Decomposition characteristics of C₄F₇N/CO₂ mixture under AC discharge breakdown

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Boya Zhang, Chenwei Li, Jiayu Xiong, Ziyue Zhang, Xingwen Li, and Yunkun Deng
Decomposition characteristics of C\textsubscript{4}F\textsubscript{7}N/CO\textsubscript{2} mixture under AC discharge breakdown

I. INTRODUCTION

For decades, sulfur hexafluoride (SF\textsubscript{6}) has been widely used in the high-voltage and medium-voltage (HV and MV) gas-insulated switchgears (GISs), gas circuit breakers (GCBs), gas-insulated transformers (GITs), and gas-insulated transmission lines (GILs) due to its superior technical performance. SF\textsubscript{6} has excellent dielectric strength, arc quenching capability, and other unique physicochemical properties, which offer the most compact and reliable design options for gas-insulated systems. However, the global warming potential (GWP) value of SF\textsubscript{6} is extremely high, which is 23,900 times greater than that of CO\textsubscript{2}. Although the proportion of SF\textsubscript{6} in the total greenhouse gas emission is quite small, it will certainly have an awful impact on the environment due to its long atmospheric lifetime and the cumulative effect. The Kyoto Protocol, signed in 1997, has clearly listed SF\textsubscript{6} as one of the six greenhouse gases that are restricted worldwide. Besides, the Paris Agreement of 2016 explicitly calls for zero net greenhouse gas emission in the second half of this century.\textsuperscript{2,4} Therefore, searching for ecofriendly gases to replace SF\textsubscript{6} has become one of the most important tasks in the power industry.

The search for a suitable substitute of SF\textsubscript{6} started from studying natural gases such as nitrogen (N\textsubscript{2}), carbon dioxide (CO\textsubscript{2}), and dry air.\textsuperscript{1–4} N\textsubscript{2} and dry air have been successfully used for the MV switch apparatus, e.g., 12 kV/24 kV cubic type GIS, and CO\textsubscript{2} has been used for HV GCB up to 72.5 kV. However, their dielectric strength is only a third that of SF\textsubscript{6}, which requires a relatively higher filling pressure and a larger device footprint to achieve acceptable dielectric withstand levels. SF\textsubscript{6} mixtures with N\textsubscript{2} or CF\textsubscript{4} have also been considered to reduce the amount of SF\textsubscript{6}; however, they cannot fully solve the environmental problem of SF\textsubscript{6}. The same is true for perfluorocarbons (PFCs). Some PFCs offer dielectric strengths that are of interest,\textsuperscript{1} but their GWPs are typically in the range 5000–12 000, eliminating them from consideration. CF\textsubscript{3}I presents good dielectric
strength and minimal greenhouse effect,\textsuperscript{10} while it is classified as the mutagenic category, which makes it still questionable for industrial purposes. Moreover, another drawback of PFCs and CF\textsubscript{4} is the formation of solid conductive carbon and iodine under discharge conditions.

Recently, it has been proved that the fluoronitrile compound C\textsubscript{4}F\textsubscript{5}N, developed by 3M Company, has a dielectric strength more than twice that of SF\textsubscript{6}.\textsuperscript{11} It is nontoxic, is nonflammable, and has a low GWP value of only 2400. Due to the high boiling point of C\textsubscript{4}F\textsubscript{5}N, buffer gases such as CO\textsubscript{2} should be added to reduce the liquefaction temperature for industrial applications.

