Decomposition Properties of Trifluoriodomethane under Discharges and Interruptions

Fan-Yi Cai*, Dong-Xian Tan**, Bai-Jie Zhou*, Jian Xue* and Deng-Ming Xiao‡

Abstract – This paper is devoted to detecting decomposition characteristics of Iodotrifluoromethane (CF$_3$I) under alternating current (AC) discharges or load current interruptions. The decomposition products are measured utilizing chromatography-mass spectroscopy. It is found that less than 1% CF$_3$I gas decomposed after several interruptions at load current of 200 A or hundred times of AC discharges. However, under interruptions at a current of 400 A, more than 95% CF$_3$I gas decomposed into carbon tetrafluoride (CF$_4$) and hexafluoroethane (C$_3$F$_6$). The equilibrium compositions based on Gibbs free energy minimization of CF$_3$I was calculated to explain the decomposition mechanism.

Keywords: CF$_3$I, Decomposition products, Interruption.

1. Introduction

Due to excellent comprehensive qualities including insulating performance, arc-quenching capability, nontoxic, non-flammable and thermal stable, SF$_6$ (sulfur hexafluoride) has been considered the most common gaseous insulation or interrupting medium for high voltage power systems, such as transformers bushings, gas-insulated transmission lines (GIL), and gas-insulated switchgear (GIS) [1]. However, SF$_6$ is a strong greenhouse gas with high global warming potential (GWP) of 23,500 [2]. Therefore, the usage of SF$_6$ has been restricted on Kyoto Protocol [3] and the power industry has been intensively searching for an environmentally friendly gas to replace SF$_6$ in a long time.

In recent years, many scientists claimed that CF$_3$I is a potential alternative gas to SF$_6$ [4-7]. CF$_3$I gas has superior insulating performance and several other advantages of physical and chemical properties. Specifically, it is a colorless, odorless gas and has no damage to the ozone layer [8]. Compared to SF$_6$, the major advantage of CF$_3$I is a very low GWP, which is about 1.5 times than that of carbon dioxide (CO$_2$). Thus, CF$_3$I has been listed in the potential environmentally friendly alternative refrigerant products catalog by United Nations Environment Programme [4, 9].

The main reason for the low GWP value of CF$_3$I is the molecular structure and its relatively unstable chemical properties. The solar radiation and even visible light can make the C-I bond breaking, which leads to the decomposition of CF$_3$I molecule. So CF$_3$I can only present in the atmosphere for a short time, which leads a slight feature on environmental impact. Due to this, it is essential to investigate the by-products of CF$_3$I, particularly in terms of discharges and interruptions.

Donnelly and his co-works found that CF$_3$I gas could remain stable after a 5-year ambient temperatures storage period from 1997-2002 [10]. M. S. Kamarudin discovered that solid by-product after more than 1400 times breakdown tests [11] was iodine (I$_2$). Moreover, the deposition of iodine on the electrode affected insulation performance by more than 10%. Investigations on gaseous decomposition of CF$_3$I after partial discharges (PD) and sparkovers have been carried out by M. Jamil et al [12] and Takeda et al respectively [13]. In their measurements, C$_2$F$_6$, C$_2$F$_4$, CHF$_3$, C$_3$F$_6$, C$_3$I$_6$, and C$_3$I$_4$ were detected as gaseous by-products. The dominant gaseous by-products were C$_2$F$_4$. Tu et al also analyzed the gas discharge by-products of CF$_3$I/Nitrogen (N$_2$) gas mixtures at high-pressure [14]. They found that the dominant gaseous by-products were C$_3$F$_3$I and finally converted to I$_2$ and CF$_3$I. The formation mechanism of CF$_3$I discharge components and effect of trace water and oxygen on decomposition were studied by Zhang et al [15, 16]. The results show that the decomposition rate of CF$_3$I was accelerated in the presence of trace water and oxygen and some harmful gas such as carbonyl fluoride (COF$_2$) was produced.

Though there are many researches on the by-products of the substitute gas after discharges, reports the by-products under interruptions are few, qualitative and lack of data. H. Katagiri found that CF$_3$I decomposed significantly and the decomposition products contained solid iodine, which attached to the gas hose making it yellow after CF$_3$I extinguishing capability test with large current arcs [7]. H. Kasuya measured the decomposed gas density after current interruptions with CF$_3$I spectra, their results revealed that fluorine release from CF$_3$I was less than that from SF$_6$ [17].

In this paper, the species and quantities of decomposition products are detected by interrupting discharges at 200 A for a few hundred times at load current interruptions are few, qualitative and lack of data. H. Katagiri found that CF$_3$I decomposed significantly and the decomposition products contained solid iodine, which attached to the gas hose making it yellow after CF$_3$I extinguishing capability test with large current arcs [7]. H. Kasuya measured the decomposed gas density after current interruptions with CF$_3$I spectra, their results revealed that fluorine release from CF$_3$I was less than that from SF$_6$ [17].

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products of CF₃I after small current interruptions were tested by means of gas chromatography-mass spectrometer (GC-MS). The arc experiments were carried out in an industrial load switch for SF₆ gas and the gas chamber was replaced with pure CF₃I gas were experimentally verified. The by-products of CF₃I after different times of AC breakdown discharges were also detected as a reference.

The organization of this paper is as follows: Section 2 specifically describes the materials for the tests, experimental setup and methodology. Interruption and decomposition results were demonstrated in Section 3. The proposed mechanism and the poison level of the by-products of CF₃I is discussed in detail in Section 4. Section 5 concludes the paper.

2. Materials and Methods

2.1 Materials

CF₃I gas was supplied by Beijing Yuji Science and Technology Co., Ltd with purity surpass 99.5%. Main impurities are C₃HF₅ (1,1,3,3,3-Pentafluoro-1-propene), CHF₃ (Trifluoromethane), C₂HF₅ (Pentafluoroethane) and C₄F₈ (Perfluoro-2-butene). Water (H₂O) content of the gas was about 0.05 wv%.

