The Influence of \( \text{O}_2 \) on Decomposition Characteristics of c-C\(_4\)F\(_8\)/N\(_2\) Environmental Friendly Insulating Gas

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Abstract: The c-C\(_4\)F\(_8\) gas is considered to have great potential as a gaseous medium for gas-insulated equipment, due to its good insulation properties and its relatively low greenhouse gas potential (GWP) relative to SF\(_6\). However, the decomposition is an important indicator of its use in equipment. In this paper, the decomposition characteristics of c-C\(_4\)F\(_8\) and the influence by oxygen have been explored through experiments and theoretical calculations. Firstly, the breakdown test of mixed gas was carried out and the precipitated elements of the electrodes and breakdown products of gas mixture were analyzed by X-ray photoelectron spectroscopy (XPS) and gas chromatography mass spectrometry (GC-MS). At the same time, the differences in decomposition products have also been studied when a small amount of \( \text{O}_2 \) was present. The path and mechanism of c-C\(_4\)F\(_8\) decomposition is then discussed, based on density functional theory (DFT). The results show that the black powdery substance descends on the electrode surface after the breakdown of the mixture of c-C\(_4\)F\(_8\)/N\(_2\) gas containing \( \text{O}_2 \), and its main constituent elements are C, O and F. \( \text{O}_2 \) can promote the decomposition of c-C\(_4\)F\(_8\). The mixture with \( \text{O}_2 \) produced a large number of additional toxic and corrosive COF\(_2\) in addition to generating more CF\(_4\), C\(_2\)F\(_4\), C\(_3\)F\(_6\), C\(_2\)F\(_6\), C\(_3\)F\(_8\) and C\(_3\)F\(_8\). The GWP values of the products are lower than SF\(_6\). Comprehensive insulation properties and decomposition characteristics, c-C\(_4\)F\(_8\) should not be mixed with dry air for use, and the oxygen content should be strictly controlled in c-C\(_4\)F\(_8\) mixed gas.

Keywords: SF\(_6\) alternative gas; c-C\(_4\)F\(_8\)/N\(_2\) gas mixture; breakdown characteristics; decomposed component; greenhouse effect

1. Introduction

Sulfur hexafluoride (SF\(_6\)) has been widely used in the power industry due to its excellent insulation and arc extinguishing properties. A total of 80% of the SF\(_6\) is used in high voltage circuit breakers and other high-pressure gas insulation equipment [1]. However, SF\(_6\) was listed as one of the six major greenhouse gases with a GWP (Global Warming Potential) of 23,500 and an atmospheric lifetime of 3200 years in the 1972 Kyoto Protocol [2,3]. Although the atmospheric concentration of SF\(_6\) is relatively low, contributing to 0.1% of the total anthropogenic radiative forcing, the concentration is growing continuously because of the compound’s long lifetime of ∼3200 years [4,5]. Over the past five years, the content of SF\(_6\) in the global atmosphere has increased by 20% [6]. California proposed that the use of SF6 in the electrical field should be reduced annually from 2020 and the European Union
plans to reduce SF6 emissions to 2/3 between 2014 and 2030 [7]. In order to ensure the sustainable development of the power industry, reducing the use of SF6 has become an important task in the current production and use of power equipment. In addition, SF6 could generate a variety of harmful gases such as SO2, SO2F2, SO3F2, S2F10, under partial discharge, spark discharge or arc discharge [8–10]. Therefore, looking for an environmentally friendly and safe gas as an alternative insulation medium in power equipment, has become a sought-after solution.

In the current research, the ideal substitutes for SF6 include perfluorocarbons (PFCs), trifluoriodomethane (CF3I), and other gases. Among them, the C-I bond of CF3I can easily be broken to produce iodine solid, which produces toxic gases such as CH3I, COF2 after discharge, which is not conductive to the long-term safe operation of the equipment [11,12]. Of course, the adsorbent can adsorb by-products, but finding a suitable adsorbent and whether the adsorbent has an effect on the insulation is also a problem. PFCs mainly include C2F6, C3F8, c-C4F8, among which c-C4F8 is the most excellent insulating property (about 1.18 times that of SF6). It is non-toxic to humans and the environment with the GWP of 8700 and the liquefaction temperature of −6 ºC [13]. Although c-C4F8 also has greenhouse effect, its global warming potential is much lower than SF6 (23,000). Replacement of SF6 with c-C4F8 in power equipment will significantly reduce the greenhouse effect. So far, there are still many scholars to study the possibility of replacement SF6.