As one of the most promising SF\textsubscript{6} alternatives at present, the C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixture has attracted much attention in the power industry. So far, numerous studies have been performed, especially on its insulation performance. For example, Nechmi \textit{et al.} measured the breakdown voltage of the C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixture under AC and lightning impulse voltages.\textsuperscript{12} Zhang \textit{et al.} explored the influence of field inhomogeneity on the breakdown voltage of the C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixture and also the partial discharge behavior under a highly nonuniform electric field.\textsuperscript{13} Franck \textit{et al.} reported the effective ionization rate, transport coefficients, and the density-reduced critical breakdown strength of pure C\textsubscript{4}F\textsubscript{5}N and C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixtures.\textsuperscript{14,15}

For applications, General Electric Co. (GE) has now made several C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixture-compatible products commercially available: 245 kV current transformer, 420 kV GIS, and 145 kV GIS.\textsuperscript{16,17}

Apart from the electrical performance of insulation gases, the decomposition characteristics of the new gases under abnormal conditions are also critical to the stable operation of the apparatus, since the by-products can be hazardous and may also cause insulation failure and degradation of materials in the long run. Some efforts have been made to investigate the decomposition characteristics of C\textsubscript{4}F\textsubscript{5}N. The thermal stability test of the C\textsubscript{4}F\textsubscript{5}N and C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixture was first studied by GE and 3M,\textsuperscript{18} which shows that C\textsubscript{4}F\textsubscript{5}N starts to decompose at approximately 650 °C and is fully decomposed at 880 °C. The main decomposition products are CO\textsubscript{2}, C\textsubscript{2}F\textsubscript{5}O, C\textsubscript{2}F\textsubscript{5}CN, and C\textsubscript{2}F\textsubscript{5}N. Decomposition under partial discharge activity of the C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixture was investigated by Asea Brown Boveri Ltd. (ABB).\textsuperscript{19} The analysis shows that pure CO\textsubscript{2} mostly recombines after the partial discharge decomposition, which is in contrast to the mixtures where decomposed CO\textsubscript{2} reacts with decomposed fluorinated additives forming various by-products, including some toxic compounds such as CO, C\textsubscript{2}F\textsubscript{5}O, C\textsubscript{2}F\textsubscript{5}O, C\textsubscript{2}F\textsubscript{5}CN, and C\textsubscript{2}F\textsubscript{5}N. Researchers from ABB have also performed switching test of the C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixture and analyzed the composition after arcing. A large number of chemical species are identified, and the decomposition rate is estimated to be approximately 0.24 mol/MJ.\textsuperscript{20} In addition, Zhang \textit{et al.} have studied the decomposition characteristics of the C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} gas mixture theoretically and found that the main decomposition species are CF\textsubscript{3}, F, CF, CNF, and CN.\textsuperscript{21}

In general, based on preliminary studies, the decomposition characteristics of C\textsubscript{4}F\textsubscript{5}N mixtures are different under different conditions and vary with different buffer gases and mixing ratios. However, the content variation and quantitative study on the decomposition products of the C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixture are still not comprehensive. Particularly, reports on the decomposition characteristics after AC breakdown are still scarce. Therefore, in this paper, a power frequency AC discharge platform was built and the
decomposition products of the C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixture after multiple AC breakdowns were analyzed both qualitatively and quantitatively using a gas chromatography-mass spectrometer (GC-MS). Besides, the decomposition processes of the C\textsubscript{4}F\textsubscript{5}N gas were studied based on quantum chemical calculation. The results in this paper will reveal the chemical stability of the C\textsubscript{4}F\textsubscript{5}N gas under AC discharge conditions, which is useful for electrical engineers in the operation and maintenance of future ecofriendly gas-insulated equipment.

II. METHODS

A. Experimental platform

The experimental platform used in this study is shown in Fig. 1. An inductive voltage regulator (0–380 V) was used to control the output of the transformer with the rating voltage of 0.38/100 kV, the rating current of 131.5/0.5 A, and the rating capacity of 50 kV A. A resistor was used to protect the circuit from overcurrent. The discharge chamber was made of stainless steel, with a volume of 10 l and with polytetrafluoroethylene (PTFE) coating on its inner wall. The PTFE is extremely chemically inert, which can effectively prevent any possible absorption and corrosion by the decomposition by-products. A needle-to-plate electrode configuration was used to discharge the gas, and the separation between the two electrodes was set 10 mm in all the experiments. The electrodes were made of brass. Their geometry and size are given in the inset of Fig. 1, and the radius of curvature of the needle tip was 0.25 mm. The decomposition products of the C\textsubscript{4}F\textsubscript{5}N/CO\textsubscript{2} mixture were analyzed by a gas chromatograph-mass spectrometer (GC-MS, Shimadzu GCMS-QP2010 Plus).

