain flame height, and flame height (h) was defined as the vertical distance from the nozzle to the flame tip[19, 20]. First, the original images were converted to gray scale images. each pixel point had its own luminance value in the gray scale image and the threshold value of the image was obtained objectively by using Otsu method. Then based on the luminance value and threshold value, the binary image could be obtained[21]. Finally, the binary image was processed to become the intermittency distribution image by processing program (Figure 2), which showed the probability of the flame occurring.

2.2 Theoretical calculations

In order to explore the detailed path of the fire extinguishing mechanism, Gaussian 16 was used for theoretical calculations, and Gauss view was used to view the optimized geometries of space[22, 23]. On the basis of DFT calculations, B3LYP/6-311++G (d, p) base sets were used for calculations. Reactants, products, transition states (TSs) and intermediates (IMs) were analyzed by DFT calculations, and the above calculation results were verified by using virtual frequencies, and there were no virtual frequencies for reactants, IMs and products, but only TSs had virtual frequencies[24, 25]. Then, the relationship and transformation relationship between the reactants and the products were analyzed using IRC theory. Meanwhile, in order to verify the accuracy of the reaction energy calculation value, single-point energy calculation and zero-point energy correction were performed on all stationing points. A more precise energy value was calculated at the CCSD/aug-cc-pVDZ level, the optimized structures were also employed in a series of single-point energy calculations by using coupled-cluster theory, and the correctness of each reaction path was verified to calculate the zero-point vibrational energy (ZPE) at the CCSD/aug-cc-pVDZ level[26, 27]. The energy barrier is the energy difference between the TSs and the reactants.

3. Results and discussion

3.1 Fireextinguishing concentration

On account of the boiling point of R123 (27.9 °C) exceed normal temperature, the fire-extinguishing experiment was performed under the heating condition. Herein, the calculation of minimum extinguishing concentration (MEC) should consider the temperature and pressure compensation. The temperature mainly influenced the gas flowed, so except for the flowmeter's conversion coefficient, the calculation required temperature and pressure compensation to calculate the actual flow. Based on the above consideration, the average MEC of R123 on methane fire was calculated as 7.31 %, the result is similar to reported results. By using the same cup burner test, the extinguishing concentration of R125 on methane fire under the normal temperature and pressure was 8.91 % by standard method calculated. Compared with the results of R125, R123 has a lower MEC, which indicates the better efficiency of fire suppression of R123.

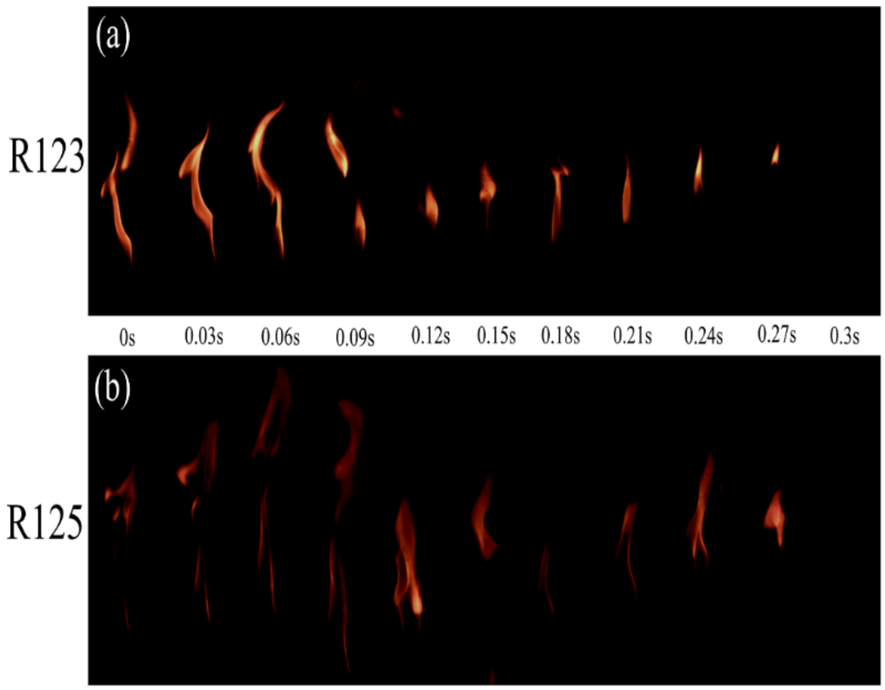

Figure 3 Flame appearances of R123 (a) and R125 (b) recorded by using a high-speed camera.