Concerning the new environmentally friendly insulation gas produced by 3M, apart from the C5F10O (Novec 5110) mentioned by reviewers, there is also C4F7N (Novec 4710) [14,15]. Both of these gases are hot in the current stage of research. We do not deny the superior performance of these two gases. However, gas liquefaction temperatures such as C5F10O are too high to be suitable for all types of gas-insulated equipment. In recent years, many researchers have studied the insulation performance of c-C4F8 with N2, CO2 and other mixed gases under DC, AC and lightning impulse voltage. It is concluded that the electrical strength of c-C4F8-N2 mixtures can only reach approximately 0.57 times that of pure SF6 at 0.5 MPa with c-C4F8 concentrations of 20% [16], but 15–20% c-C4F8 gas mixture meets the requirements of electrical equipment, and mixtures can greatly reduce the impact of insulating gas on the environment [17–19]. Li et al. calculated the mixtures between c-C4F8 and variety of gases in order to determine the mixed gas insulation. For example, the critical breakdown strength of c-C4F8-N2 and c-C4F8-air are similar and significantly higher than other mixed gases. When the content of c-C4F8 exceeds 80%, the insulation property of mixture can reach the level of pure SF6 but there is a lack of experimental data for validation [20]. Some studies on the decomposition characteristics of c-C4F8 have achieved some results. Li et al. [21] explored the decomposition products of c-C4F8 under various typical faults based on the gas chromatograph-mass spectrometer test. It was found that the decomposition of c-C4F8 mainly produced CF4, C2F6 and C2F4, C3F8, C4F8. Hayashi et al. [22] discussed the main pathways for the dissociation of c-C4F8 to generate free radicals CF2 based on the density functional theory (DFT), providing guidance for further investigation of the decomposition mechanism of c-C4F8. As the core insulating gas, c-C4F8 may need to be mixed with other gases due to the liquefaction temperature, and dry air is the common buffer gas. The theoretical calculations and experimental studies have shown that c-C4F8-N2 has good insulation properties. Potential alternative environmentally-friendly alternative gas and dry air often are mixed as an insulating medium. Additionally, in order to promote the recovery after the arc, O2 often appears in the arc medium. However, the related research is lacking, and the toxicity and environmental safety of the decomposition products after mixing with oxygen are urgent to be investigated. Oxygen introduction is divided into passive introduction and active introduction. Passive introduction mainly refers to the introduction of trace amounts of oxygen introduced by the equipment during operations such as transportation, assembly, maintenance, and ventilation. Generally, it will not exceed 1%, which is similar to the problems faced by SF6 gas insulation equipment [23]. The other is active introduction, because the environment-friendly insulation gas may be mixed with dry air to fill the equipment. In addition to nitrogen and CO2, dry air mainly contains O2. The safety of the other two gases has been verified in many studies [24]. Therefore, the influence of O2 on the insulation performance and decomposition properties of c-C4F8 also needs to be studied, and it is very urgent.
The influence of oxygen on the decomposition of mixed gas can provide the basis for exploring c-C₄F₈-air and the performance analysis of the decomposition products is also an important indicator of evaluation gas application. In order to obtain a new insulation formula for environmental safety and to study the possible causes of hazardous products, it is necessary to test and analyze the physical and chemical processes of oxygen gas mixture discharge.

In this paper, the decomposition products of pure c-C₄F₈ and the c-C₄F₈/N₂ mixed gas are explored experimentally and the influence of oxygen are also considered. N₂ is just the buffer gas added in order to reduce the liquefaction temperature, because its physical and chemical properties are stable and not easy to decompose. After several frequency breakdown experiments, the decomposition products and electrode precipitation elements were obtained by GC-MS (gas chromatography mass spectrometry) and XPS (X-ray photoelectron spectroscopy). Based on the density functional theory, the structural characteristics of c-C₄F₈ were calculated firstly, the stability of the molecular structure and the reactive sites were analyzed. The possible dissociation pathways of c-C₄F₈ and the formation mechanism of the decomposition products were discussed. The purpose of this paper is to study the changes of decomposition products with the participation of oxygen and explore the safety and environmental protection of products. The comprehensive evaluation of the influence of oxygen on the decomposition characteristics of c-C₄F₈ provides a reference for the research of SF₆ alternative gas.