B. Experimental details

Before the experiment, the electrodes and the inner wall of the chamber were carefully cleaned with absolute ethanol. Next, the chamber and all the gas lines were vacuumed for 60 min. Then, the chamber was filled with CO\textsubscript{2} and vacuumed again. This was repeated three times in order to eliminate impurities. Finally, the chamber was filled with C\textsubscript{4}F\textsubscript{5}N (purity of 99.3%, provided by 3M) and CO\textsubscript{2} (purity of 99.99%) to 0.3 MPa with a mixing ratio of 13.3/86.7% according to their partial pressures. This pressure and ratio was chosen because it meets the requirement of the minimum operation
TABLE I. Test settings of the GC/MC.

| Parameter                        | Setting                     |
|----------------------------------|-----------------------------|
| Chromatographic column           | Agilent GS-GasPro           |
|                                  | (30 m × 0.32 mm × 0.4 μm)  |
| Carrier gas                      | 99.999% He                  |
| Carrier gas flow rate            | 2.83 ml/min                 |
| Split ratio                      | 10:1                        |
| Oven temperature                 | 45 °C for 8 min, 40 °C/min up to 160 °C for 1 min |
| Interface temperature            | 200 °C                      |
| Ion source temperature           | 200 °C                      |
| Ionization method                | EI source                   |

During the experiment, the power frequency high voltage was applied to the electrode with a constant rate until breakdown, and the instantaneous breakdown voltage value was recorded. The test was repeated 2000 times, and the breakdown voltage values are shown in Fig. 2.

The gas mixture in the chamber was sampled and detected by GC/MS every certain interval. The details of the settings for the GC/MS are listed in Table I. It should be noted that for each sampling, a 100 μl-sampling loop was used in the GC-MS. In our experiment, no more than ten times of sampling were performed. So, the pressure decrease in the chamber was approximately 10 × 100 μl/10 l = 0.1%, which has little effect on the breakdown voltage. Both SCAN and SIM (single ion monitoring) modes were used in the experiment. The SCAN mode is mainly used for the identification of unknown chemical components using a mass spectrum, while the SIM mode is better for the quantitative analysis of a target compound because it has lower detection limits and higher sensitivity.

In addition, solid by-products after 2000 times of discharge were also collected by conductive tapes for analysis. To get the morphology of the solid products, Scanning Electron Microscopy (SEM) was performed on a Gemini SEM 300 field-emission microscope operating at 15 kV. A thin Au/Pd layer was sputtered onto the samples before the imaging. The corresponding elemental mapping of the solid products was also obtained by a BRUKER XFLASH 6|60 Electron Energy Disperse X-ray Spectrometer (EDS).

C. Quantum chemical calculation

Quantum chemical calculation can effectively analyze the decomposition process of C₃F₇N and the formation process of final products at the microscopic level. Geometries of the reactants and products were optimized using density functional theory B3LYP with 6-311G(d,p) basis sets. Based on the B3LYP/6-311G(d,p) optimized geometrical parameters, the complete basis set quadratic mode (CBS-QB3) was performed to get high-precision enthalpy data.

$$E(CBS-QB3) = E_{MP2} + \Delta E_{CBS} + \Delta E_{MP4} + \Delta E_{CCSD(T)} + \Delta E_{CBS-\text{int}} + \Delta E_{\text{emp}},$$