For clearly observing the process of fire extinguising, the flame behavior in the last 0.3 s before the fire was extinguished was recorded (in Figure 3). R123 and R125 extinguished the cup-burner flame both through the process of oscillation-separation-extinction. As the concentration reached the extinction limit, the flame oscillated frequently, and the flame root began leaving the rim of the cup-burner. Due to the sudden increase in the distance between the root of the flame and the burner at a certain point, the flame cannot return to the edge of burner, the two agents eventually cause the flame to blow out.

The addition of two extinguishing agents weakened the adhesion of the flame with the rim of cup, causing the flame to vibrate continuously. However, it was also found that R123 (Figure 3a) made the flame oscillation more obvious than R125 (Figure 3b) before extinguishing. For co-flow diffusion flame in the cup burner, the reaction kernel provides a continuing ignition source in the flame base, which can consume the new incoming reactants fast and maintain combustion, thereby the trailing diffusion flame in the flow can keep holding in succession[28, 29]. However, when the flame root starts appearing the separation from the rim of cup, the reaction kernel which was at the flame base was weakened by the addition of extinguishing agents, thus the phenomenon of flame oscillation was occurred. It is indicated that the influnce of R123 on the reaction kernel is greater than R125, the addition of R123 may make the phenomenon of flame oscillation more obvious.

3.2 Flame height

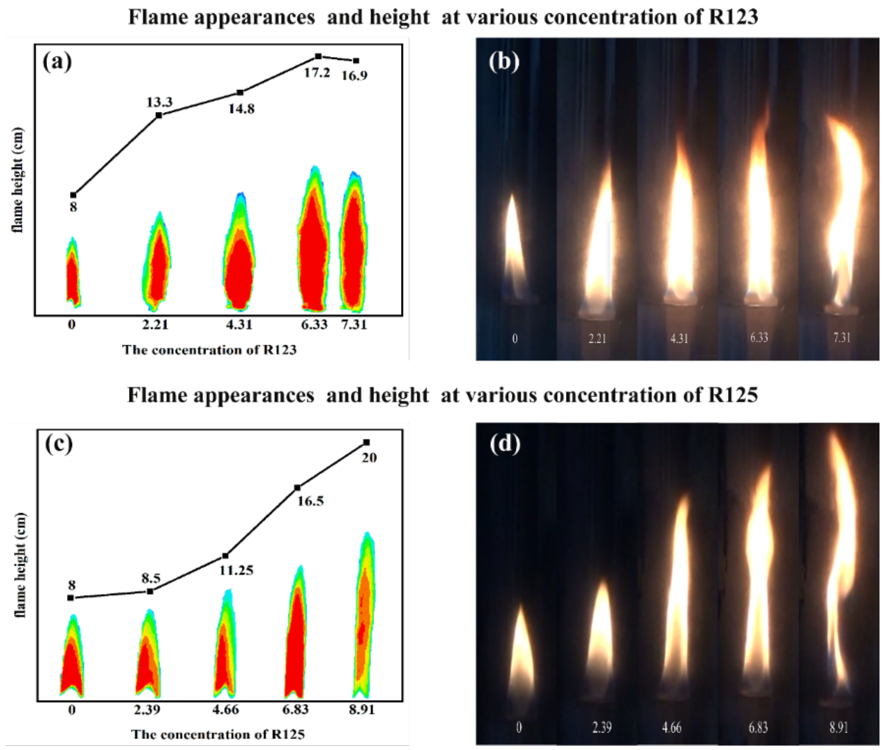

Figure 4 Flame (a) and appearances (b) at various concentration of R123 and flame appearances height (c) and appearances (d) at various concentration of R125.