2. Experimental Setup

The test was carried out at a 50 Hz AC voltage gas insulation performance test platform. In the experiment, N₂, which is stable chemically gas, was used as the buffer gas.

Before the experiment, the airtightness of the gas chamber was checked, and the sealed gas chamber was evacuated using a vacuum pump (BECKER/VT4.16, BECKER, Wuppertal, Germany) and was allowed to stand still for 60 min (less than 10 Pa). N₂ gas is used to clean the gas chamber. The above steps are repeated 2 to 3 times in order to avoid the influence of impurity gases. After cleaning, the mixed gas is introduced into the gas chamber. The ball-ball electrode was used in the experiment. The diameter of the copper ball was 50 mm with the electrode spacing of 5 mm. The range of applications for mixed gases may be medium-voltage gas-insulated devices such as switch cabinets. Because the key part of the conductivity in these devices is made of copper, it is used as the electrode material. The purity level of the c-C₄F₈ and N₂ is 99.999%.

According to the literature [24], it has been shown that the breakdown behavior of c-C₄F₈/N₂ mixture (the mixing ratio of c-C₄F₈ is 5%~20%) under uniform electric field is similar to that of SF₆/N₂ with the same mixing ratio. The Corona discharge performance of c-C₄F₈/N₂ is better than the same mixing ratio SF₆/N₂. If the c-C₄F₈/N₂ gas mixture is not liquefied at −30 °C, the content of c-C₄F₈ in the gas mixture is at most about 15% [25]. Therefore, the pure c-C₄F₈, 15% c-C₄F₈/N₂ and with 3% O₂ were selected as samples in this paper. The test was carried out by a step-and-step method, and the gas mixture was broken down 50 times to detect decomposition products. The details are shown in Figure 1.

![Figure 1. The step method.](image-url)
GC-MS is used for detection of gas mixture components after the breakdown discharge. CP Sil 5CB was selected as the column. GC analysis, the high purity He (the purity of gas is above 99.999%) gas is used as a carrier gas, and carrier gas filters (including He filter and RP oil filter) are used to filter out the impurities, which may affect the column and interfere with the experimental results. Inlet temperature is 220 °C and inlet pressure is 56.1 kPa. The injection mode uses a split flow method with a split ratio of 10:1 and an injection volume of 1 mL. The column flow rate is 1.2 mL/min, and the purge flow rate is 3.0 mL/min. The heating rate of gas into the oven is shown in Figure 2. The oven had an initial temperature of 35 °C, a final temperature of 150 °C, and a temperature increase rate of 40 °C/min. The column temperature was maintained at 35 °C for 0~8 min, and after 8 min, the temperature rose steadily to 150 °C, and the temperature rising rate was kept at 40 °C/min. MS analysis, the ion source temperature is 200 °C, the chromatographic mass spectrometry interface temperature is 220 °C, ionization mode is Electronic ionization (EI). The solvent delay time was 0.1 min; the detector voltage threshold was 100 and the voltage was 0.1 kV. The specific steps can be found in [26–30].

Figure 2. Oven temperature of GC-MS (gas chromatography mass spectrometry).

3. Experimental Results

3.1. Electrode Precipitate Component Analysis

Figure 3 shows the surface of the ball electrode before and after breakdown of pure c-C₄F₈, c-C₄F₈/N₂ gas without O₂ and with 3% O₂. It can be seen that the surface of the copper ball electrode is covered with a layer of black powdery solid. Compared to pure gas, the mixed gas deposits are significantly less. However, the addition of oxygen increases the production of solid products while there only was a clear trace of ablation on the electrode surface at absence of O₂ in mixture. The ESCALAB 250Xi photoelectron spectrometer (Thermo Scientific Corp., Waltham, MA, USA) was used to scan the black surface of the electrode by XPS. It was found that it consisted of C, F, O and N elements. Table 1 shows the content of each component in the black material, in which the C content is 58.44%, which is the main constituent element, the content of O is 17.32%, the N element content is 0.75% and the F element content is 23.49%. Figure 4 shows the C photoelectron scanning.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (%) (Precision: 0.01%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>58.44</td>
</tr>
<tr>
<td>O1s</td>
<td>17.32</td>
</tr>
<tr>
<td>N1s</td>
<td>0.75</td>
</tr>
<tr>
<td>F1s</td>
<td>23.49</td>
</tr>
</tbody>
</table>
was conducted on the mixed gas and the decomposition components of the mixed gas were detected. The test results are consistent with the literature [21].