(1)

where $E_{MP2}$ is the MP2 energy calculated with the 6-311+G(3df,2df,2p) basis set, $\Delta E_{CBS}$ is obtained from the CBS extrapolation, and $\Delta E_{CBS-\text{int}}$ and $\Delta E_{\text{emp}}$ are the empirical terms for interference correction to the pair energies and the higher-order correlation energies, respectively. $\Delta E_{MP4}$ and $\Delta E_{CCSD(T)}$ are expressed as

$$\Delta E_{MP4} = E_{MP4(\text{SDQ})/6-31+G(d,p)} - E_{MP2/6-31+G(d,p)}.$$

(2)

$$\Delta E_{CCSD(T)} = E_{CCSD(T)/6-31+G(d')} - E_{MP4(\text{SDQ})/6-31+G(d')}.$$

(3)

The CBS-QB3 method shows a good performance for thermochimistry with a high accuracy, which is suitable for this work. The enthalpy changes of the possible reaction pathways during AC discharge breakdown were obtained by the methods described above to help reveal the dissociation and recombination mechanism of C₃F₇N/CO₂. We have compared our results with the results in Ref. 24 using the PWPB95/def2-QZVPP method and the results in Ref. 25 using Gaussian-4 theory, and a good agreement is achieved. All the calculations in this paper were performed with Gaussian09 software.

III. RESULTS ANALYSIS AND DISCUSSIONS

A. Detection of decomposition products

We first analyzed the original composition of the C₃F₇N/CO₂ mixture in the chamber before the discharge breakdown. Figure 3 shows the gas chromatogram of the mixture, from which we can see that apart from CO₂ and C₃F₇N, a trace amount of heptafluoropropane (C₃HF₇) was detected. In fact, C₃HF₇ is regarded as the impurity from C₃F₇N, which has been confirmed by the supplier, namely, the 3M company. The mass spectra of C₃HF₇ and C₃F₇N are given in Fig. 4 for reference.

According to IEC 60480-2004, the H₂O content in the chambers of gas insulated equipment in operation should be less than 500 ppm. Therefore, the content of microwater in the experiment was monitored by a dew point meter and strictly controlled below 300 ppm.
FIG. 3. Gas chromatogram of the C₄F₇N/CO₂ sample before discharge.

FIG. 4. Mass spectra of C₃HF₇ and C₄F₇N.

FIG. 5. Gas chromatogram of C₄F₇N/CO₂ after multiple breakdowns.

FIG. 6. Response of reference ions at different retention times.

After multiple breakdowns, the gas mixture was sampled and analyzed by GC/MS. A large number of characteristic peaks appeared in the gas chromatogram, as shown in Fig. 5. By analyzing the mass spectrum of particle fragments in the SCAN mode and checking with the NIST (National Institute of Standards and Technology, USA) database, CO, CF₄, C₂F₆, C₃F₆, C₂F₄, CF₂CN, C₄F₁₀, C₂N₂, C₂F₆, C₂F₅CN, HCN, and C₂F₃CN were detected. Among them, compounds CO, CF₄, C₂F₆, C₃F₆, and C₂F₄ were also confirmed by comparing the retention time of the corresponding standard gases. Besides, it should be admitted that three other compounds with small characteristic peaks in the gas chromatogram cannot be confirmed at present by using the above method, so they will not be involved in the following discussions.

In addition, it should be noted that only using the SCAN mode cannot distinguish C₂F₄, C₂F₆, and CO₂ in the gas chromatogram because the response peaks of C₂F₄ and C₂F₆ are hidden behind that of CO₂ due to its large content and long retention time. Therefore, the SIM mode was used. By inputting the reference ions that were detected in the SCAN mode into the SIM mode, the variations of the mass spectrum of these reference ions were obtained, as shown in Fig. 6. It clearly reveals that there are other two substances in the period of 1.2–1.8 min in addition to CO₂, whose information has been summarized in Table II.