Figure 4 shows the evolution of the flame height after adding different volume concentrations of two extinguishing agents. With the addition of R123 (Figure 4a and b), the flame height occurred the process of rapid increase (0-2.21 %, 8 to 13.3 cm), slow increase (2.21-6.33 %, 13.3 to 17.2 cm) and slight decrease (7.31 %, 17.2 to 16.9 cm). There is a reason for the increased height that R123 can increase the O_2 demand of combustion system and make unfired gas buoyancy to burn with O_2[6, 30]. The density of the agent and its decomposition products, and their heat-release all effect the buoyancy forces, then may affect the flame height variations and flame oscillations[9]. Furthermore, after the R123 concentration exceeded 6.33 %, the flame height decreased from 17.2 to 16.9 cm. From Figure 4b, as the concentration of R123 above 6.33 %, flame oscillation become more evident. The decreased height and oscillation of flame mainly result from two theory. On one hand, abundant fluorine-containing or chlorine-containing groups were generated with plenty of R123 inhibiting combustion reactions, further effectively inhibiting the combustion chain reactions[31]. On the other hand, R123 and oxidizers was flowing on both sides of the nozzle, and they entered the reaction zone from the root of flame, thus the reaction kernel would be affected and weakened. Therefore, the reaction kernel is too weak to maintain the flame stable, and the balance location of the reaction time and the residence time becomes difficult to obtain. Eventually, the flame oscillated violently, then blown out.

In comparison with R123, R125 made the flame height increase continuously (0-8.91 %, 8 to 20 cm). Apart from the different changes of flame height, the flame width did not have obvious change with the addition of R125 (Figure 4c and d), but the flame was widened with the addition of R123 (Figure 4a and b). For the co-flow diffusion flame in cup burner, the flame width was wider, the combustion reaction was slower[32], thus the addition of R123 made total combustion reactions slow, which may accelerate the process of the fire extinction[33]. Consistent with the results of the minimum fire extinguishing concentration calculated earlier, the extinguishing performance of R123 is better than that of R125.

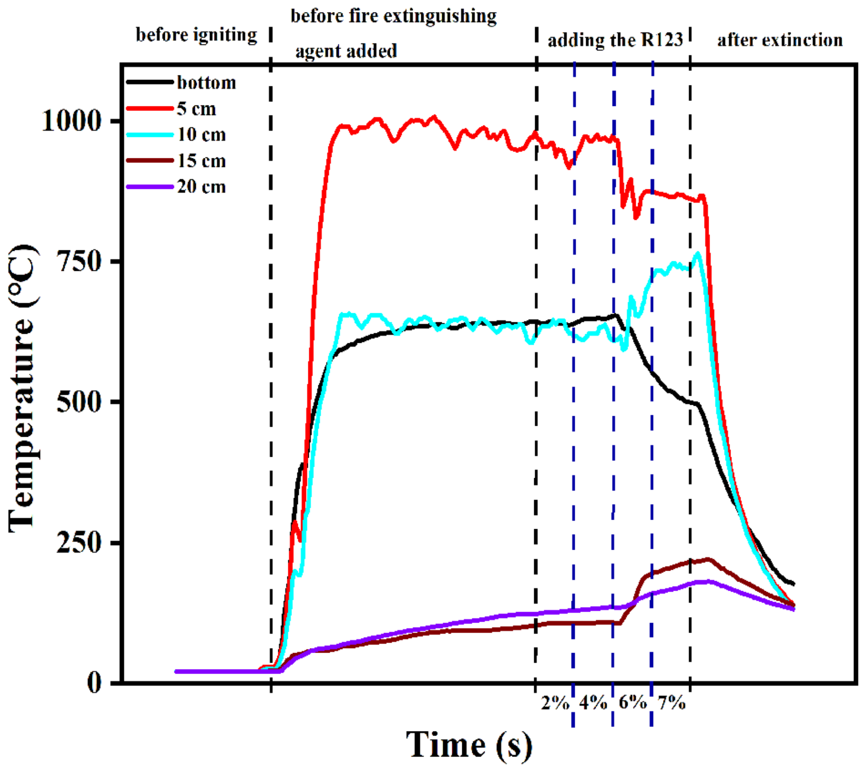

Figure 5 Temperature at various concentration of R123.