In order to further verify the accuracy of the experimental results, the gas-insulated test platform was used to conduct continuous, 50 rounds of pure c-C4F8, c-C4F8/N2 mixed gas with 0% and 3% O2 content breakdown tests and analysis of discharge breakdown components. The breakdown test was conducted on the mixed gas and the decomposition components of the mixed gas were detected. Figure 5a,b shows the GC-MS chromatograms (Varian Medical Systems, Inc., Palo Alto, CA, USA) of the two mixed gases after breakdown. Qualitative analysis is carried out using the combined methods of the United States National Institute of Standards and Technology (Nist14.0) database, and standard gas chromatography scanning.

Figure 3. The spherical electrode before and after breakdown of c-C4F8/N2 gas. (a) the ball electrode before breakdown; (b) 15% c-C4F8/85% N2; (c) 100% c-C4F8; (d) 15% c-C4F8/82% N2/3% O2.

As shown in Figure 4, the maximum intensity of the corresponding C element binding energy is about 285 eV, corresponding to the chemical structure of the C–C single bond structure, which constitutes the C elemental elements. With C element loss of electrons, the binding energy can increase to 290 eV, corresponding to the chemical structure of O–C=O, which may constitute a variety of carbon oxides. Through XPS analysis, the black surface of the electrode may show a single element of C and various oxyfluorides of carbon. The test results are consistent with the literature [21].

3.2. Experimental Analysis of the Decomposition Products of c-C4F8 under Micro-Oxygen Condition

In order to further verify the accuracy of the experimental results, the gas-insulated test platform was used to conduct continuous, 50 rounds of pure c-C4F8, c-C4F8/N2 mixed gas with 0% and 3% O2 content breakdown tests and analysis of discharge breakdown components. The breakdown test was conducted on the mixed gas and the decomposition components of the mixed gas were detected. Figure 5a,b shows the GC-MS chromatograms (Varian Medical Systems, Inc., Palo Alto, CA, USA) of the two mixed gases after breakdown. Qualitative analysis is carried out using the combined methods of the United States National Institute of Standards and Technology (Nist14.0) database, and standard gas chromatography scanning.
The presence of O₂ promotes the decomposition of c-C₄F₈/N₂. The mass-to-charge ratio M/Z = 1 was selected as the base peak. As shown in Figure 5a, the chromatograms of the two mixed gases showed the characteristic peaks of CF₄, C₂F₆, C₂F₄ and C₃F₆. The characteristic peak of COF₂ also appears with O₂ of 3%. COF₂ is a highly toxic gas with a strong irritating effect on the skin and respiratory mucosa. It is also corrosive and can irreversibly damage equipment insulation. In order to display all products containing CF₃• groups, the results of the scan were analyzed using M/Z = 69 as the base peak, as shown in Figure 5b. Chromatogram in addition to CF₄, C₂F₆, C₂F₄, C₃F₆, C₃F₈ also appeared characteristic peaks. From the test results, the main decomposition products are from the c-C₄F₈ molecules, and N₂ in the mixed gas did not participate in the chemical reaction.

Test results show that pure gas is more likely to decompose and the intensity of each decomposition product monitored was higher than that of c-C₄F₈/N₂. In order to investigate the effect of O₂ on the decomposition of c-C₄F₈/N₂ gas mixture in more detail, Table 2 shows the peak intensities of the decomposition components of c-C₄F₈/N₂ gas mixture at 0% and 3% O₂. It can be seen that with the addition of O₂, the peak intensities of CF₄, C₂F₆, C₃F₈ and C₂F₄ all have large changes, and the peak intensity of CF₄ produced by c-C₄F₈/N₂ with 3% O₂ increased by 275.34%, C₂F₆ relative increase of about 200%, C₂F₄ and C₃F₈ relative growth of about 140%. The growth rate of CF₄ and C₂F₆ is higher than that of C₃F₈. The above analysis shows that the decomposition of c-C₄F₈ is more likely to produce small molecule products and the mixed gas containing O₂ generates extra COF₂. The presence of O₂ promotes the decomposition of c-C₄F₈/N₂.
Table 2. Peak strength of c-C$_4$F$_8$/N$_2$ mixed gas decomposition products under different O$_2$ contents.