Moreover, since hydrogen fluoride (HF) could not be detected accurately through GC/MS, a specific HF detection tube (GASTEC, Japan) was used after the breakdown. The indicator changed from yellow to dark purple immediately (Fig. 7), indicating that HF was produced during the decomposition. The generation of HF should be related to the hydrolysis reactions with inevitable trace water in the chamber. Since HF is corrosive and can be harmful to the equipment, much effort should be made to control the amount of trace water in the applications, just as what we do for the SF₆-filled equipment.

By comparing Figs. 3 and 5, perfluorocarbon gases were found to be the main decomposition products, including CF₄, C₂F₆, C₂F₄, C₃F₇, C₄F₉, C₂F₃CN.
TABLE II. Characteristic mass spectrum of target substances.

| Target substance | Mass spectrum of reference ions | Retention time (min) |
|------------------|---------------------------------|---------------------|
| C2F4             | 31 (CF2+, 50 (CF2+)3, 81 (C2F4+)1, 100 (C2F4+)1) | 1.635               |
| C2F6             | 31 (CF2+, 50 (CF2+)3, 69 (CF3+)3, 119 (C2F5+)1) | 1.485               |

C2F4, C2F6, C4F6, and C4F10. Nitriles with CN groups are also dominant in the decomposition products, including CF3CN, C2F3CN, C2F3NF, C2N2, and HCN. The electrical strength (relative to SF6) and boiling point of some of the decomposition products are given in Table III. We can see that the boiling point of all these products is lower than that of C2F2N, which indicates that none of them were liquefied under the experimental condition. Meanwhile, it can be found that the electrical strength of the produced perfluoroniclitriles C2F3CN and C2F3CN is lower than that of C2F2N but is still much higher than that of SF6. Except for CF4, most of the produced perfluorocarbon gases have equivalent or slightly higher electrical strength than that of SF6. The decomposition product of CO2, namely, CO, has an electrical strength slightly higher than that of CO2. Therefore, the overall electrical strength of the decomposed C2F2N/CO2 mixture should be little poorer than that of the original. However, if considering only a small fraction of the gas is decomposed during each breakdown, the deterioration of the insulation performance should be still acceptable if the volume of the chamber is large enough compared to the discharge channel. Actually, Fig. 2 shows that the breakdown voltage of the gap drops with the increase in breakdown times, but the deterioration is not that severe even after 2000 breakdowns.

As aforementioned, C2F2N is nontoxic and has an occupational exposure limit time of ~65 ppm. Its 4-h rodent (rat) LC50 (lethal concentration at 50% mortality) is between 10 000 ppm and 15 000 ppm, which is lower than that of SF6 (500 000 ppm/4 h). Considering the small content of C2F2N in the gas mixture, the safety of C2F2N/CO2 is almost the same as the widely used SF6 gas. However, some of the decomposition products are found toxic, and the toxicity of these products are given in Table III. For example, the LC50 of C2F6 is 750 ppm (4 h, rat), and a large number of short-term inhalation will produce dizziness, weakness, poor sleep, and other symptoms. Trifluoroacetonitrile CF3CN is also an acute toxic gas, which can be fetal if inhaled. In addition, CO, C2N2, HF, and HCN are all common toxic gases. Therefore, from the perspective of human safety, special care must be taken when handling the C2F2N/CO2 mixture after discharges.

**B. Relative content change of decomposition products**

The content change of the decomposition products was studied by the SIM mode of GC-MS. The absolute content of CO, CF4, C2F6, and C3F8 was determined quantitatively by using the “standard curve method” in which the corresponding standard gases were used to calibrate GC-MS, while the contents of other gases were characterized by the peak area of the corresponding reference ion. The selected reference ion and retention time of the decomposition products are given in Table IV. Figure 9 shows the concentration variation of CO, CF4, C2F6, and C3F8 with the increase in breakdown times. After the first 200 times of breakdowns, the concentration of CF4 and CO in the chamber was around 550 ppm by volume; the concentration of C2F6 and

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### FIG. 7. Detection of HF by using a specific HF detection tube.