To further explore the effect of the addition of R123 on the flame, it is necessary to investigate the temperature change. Figure 5 shows the flame temperature at different heights changed over time. It is well known that both the heat-release rate per unit volume along the zone and the flame size affect the total quantity of heat[13, 30]. On the other hand, halogenated extinguishment added causes the flame reaction kernel weakened, which can decrease the heat of reaction. As shown in Figure 5, It can be clearly observed that R123 went from 0 to 4 %, and the temperature fluctuated in the range of 890 °C. Then the temperature of the spout and 5 cm height decreased as the addition exceeded 6 % until extinguishment, but the temperature of 10 cm, 15 cm and 20 cm height was increased, especially the 10 cm height increased from about 550 °C to about 750 °C. Therefore, it is speculated that the reaction kernel with the premixed flame structure was weakened and moved up by R123 addition, the temperature decreased, and the flame became unstable. At the same time, the addition of R123 would provide more reactants for the combustion of the trailing diffusion flame, thereby releasing additional heat and increasing the temperature at the tail flame.

3.3 R123 of thermal decomposition and reaction with active radicals

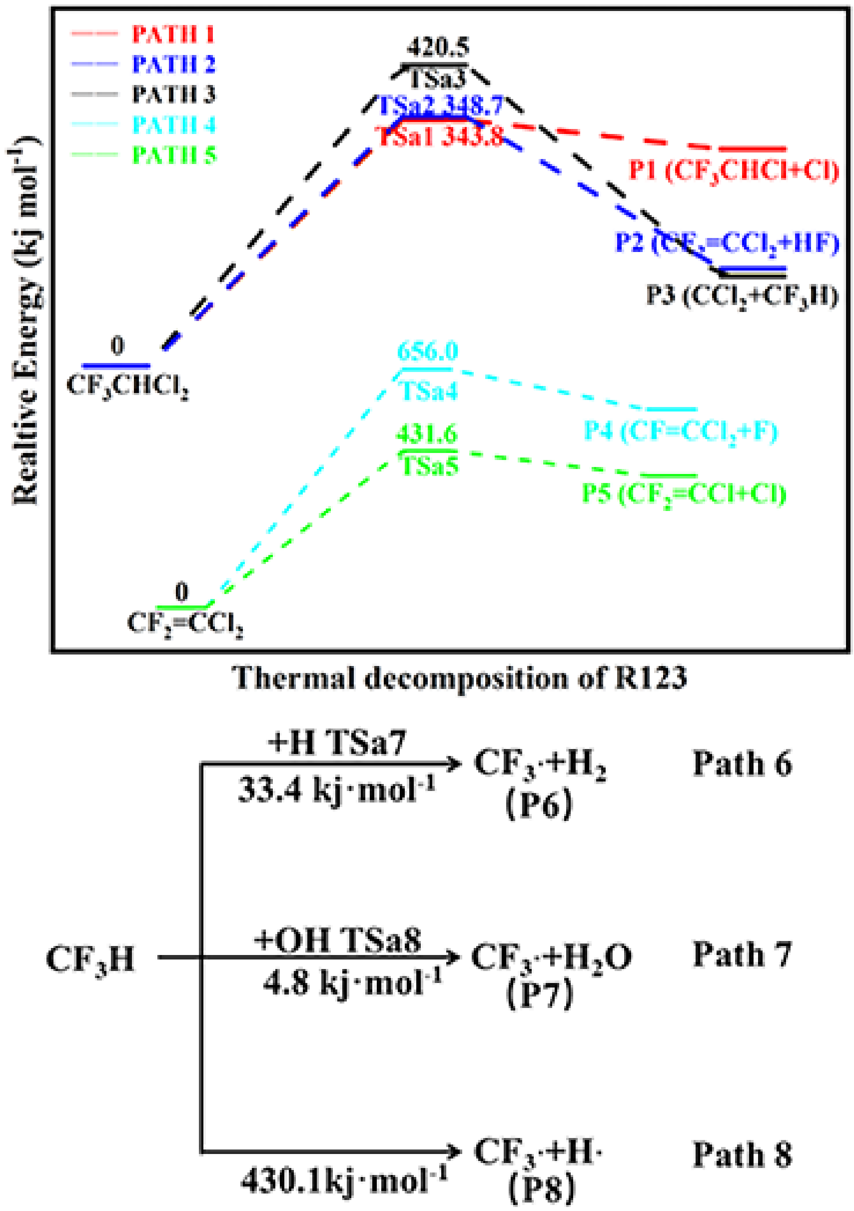

Figure 6 Energy diagram of R123 decomposition pathway.

In order to unravel the fire extinguishing mechanism of R123, the reaction pathways of R123 with H and OH radicals and the direct decomposition pathway of R123, were separately explored. the B3LYP/6-311++G(d,p) method was used for structural optimization of transition states, and the CCSD/aug-cc-pVDZ method was used for correlation energy calculations.