<table>
<thead>
<tr>
<th>Products</th>
<th>0% O$_2$</th>
<th>3% O$_2$</th>
<th>The Growth Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_4$</td>
<td>1,052,859</td>
<td>2,898,954</td>
<td>275.34</td>
</tr>
<tr>
<td>C$_2$F$_6$</td>
<td>1,944,746</td>
<td>3,808,650</td>
<td>195.84</td>
</tr>
<tr>
<td>C$_3$F$_8$</td>
<td>196,263</td>
<td>275,746</td>
<td>140.50</td>
</tr>
<tr>
<td>C$_2$F$_4$</td>
<td>8,377,435</td>
<td>11,928,574</td>
<td>142.39</td>
</tr>
<tr>
<td>C$_3$F$_6$</td>
<td>1,479,519</td>
<td>1,627,829</td>
<td>110.02</td>
</tr>
</tbody>
</table>

4. Discussion

In order to explore the discharge decomposition path of c-C$_4$F$_8$ and the effect of O$_2$ on its decomposition, a thermodynamic and kinetic combination method was used to analyze the orientation and mechanism of the reaction based on density functional theory (DFT). With regard to theoretical knowledge of calculations, it has been described in detail in our previous work [30,31]. The Dmol3 package was used to process exchange-related interactions using a local density approximation (LDA-PWC) approach to optimize the structure of c-C$_4$F$_8$ and O$_2$ [25]. To model the possible reaction path, the stable molecular configuration with the lowest energy is needed for selection. By calculating the energy of reactants and products, we can get the energy change before and after the reaction, and judge the difficulty of the reaction from the thermodynamic point of view. In addition, the constructed non-decomposing reaction path needs to be searched for transition state [32]. Because during the process of chemical bond breaking and rearrangement, the intermediate activated complexes will be absorbed by the reactants to produce a certain amount of energy, and the process of generating activated complexes often determines the reaction rate. Therefore, the transition state structure and the corresponding activation energy are helpful to evaluate the reaction from the kinetic point of view. Finally, combined with the test results, the dynamic equilibrium process of particles during the decomposition of c-C$_4$F$_8$ with O$_2$ was analyzed.

4.1. The Basic Properties of c-C$_4$F$_8$

Figure 6 shows the geometry of optimized c-C$_4$F$_8$ molecule structure, where the bond length is Å and the bond angle is °. The c-C$_4$F$_8$ molecule has a high degree of symmetry. The C-C bond length is 1.583 Å and the C-F bond length is 1.350 Å. The F-C-F bond angle is 110.150° and the F-C-C bond angle is 113.587°.

The bond level is a physical quantity that describes the bond strength between adjacent atoms in the molecule, indicating the relative strength of the bond. In the collision of electrons and other particles or under high temperature conditions, the chemical bond may be broken, wherein the strength of the chemical bond relative to the strength of the smaller chemical bonds more difficult to break. Figure 7 shows the calculated chemical bond levels for the c-C$_4$F$_8$ and SF$_6$ molecules. According to the calculation results, the C-C bond in the c-C$_4$F$_8$ molecule has a bond level value of 0.924 and the C-F
bond with a value of 0.896. The intensity of the C-F bond in the c-C₄F₈ molecule is weaker than that of the C-C bond. Therefore, the C-F bond is more likely to dissociate than the C-C bond. In the SF₆ molecule, the S-F bond level value of the four co-planar F atoms and the S atom is 0.826, and the other the S-F bond level value is 0.829. Overall, the bond level of the chemical bonds in the SF₆ molecule is smaller than the bond order of the chemical bonds in the c-C₄F₈ molecule, indicating that the stability of the molecular structure of the SF₆ is inferior to that of the c-C₄F₈ molecule, which explains the c-C₄F₈ gas dielectric strength is superior to SF₆ gas.