![Detection of HF by using a specific HF detection tube.](image)

### FIG. 8. The electrical strength (relative to SF6) and boiling point of SF6, CO2, C2F2N, and some decomposition products.

![The electrical strength (relative to SF6) and boiling point of SF6, CO2, C2F2N, and some decomposition products.](image)

### TABLE III. Toxicity of the decomposition by-products.

| Products | CAS number | LC50    |
|----------|------------|---------|
| CO       | 630-08-0   | 1807 ppm/4 h |
| C2F6     | 116-15-4   | 750 ppm/4 h   |
| C2F4     | 116-14-3   | 40 000 ppm/4 h |
| C2F2     | 76-16-4    | 20 ppm/2 h    |
| C4F6     | 692-50-2   | 82 ppm/4 h    |
| C2N2     | 460-19-5   | 350 ppm/1 h   |
| CF3CN    | 353-85-5   | 500 ppm/1 h   |
| HF       | 7664-39-3  | 484 ppm/4 h   |
| HCN      | 74-90-8    | 160 ppm/30 m  |

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C$_2$F$_8$ was 20 ppm and 44 ppm, respectively. It can be seen that the concentration of these gases is approximately proportional to the number of breakdowns. With the increase in breakdown times, the concentration of CO increases the fastest, reaching 4200 ppm after 2000 breakdowns. This is because CO stems from the decomposition of CO$_2$, whose content is the highest in the chamber. CF$_4$ is the second dominant decomposition product. Its concentration reached 2500 ppm after 2000 breakdowns. While the concentration of C$_3$F$_8$ is the lowest, only 180 ppm is produced after 2000 breakdowns.

The relative content variations of C$_2$F$_5$CN, C$_2$N$_2$, CF$_3$CN and HCN, C$_3$HF$_7$ are shown in Fig. 10. The content of these products also increases almost linearly with the increase in breakdown times, except for C$_3$HF$_7$, whose concentration drops gradually. This is because C$_3$HF$_7$ is the impurity of the original C$_4$F$_7$N and it also decomposed during the discharges.

### C. Analysis of solid products

After multiple breakdowns for 2000 times, a layer of powdery solid with pale yellow color was found on the inner wall of the chamber and the surface of the electrode, as shown in the inset of Fig. 11(a). These solid products were carefully collected by conductive tapes and analyzed by SEM and EDS. From the SEM image of Fig. 11(a), we can see that these solid particles have amorphous shape with a size ranging from a few hundred nanometers to tens of micrometers. In Figs. 11(b)–11(e), EDS analysis shows that the solid particles contain the elements Cu, N, F, and Si. From the EDS...
analysis, we cannot confirm whether the particles contain C element or not because the large amount of C element in the substrate tap masked the response of possible C element from the particles. To determine the exact compositions of these solid particles is a rather tough job since their chemical constitutions can be multi-tudinous and complicated. Nevertheless, we can still infer that the gaseous decomposition products of C₄F₇N probably react with the brass electrode and form copper fluoride and copper cyanide, since the N and F elements are certainly from C₄F₇N. The Si element may be from the quartz glass window of the chamber, indicating that the decomposition product of the C₄F₇N gas may react with the glass. It may also be from the additives in the brass, which needs further verification. It should be noted that there are few black carbon particles generated in this experiment.

IV. FORMATION MECHANISM OF THE DECOMPOSITION PRODUCTS

In the AC breakdown experiments, the discharge channel can be regarded as a source of energy injection. The discharges not only lead to local heating but also generate energetic electrons. The local heating will cause thermal degradation of the gas, while electron impact processes will cause ionization and dissociation of the gas molecules, which makes the decomposition mechanism more complicated. In order to better understand the formation of final products detected by GC-MS, the main dissociation and recombination reactions of C₄F₇N are shown in Tables V and VI, respectively. The corresponding enthalpy changes of these reactions at the standard condition are also calculated.