The decomposition pathway of the ground state of R123 should be first considered. As revealed in Figure 6, there are three main pyrolysis paths for R123, and path 4 and 5 are the subsequent reactions of the pyrolysis products. In path 1, the break of the C-Cl bond occurred, the products $CF_3CHCl\cdot$ and $Cl\cdot$ (P1) are obtained by overcoming an energy barrier of 343.78 kj·mol^{-1}. Path 2 predominantly undergoes the elimination reaction, the path eliminates from R123 to form a HF molecule and $CF_2{=}CCl_2$ by overcoming an energy barrier of

348.68 kj·mol-1. There are two paths for the decomposition of $CF_2{=}CCl_2$. The $CF_2{=}CCl_2$ can consume 656.02 kj·mol-1 energy to produce $CF{=}CHCl_2$· and F· via the transition state of TSa4 in path 4, or consume 431.56 kj·mol-1 energy to produce $CF_2{=}CHCl$· and Cl· via the transition state of TSa5 in path 5. In addition, it is found that the above paths are endothermic reactions, indicating that R123 can play a physical fire extinguishing method of cooling in fire extinguishing. In path 3, the products CF_3H and CCl_2 are obtained by overcoming an energy barrier of 420.5 kj·mol-1. As shown in path 6˜8, CF_3H has three paths to generate plentiful CF_3· free radicals, where CF_3H decomposition produces CF_3· without transition state generation. It is worth noted that CF_3· is one of the free radical groups that will play an important role in the process of fire suppression. According to the literature[34, 35], CF_3· free radicals can effectively capture both H· and OH· in combustion, thereby interrupting the combustion chain reaction. R123 is capable of producing enough CF_3·, indicating that R123 has the potential to extinguish fire as an alternative extinguishing agent. According to the literature, R125 mainly occurs C-C fracture reactions reaction and elimination reaction, wherein the product contains CF_3· and CF_2·. Like the pyrolysis products of R123, these pyrolysis products are very easy to react with H· and OH· free radicals, interrupting the combustion chain reaction.

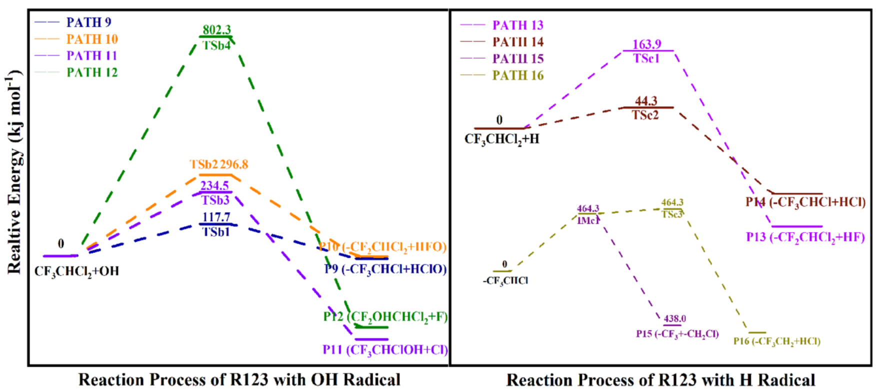

Figure 7 Potential energy diagram of the reactions between R123 and H·, OH·.