**Figure 7.** c-C₄F₈ and SF₆ bond-level distribution.

The distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of c-C₄F₈ is calculated from the orbital distribution of the molecules, as shown in Figure 8. The corresponding energies are $−0.298645$ Ha and $−0.086768$ Ha, respectively. The energy difference between LUMO and HOMO characterizes the stability of the gas involved in the chemical reaction. The larger the difference is, the larger the energy required for the electron transition in the molecule is and the more stable the molecule is.

**Figure 8.** c-C₄F₈ molecular orbital distribution.

4.2. The Decomposition Path of c-C₄F₈ and the Main Product Generation Mechanism

Electrons are the main factors that cause collision ionization and dissociation in the electric field. Under the high-energy electric field or local overheating, the chemical bonds in the molecular structure of c-C₄F₈ will be cleaved, generating various types of free radicals, thereby damaging the insulation structure. In combination with the molecular structure of c-C₄F₈, Table 3 shows the major pathways for the decomposition during the discharge process.
Table 3. c-C\textsubscript{4}F\textsubscript{8} discharge decomposition path.

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Chemical Equation</th>
<th>Reaction Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>c-C\textsubscript{4}F\textsubscript{8} → C\textsubscript{2}F\textsubscript{4} + C\textsubscript{2}F\textsubscript{4}</td>
<td>173.8539</td>
</tr>
<tr>
<td>(2)</td>
<td>c-C\textsubscript{4}F\textsubscript{8} → C\textsubscript{3}F\textsubscript{6} - + CF\textsubscript{2} -</td>
<td>342.3815</td>
</tr>
<tr>
<td>(3)</td>
<td>c-C\textsubscript{4}F\textsubscript{8} → C\textsubscript{4}F\textsubscript{7}· + F·</td>
<td>434.8436</td>
</tr>
</tbody>
</table>

The decomposition pathway (1) refers to the process of two C-C bonds that located at the relative positions of the c-C\textsubscript{4}F\textsubscript{8} molecule being disconnected to form free radicals. The pathway (2) refers to the disconnecting process of C-C bonds which are adjacent in the C-C\textsubscript{4}F\textsubscript{8} molecule. The absorption energy required for pathway (1) is 173.8539 kJ/mol, which is lower than the 342.3815 kJ/mol required for pathway (2). The pathway (3) refers to the process of c-C\textsubscript{4}F\textsubscript{8} which cleaves the C-F bond to produce C\textsubscript{4}F\textsubscript{7}· and F· free radicals, and the process need to absorb energy of 434.8436 kJ/mol, higher than pathway (1) and pathway (2).

Figure 9 shows the change trend of reaction energy of three decomposition paths (in Table 3) with temperature. As the temperature increases, the energy required for molecular decomposition decreases gradually, and the increase of temperature is in favor of the reaction. The effect of temperature is considered mainly because the temperature changes during the discharge. In particular, there will be a significant increase in the temperature at the moment of breakdown, and the temperature at the center of the breakdown arc may reach 1000 k.

![Figure 9](image-url)  
*Figure 9. The reaction energy of decomposition paths with temperature.*

All kinds of free radicals generated by ionization or dissociation of c-C\textsubscript{4}F\textsubscript{8} molecules can produce a series of new products by secondary reactions, mainly CF\textsubscript{4}, C\textsubscript{2}F\textsubscript{6}, C\textsubscript{3}F\textsubscript{8}, C\textsubscript{2}F\textsubscript{4} and C\textsubscript{3}F\textsubscript{6}. Figure 10 shows the molecular model of the above decomposition product after optimization, and the bond length bond angle parameter is basically the same as that given in [30].