In Table V, the dissociation pathways D1–D4 are the preliminary dissociation reactions. The value of enthalpy changes of D1 and D4 is relatively high, which means that the corresponding bond cleavage needs more energy. An energy of 352.6 kJ/mol is required in reaction D3, which is the lowest in reactions D1–D4, indicating that the corresponding C–C bond is much easier to break than others. Considering that the majority electron energy of low-temperature plasma ranges within 416.3–1056.2 kJ/mol, reactions D1–D4 could take place simultaneously with enough energy influx during the discharge, while D3 may be the dominant process due to its lower enthalpy changes and the free radicals CF₃CFCN and CF₃ are more likely to be generated.

After the preliminary dissociation of C₄F₇N, several free radicals are produced, including CF₃, CN, F, (CF₃)₂CF, and CF₃CFCN. D5–D12 are subsequent dissociation reactions. It is noteworthy that those reactions are not a complete dissociation pathway, but reveal the possible generation of different free radicals. The values of enthalpy changes can reveal the relatively difficulty of occurrence for those reactions. The reaction D6 requires 243.6 kJ/mol, which is much lower than the others, indicating that this path is more likely to occur. Some free radicals such as CN and CF₃ could be generated at different stages of dissociation with relatively low enthalpies; therefore, these radicals may dominate the recombination processes after the discharge. Besides, the decomposition process of trace water (D13) could not be ignored, since it is also relevant to some decomposition products, such as HF.

After the dissociation, the generated free radicals start to recombine without energy injection. Some typical recombination reactions of free radicals are given in Table VI, in which the products are closely related to the decomposition products detected in the experiments. All the reactions in Table VI are exothermic and barrierless reactions, which means that they can occur spontaneously at normal temperature. According to the experimental results, various perfluorocarbons formed after discharges. R1–R6 show the possible formation process of some perfluorocarbon products. CF₃ and (CF₃)₂CF stem from the dissociation processes such as D1 and D3, while CF₂ and F are formed by D11 and further decompositions after D1–D4. It is found that the enthalpy of reaction R2 is much higher than that of R1, R3, and R4, which indicates that the formation of the C=C double bond is more difficult than that of the C–C single bond. So the formation of unsaturated fluorocarbon C₃F₃ is more difficult than that of the saturated ones, such as CF₄, CF₂, and CF₃. CN radicals can bind to itself and also to fluorocarbon radicals, leading to the formation of C₂N₂ and C₂F₃CN, and CF₇CN. The influence of trace water on the final products is shown as R11 and R12. H radicals caused by dissociation of H₂O can bind to F atoms and CN radicals, forming poisonous HCN and HF.

As discussed above, the possible dissociation and recombination pathways of C₄F₇N are summarized in Fig. 12. The

| Path | Reaction of free radicals | ΔH°,298 K (kJ/mol) |
|------|---------------------------|--------------------|
| D1   | C₄F₇N → (CF₃)₂CF + CN     | 471.5              |
| D2   | C₄F₇N → (CF₃)₂C(CN) + F   | 417.2              |
| D3   | C₄F₇N → CF₃CFCN + CF₃     | 352.6              |
| D4   | C₄F₇N → (CF₃)(CF₂)CFCN + F | 476.3              |
| D5   | (CF₃)₂CF → (CF₃)₂C + F    | 540.9              |
| D6   | (CF₃)₂C → CF₃ = C−CF₃ + F | 243.6              |
| D7   | CF₂=CF→CF₂ = CF₂ = CF₃ + CF₃ | 465.0              |
| D8   | CF₃CFCN → CFCN + CF₃      | 388.3              |
| D9   | CF₃CFCN → CN + CF₃CF      | 486.6              |
| D10  | CF₃CF → C−CF₃ + F         | 613.3              |
| D11  | CF₃ → CF₂ + F             | 357.6              |
| D12  | CF₂ → CF + F              | 522.1              |
| D13  | H₂O → HO + H              | 498.4              |