The analysis of the reaction of fire extinguishing agent and its decomposition derivatives with H· and OH· is also an important aspect of revealing the fire extinguishing mechanism of fire extinguishing agent, hence the reactions of R123 with H· and OH· radicals are theoretically simulated in detail (Figure 7). OH· radical interacts with different atoms in R123 to form different products. The C-Cl bond homolysis reaction occurs in path 9, the OH· can absorb an Cl atom of R123 to generate CF_3CHCl· and HClO through the TSb1, overcoming the energy barrier of 117.7 kj·mol-1. The C-F bond homolysis reaction occurs in path 10, R123 interacts with OH· through abstraction reaction to generate CF_2CHCl_2· and HFO, the reaction to occur requires the absorption of about 296.8 kj·mol-1 energy. Furthermore, there are two paths about substitution reaction. In path 11 and path 12, OH· radical can replace the Cl· and F· atoms in R123 to form $CF_3CHClOH$ and $CF_2OHCHCl_2$, respectively, the products are generated via the TS of TSb3 and TSb4 with the energy barriers of 234.5 and 802.3 kj·mol-1, the Cl· and F· atoms will be very easy to react with free radicals such as H· and OH·, reducing the chain reactions in combustion. For the reaction of R123 with H·, two abstraction reaction paths are theoretically exhibited in Figure 7. P13 (path 13) and P14 (path 14) are generated via TSc1 and TSc2 by conquering the energy barriers of 136.9 and 44.6 kj·mol-1 separately. According to the energy barrier, it can be seen that P13 is more likely to generate than P14. And through further simulation calculations it is found that CF_3CHCl· can generate CF_3· via C-C bond fracture, the specific reaction is shown in path 15 and path 16. The generation of CF_3· promotes the chemical action of R123 in fire extinguishing and also accelerates the speed of fire extinguishing.

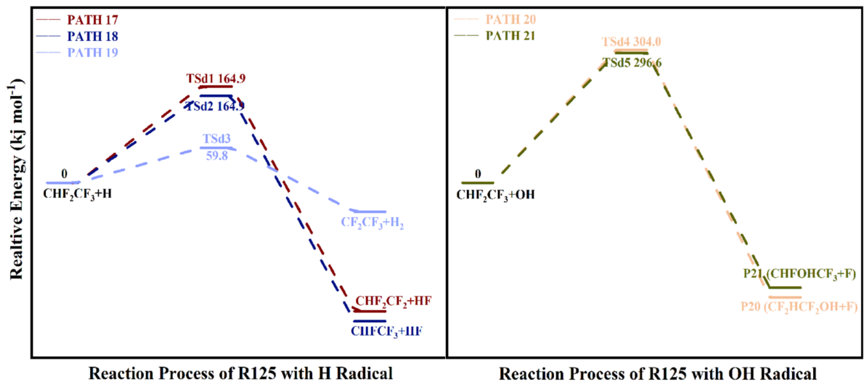

Figure 8 Potential energy diagram of the reactions between R125 and H·, OH·.