Table 4 shows the chemical equations of decomposition products, energy changes and activation energy. Among them, the processes of free radical recombination are exothermic reactions to generate CF\textsubscript{4}, C\textsubscript{3}F\textsubscript{8}, C\textsubscript{2}F\textsubscript{4}, C\textsubscript{3}F\textsubscript{6} and C\textsubscript{2}F\textsubscript{6}. From a thermodynamic point of view, CF\textsubscript{4}, C\textsubscript{2}F\textsubscript{6}, C\textsubscript{2}F\textsubscript{4} are relatively easy to form, and C\textsubscript{3}F\textsubscript{8} generation is more difficult.
According to the kinetic analysis, the path B1 to B5 reaction without energy barrier, are the processes of free radical complex into molecules, without activation spontaneously. The formation process of C3F6 release more energy, and the reaction is more prone to occur. The path B2 needs to release 83.7318 kJ/mol, which is the most difficult to occur with the least energy. Figure 11 shows the energy changes of reactions with temperature. With the increase of temperature, the absolute value of the reaction enthalpy showed a different degree of decline. That is, the temperature is conducive to the reaction.

Path B6 reaction requires the formation of an activated complex transition state (TS). The reactant absorbs energy of 80.97188 kJ/mol, and then the activated complex TS releases energy to form the final product. The progress of the reaction is shown in Figure 12. Small molecule product formation process

<table>
<thead>
<tr>
<th>No</th>
<th>Chemical Equation</th>
<th>Energy Changes (kJ·mol⁻¹)</th>
<th>Activation Energy (kJ·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>CF₂⁺ + F⁻ → CF₃⁻</td>
<td>−307.27</td>
<td>—</td>
</tr>
<tr>
<td>B2</td>
<td>C₂F₇⁺ + 2F⁻ → C₂F₈</td>
<td>−83.7318</td>
<td>—</td>
</tr>
<tr>
<td>B3</td>
<td>CF₃⁻ + F⁻ → CF₄</td>
<td>−190.262</td>
<td>—</td>
</tr>
<tr>
<td>B4</td>
<td>2CF₂⁻ → C₂F₄</td>
<td>−332.313</td>
<td>—</td>
</tr>
<tr>
<td>B5</td>
<td>2CF₃⁻ → C₂F₆</td>
<td>−373.811</td>
<td>—</td>
</tr>
<tr>
<td>B6</td>
<td>C₃F₆⁻ → C₃F₈</td>
<td>−81.21444</td>
<td>80.97188</td>
</tr>
</tbody>
</table>
releases more energy, so it can be concluded that free radicals such as F·, CF2·, CF3· generated by the decomposition of c-C₄F₈ molecules tend to recombine into small molecules, resulting in a large content of small molecule products, which is in good agreement with the previous experimental results.

![Reaction process graph](image)

**Figure 12.** Reaction process of pathway B6 (TS: transition state).

In order to study the effect of O₂ on the decomposition of c-C₄F₈, the discharge decomposition path of O₂ must be studied first. In [20], the main pathways for generating O· are given by O₂→2O· and O₂ + e→O· + O. It is also pointed out that the free radicals CF₂ and C₂F₄ are oxidized to COF₂ under O₂ conditions. Figure 12 shows the geometrically optimized COF₂ molecular structure model. Table 5 shows the reaction equations and energy changes for the free radical binding to COF₂ produced by c-C₄F₈ [20]. The reaction is an exothermic reaction. O₂ can oxidize CF₂· to form COF₂ and O· oxidize C₂F₄· to generate COF₂ and CF₂·. The structure of COF₂ is shown in Figure 13.

<table>
<thead>
<tr>
<th>No</th>
<th>Chemical Equation</th>
<th>Energy Changes (kJ·mol⁻¹)</th>
<th>Activation Energy (kJ·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>CF₂· + O₂→COF₂ + O·</td>
<td>-138.52</td>
<td>180.18</td>
</tr>
<tr>
<td>C2</td>
<td>C₂F₄· + O→COF₂ + CF₂</td>
<td>-112.64</td>
<td>184.61</td>
</tr>
</tbody>
</table>

![COF₂ molecular structure model](image)

**Figure 13.** COF₂ molecular structure model.

4.3. The Basic Properties of the Main Products

According to the experimental measurement and calculation results, it can be seen that the main decomposition products are CF₄, C₂F₄, C₂F₆, C₃F₆ and C₃F₈, and COF₂ is produced when O₂ is involved. Figure 14 shows the molecular orbital energies of the main product. Based on the molecular orbital gap value, the main decomposition products have good stability. The C₂F₄, C₃F₆ and COF₂ containing double bonds are poorly stable in the chemical reaction.