| Path | Reaction of free radicals | ΔH°,298 K (kJ/mol) |
|------|---------------------------|--------------------|
| R1   | CF₃ + F → CF₄             | −550.4             |
| R2   | CF₂ + CF₂ → C,F₄          | −292.9             |
| R3   | CF₃ + CF₃ → CF₆           | −416.7             |
| R4   | (CF₃)₂CF + F → CF₃F₆     | −502.4             |
| R5   | CF₅−CF−CF₃ + F → CF₃F₆   | −508.3             |
| R6   | CF₃ + CF₃(CF₂)₂ → CF₃(CF₂)₂CF₃ | −395.8        |
| R7   | CF₃ + CN → CF₃CN          | −478.1             |
| R8   | CF₃CF−CN + F → CF₃F₃CN    | −453.2             |
| R9   | CF₂=CF +CN → CF₂=CFCN     | −559.0             |
| R10  | CN + CN → C₂N₂           | −579.4             |
| R11  | H + CN → HCN             | −531.3             |
| R12  | F + H → HF               | −573.5             |
FIG. 12. Summarization of some possible decomposition pathways of C₄F₇N.

isomerization of perfluorocarbons leads to more products, which is not included in the figure. In fact, under AC discharge breakdown, the real decomposition pathway could be much more intricate. Various free radicals could be produced from different dissociation processes and recombine to each other simultaneously through different pathways. The occurrence of those reactions has different degrees of difficulty, leading to different contents of radicals and unstable intermediate products. Although quantum chemistry calculation can hardly draw a full picture of radical reactions and electron impact processes, it helps us to get an insight into the decomposition processes during discharge breakdown of C₄F₇N/CO₂ mixtures and gives a good explanation of the formation of final products detected in our experiments. Admittedly, to accurately interpret the decomposition processes in a gas discharge, kinetic models should be built taking into account more reactions, including ionization, adsorption, excitation, and ion conversion reactions. The decomposition products could be influenced by electric field, discharge energy, and trace water, which will be studied in detail in the future.

V. CONCLUSIONS

In this paper, the decomposition characteristics of the C₄F₇N/CO₂ mixture under power-frequency AC discharge breakdown were studied by GC-MS. Besides, the corresponding decomposition mechanism was explored by the quantum chemistry calculation method. The main conclusions are as follows:

1. A small amount of C₃HF₇ was detected as the impurity in the C₄F₇N gas. The main decomposition products of the C₄F₇N/CO₂ mixture under AC breakdown are mainly perfluorocarbons and perfluoronitriles, including CO, CF₃, C₂F₄, C₃F₆, C₂F₆, C₂F₄, C₃F₆, C₆F₆, C₆F₆, C₉F₆, C₁₂N₂, CF₃CN, C₂F₅CN, C₂F₃CN, HCN, and HF. Since most of the products have a lower electrical strength than C₄F₇N, the insulation performance of the C₄F₇N/CO₂ mixture after multiple breakdowns can gradually become degraded. Besides, some of the decomposition products are toxic, so special care should be taken when handling the decomposed gases.

2. The content change of the decomposition products was studied by the SIM mode of GC-MS. The absolute content of CO, CF₃, C₂F₄, and C₃F₆ was determined quantitatively by using standard gases. The content of all the products increases linearly with the increase in breakdown times. After 2000 breakdowns, the concentration of CO reaches up to 4200 ppmv, which is the most among the decomposition products. While the concentration of C₃F₆ is the lowest, only 180 ppmv is produced.

3. After 2000 times of breakdowns, a layer of powdery solid with pale yellow color was found on the inner wall of the chamber and the surface of the electrode. Elements Cu, F, N, and Si were found to be the main components of these solids.

4. For the formation mechanism of the detected products, the enthalpies of possible dissociation and recombination reactions were obtained by using quantum chemical calculation. It shows that the breaking of the C−C bond in reaction D3 to produce CF₃ radicals is easier than others and the formation of unsaturated fluorocarbon is more difficult than the saturated ones.
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