In order to further explore the fire extinguishing mechanism of R123, the reactions of R125 with H· and OH· radicals are also calculated as a comparison (Figure 8). The same as R123, R125 and free radicals mainly undergo substitution reactions and abstraction reactions. For the reaction of R125 with H·, three additive reaction paths are theoretically exhibited, with P17 (path 17), P18 (path 18) and P19 (path 19) separately generated via TSd1, TSd2 and TSd3 by consuming 164.9, 148.6 and 59.8 kj·mol^{-1}. And two substitution reactions occur about R125 with OH·, which consumes 304.0 and 296.6 kj·mol^{-1} respectively, these reactions can generate more F· atoms. However, the product of R123 contains not only F· atoms but also Cl· atoms, Cl· atoms are easier to generate than F· and CF_3· atoms, and the energy barriers that need to be overcome are lower, so the fire extinguishing performance of R123 is better. The introduction of fluorine-species reactions and chlorine-species reactions in literature, it is indicated that fluorine-species reactions have less sensitive to the burning velocity. For the chlorine-species reactions, the burning velocity is sensitive to three reactions of the initial break-down of R123, such as CF_3CH_2Cl=CF_3+CH_2Cl, CF_3CHCl_2+H= CF_3CHCl+HCl[18]. And two of the reactions in the catalytic radical recombination cycles (HCl + OH = Cl + H_2O, and Cl + HCO = CO + HCl) are affecting the burning velocity[36, 37]. In general, the chlorine-species reactions have more obvious inhibitory effect on the burning velocity.

4. Conclusion

For finding an alternative halon fire extinguishing agent for use in aircraft cargo compartments, R123 may have advantages over R125 as fire suppressants. To understand the different between R123 and R125, Fire extinguishing experiments with the addition of R123 and R125 to methane/air combustion systems were carried out, and detailed studies were also carried out in the thermal decomposition mechanism and fire extinguishing mechanism.

To explore the fire-extinguishing effectiveness of R123 and R125, the MEC, flame shape, flame height and temperature changes were studied through the cup-burner experiments. The MEC of R123 and R125 on suppressing the methane-air flame were 7.31 % and 8.91 % respectively, the comparison of flame shape and flame height variations showed that R123 had excellent fire extinguishing performance. The temperature change is not obvious when the concentration of R123 is less than 6 %, and the temperature changes sharply when approaching the fire extinguishing concentration indicate that the addition of R123 prompts the flame reaction kernel to move until extinguished.

The theoretical results directed that R123 by pyrolysis or reaction with free radicals would produce F·, Cl· and CF_3· groups, these groups were very easy to react with H· and OH· to interrupt the combustion chain reaction. By analyzing the calculation of the reaction of R123 and R125 with free radicals, respectively, the Cl· produced by R123 had a greater impact on flame extinguishing than F·. Noteworthy, the theoretical calculation results are in good agreement with the experimental results.

Declaration of Competing Interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version

Reference

[1] X. Wang, R. Wu, L. Cheng, X. Zhang and X. Zhou,*Thermochim. Acta* **2020** , 683.

[2] R. Wu, X. Wang, L. Cheng, C. Ren, X. Wei and X. Zhang, *New J. Chem.* **2020** , 44, 12932-12941.

[3] J. W. Reinhardt, D. Blake and T. Marker, Development of a Minimum Performance Standard for Aircraft Cargo Compartment Gaseous Fire Suppression Systems, **2000** .

[4] J. W. Reinhardt, Behavior of Bromotrifluoropropene and Pentafluoroethane When Subjected to a Simulated Aerosol Can Explosion,**2004** .

[5] J. W. Reinhardt, Minimum Performance Standard for Aircraft Cargo Compartment Halon Replacement Fire Suppression Systems (2012 Update),**2012** .

[6] J. W. Reinhardt, Minimum Performance Standard for Aircraft Cargo Compartment Halon Replacement Fire Suppression Systems (2nd Edition); Technical note, **2005** .

[7] T. Marker, Initial development of an exploding aerosol can simulator, **1999** .

[8] Linteris, Gregory, Takahashi, F., Katta, V., Chelliah, H., Meier and O., *Fire Safety Science* **2011** , 10, 307-320.

[9] G. T. Linteris, D. R. Burgess, F. Takahashi, V. R. Katta, H. K. Chelliah and O. Meier, *Combust. Flame* **2012** , 159, 1016-1025.