At the same time, the relative insulation properties of the decomposition products were compared. The environmental values and ecological toxicity are shown in Table 6.
Figure 13. COF2 molecular structure model.

Table 6. Parameters of decomposition products.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SF6</td>
<td>1</td>
<td>−63</td>
<td>23,900</td>
<td>3200</td>
<td>&gt;500,000 ppm/4 h, LC50</td>
</tr>
<tr>
<td>c-C4F8</td>
<td>1.12</td>
<td>−6</td>
<td>8700</td>
<td>2600</td>
<td>78 ppm/2 h, LCLo</td>
</tr>
<tr>
<td>CF4</td>
<td>0.39</td>
<td>−186.8</td>
<td>6300</td>
<td>50,000</td>
<td>885,000 ppm/15 min, LCLo</td>
</tr>
<tr>
<td>C2F4</td>
<td>0.78–0.79</td>
<td>−78</td>
<td>9200</td>
<td>10,000</td>
<td>&gt;20 ppm/2 h, LC</td>
</tr>
<tr>
<td>C3F6</td>
<td>0.96–0.97</td>
<td>−37</td>
<td>7000</td>
<td>2600</td>
<td>750 ppm/4 h, LC50</td>
</tr>
<tr>
<td>C2F6</td>
<td>—</td>
<td>−28</td>
<td>—</td>
<td>&lt;10</td>
<td>750 ppm/4 h, LC50</td>
</tr>
<tr>
<td>COF2</td>
<td>—</td>
<td>−76.3</td>
<td>0</td>
<td>1.9 days</td>
<td>40,000 ppm/4 h, LC50</td>
</tr>
<tr>
<td>COF2</td>
<td>—</td>
<td>−84</td>
<td>0</td>
<td>—</td>
<td>270 mg/m3, 4 h, LC50</td>
</tr>
</tbody>
</table>

Note: GWP—global warming potential; LCLo—Lowest published lethal concentration; LC50—Lethal concentration, 50 percent kill; LC—Lethal concentration; The measurement of acute toxicity in the table is the test value of rat inhalation.

The insulation strength of CF4 gas is about 39% of that of SF6 and the insulation performance of C2F6 is about 76% of that of SF6. The insulation performance of C3F8 is close to that of SF6, and the C4F10 has better insulation performance than SF6. The resulting decomposition products basically maintain the original mixed gas insulation properties. The GWP of all the products are lower than that of SF6, and the concentration of the product is very small, so the product could be considered as not harmful to the environment. However, when oxygen is involved in the mixed gas discharge process, COF2 will be generated, which is toxic and corrosive and harmful to the insulation equipment and operators. Therefore, oxygen content should be strictly controlled in the equipment.

5. Conclusions

(1) During the breakdown process of the c-C4F8/N2 mixed with O2 included, a large amount of black powdery substance precipitates on the surface of the ball electrode, which are mainly composed of C, O, F, and O element content accounted for 17.32%.

(2) The main products produced by c-C4F8 discharge decomposition are CF4, C2F4, C2F6, C3F6 and C3F8 and small molecules such as CF4, C2F4 and C2F6 are generated more easily. The addition of N2 weakened the decomposition of c-C4F8 gas. The decomposition products mainly come from c-C4F8 and N2 in the mixed gas does not participate in the chemical reaction. The product has good insulation properties. The presence of O2 causes the promotion of c-C4F8 decomposition and produces COF2. The increase of temperature can promote the reaction.

(3) The main products produced by c-C4F8 discharge have good insulation properties, and the products basically maintain the insulation properties of the original mixed gas. However, when O2 was involved, COF2 gas was detected, which is toxic and corrosive and would be hazardous to insulation equipment and operators.
In summary, c-CsF should not be mixed with dry air. In order to ensure the safe and reliable operation of equipment, the oxygen content in the c-CsF mixed gas should be strictly controlled.

Author Contributions: Conceptualization, S.T. and S.X.; Methodology, S.T.; Software, Z.D.; Validation, Y.C.; Writing-Original Draft Preparation, S.T.; Writing-Review and Editing, S.T.; Visualization, Y.L.; Supervision, X.Z.; Project Administration, J.T.

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Conflicts of Interest: The authors declare no conflict of interest.

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