[10] G. T. Linteris, V. I. Babushok, P. B. Sunderland, F. Takahashi, V. R. Katta and O. Meier, *Proc. Combust. Inst.* **2013** , 34, 2683-2690.

[11] V. I. Babushok, G. T. Linteris and O. C. Meier, *Combust. Flame* **2012** , 159, 3569-3575.

[12] V. I. Babushok, G. T. Linteris, O. C. Meier and J. L. Pagliaro,*Combust. Sci. Technol.* **2014** , 186, 792-814.

[13] F. Takahashi, V. R. Katta, G. T. Linteris and V. I. Babushok,*Proc. Combust. Inst.* **2015** , 35, 2741-2748.

[14] G. Holmstedt, P. Andersson and J. Andersson, Investigation of Scale Effects on Halon and Halon Alternatives Regarding Flame Extinguishing, Inerting Concerntration and Thermal Decomposition Products, **2018** .

[15] V. R. Katta, F. Takahashi and G. T. Linteris, *Combust. Flame* **2004** , 137, 506-522.

[16] G. T. Linteris, V. R. Katta and F. Takahashi, *Combust. Flame* **2004** , 138, 78-96.

[17] G. T. Linteris, F. Takahashi and V. R. Katta, *Combust. Flame* **2007** , 149, 91-103.

[18] J. L. Pagliaro, G. T. Linteris and V. I. Babushok,*Combust. Flame* **2016** , 163, 54-65.

[19] P. He, P. Wang, K. Wang, X. Liu, C. Wang, C. Tao and Y. Liu,*Fuel* **2019** , 237, 486-493.

[20] C. Tao, B. Liu, Y. Dou, Y. Qian, Y. Zhang and S. Meng,*Fuel* **2021** , 290.

[21] N. Otsu, *IEEE Transactions on Systems, Man, and Cybernetics* **1979** , 9, 62-66.

[22] R. R. Yu, W. H. Hu, X. Zhang, X. Y. Wang and Z. Y. Tan,*Int. J. Quantum Chem.* **2022** , 122.

[23] Y. Wang, X. Y. Wang, X. Zhang, H. L. Fu, Z. Y. Tan and H. J. Zhang, *Int. J. Quantum Chem.* **2020** , 120.

[24] C. Gonzalez, J. J. W. Mcdouall and H. B. Schlegel, *J. Phys. Chem.* **1990** , 94, 7467-7471.

[25] C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.***1989** , 90, 2154-2161.

[26] X. Zhou, W. Chen, M. Chao and G. Liao, *J. Phys. Chem.***2013** , 153, 101-106.

[27] R. Zhai, Z. Yang, Y. Chen, B. Feng and W. Zhao, *Energy***2019** , 189, 116087-.

[28] F. Takahashi, W. John Schmoll and V. R. Katta, *Symposium (International) on Combustion* **1998** , 27, 675-684.

[29] V. Katta, *Combust. Flame* **2004** , 137, 506-522.

[30] F. Takahashi, G. T. Linteris and V. R. Katta, *Combust. Flame* **2008** , 155, 37-53.

[31] S. Zhou, Q. Yang, H. Zhang and X. Zhou, *Phys. Chem. Chem. Phys.* **2021** , 23, 11411-11423.

[32] Y. H. Zhang, Z. A. Huang and Y. K. Gao, *Combustion and Explosion* , Metallurgical Industry Press, **2015** .

[33] StephenR.T, *An Introduction to Combustion Concepts and Applications (Second Edition)* , Tsinghua University publishing house co., ltd, **2009** .

[34] M. Zhang, Z. Lin and C. Song, *J. Chem. Phys* .**2007** , 126, 034307.

[35] H. J. Zhang, X. F. Meng, Q. Yang and X. M. Zhou, *ACS Sustain. Chem. Eng.* **2021** , 9, 1272-1285.

[36] J. C. Leylegian, D. L. Zhu, C. K. Law and H. Wang,*Combust. Flame* **1998** , 114, 285-293.

[37] J. C. Leylegian, C. K. Law and H. Wang, *Symposium (International) on Combustion* **1998** , 27, 529-536.