2.2 The interruption measurement system for CF₃I gas

The interruption tests of pure CF₃I gas were carried out in a commercial SF₆ arc quenching load switch (TO, Fig. 1). The rated normal current of the load switch is 630 A. Moreover, the filling pressure of the working chamber was 0.04 MPa. The sketch of the test circuit shown in Fig. 2 was used to investigate the interruption characteristics. The output current around 4~40 kA is provided by the LC oscillation circuit. A 49.2 Hz output current was produced by a 55,760 µF capacitor bank (Cs) and a 187.5 µH thyristor controlled air reactor (Ls). A 12 kV vacuum circuit breaker with the spring operating mechanism was used as the main switch (MS) while a 40.5 kV vacuum circuit breaker with the spring operating mechanism was used as the auxiliary switch (AB). Arc voltage and current were measured by the voltage transducer and the Rogowski coil, respectively. Digital memory oscillograph was used to record the experimental data. After the interruption experiment, we let the gases stand for 1 hour to ensure the decomposition further mixed in the cavity and then sample the gases with vacuum sampling bags.

2.3 The AC breakdown measurement system for CF₃I gas

The by-products of CF₃I under AC breakdown tests were...
also detected for comparison. The experimental setup was illustrated in Fig. 3. Tests were made between a stainless steel electrode and a horizontal plate electrode in a cylindrical closed chamber made of stainless steel. The diameter of the needle electrode was 1 mm and the diameter of the plate diameter was 400 mm. The discharge gap was 10 mm. Hence, the non-uniform coefficient of the electric field is 12.3. In addition, the observation window was set up to watch the discharge path during breakdown tests. A 300 kV AC transformer was used in the AC withstand test. The rising rate of AC voltage was 1 kV/s, and it was increased continuously until the breakdown took place. AC withstand voltage was obtained from the average of 10 measurements by the voltage increasing method. There was 1 min interval between each discharge to ensure the gas can recover the initial insulation conditions. In this paper, we detected the gases compositions of 5 sample groups include the origin gas and the gases after 0 to 500 times AC discharges.

2.4 Gaseous by-product measurement system for CF$_3$I

Identifications of the products after the electrical tests were achieved by GC/MS (Agilent 7890A/5975C) system equipped with a CP-Pora PLOT Q column (30 m × 0.25 mm × 0.25 μm). The column was programmed as follows: the initial temperature was set at 60 °C for 6 min; then the temperature was increased at the rate of 40°C/min, and finally reached to 200°C and held for 11 min. The instrumental parameters were set up as follows: injection port temperature, 200 °C; TCD detector, 200 °C; the carrier gas rate, 4.1 ml He/min. The GC/MS features were identified by comparing the mass fragmentation patterns of the products with patterns from the built-in Wiley/NIST library.

3. Results

3.1 Interrupting capacity of CF$_3$I gas under different load currents

In the interruption tests, the peaks of the main current were set at 200 A and 400 A. The experiment results of interruption showed that CF$_3$I gas can switch off current of 200 A, but could not switch off current of 400 A (Fig. 4). Specifically, Fig. 4(a) shows a waveform of a successful interruption at current of 200 A. The transient recovery voltage (TRV) was established at about 22 kV (50 Hz), while the total duration of the current was three half cycles of the sine wave (30 ms). Fig. 4(b) shows a waveform of a failure interruption at a current of 400 A. The time of through-flow was about eight half-cycles of the sine wave (80 ms). The energy stored in the oscillation circuit was dissipated due to the arc burning continuously.

Fig. 4. Waveform of interruption experiments, (a) the load current is 200 A, (b) the load current is 400 A

3.2 Determination of the decomposition products under load current interruption and AC breakdown tests for CF$_3$I gas

We use GC-MS to measure the ingredients of CF$_3$I gas after interruption tests. GC-MS spectrogram changes of CF$_3$I gas in different experimental conditions were shown in Fig. 5. Different molecules could be identified by retention times and the mass fragmentation patterns (Table 1). In initial state, there exist three prominent peaks for N$_2$, H$_2$O, and C$_2$F$_4$.
increased slightly while the opposite happened to the amount of $\text{C}_2\text{F}_4$. As shown in Fig. 6, the amount of $\text{CF}_3\text{I}$ increased to 400 A, more than 95% CF$_4$ and CF$_2$ could not fulfill the interruptions for 400 A in the load switch we used. Two distinct peaks of CF$_4$ and CF$_2$F$_6$ with much larger peak area than that of CF$_3$I could be observed in the GC-MS analysis (Fig. 5). The abundance ratios of CF$_2$/CF$_3$I and CF$_2$F$_6$/CF$_3$I are 8 and 9.5 respectively. In other words, more than 95% CF$_3$I was already decomposed.

Toxic decomposition products formation under arcing or discharge conditions might involve risks to the health of anyone in the immediate surroundings of electrical equipment filled, therefore the poison level of the decomposition products of CF$_3$I gas should be determined before application.

First, CF$_3$I has a very low cardiac sensitization LOAEL (Lowest Observable Adverse Effect Level), a volume fraction of 0.4 %, although the acute 4-hour rat ALC (Approximate Lethal Concentration, essentially an LC50) is much higher. CF$_3$I has toxicity higher than CF$_4$, but toxicity of these two alkyl iodides can be considered acceptable for insulation purposes [20]. The perfluorocarbons (PFCs) by-products of CF$_3$I are CF$_3$I, CF$_2$, CF$_4$, and CF$_2$I. In fact, these highly stable compounds have no measurable toxicity, they are widely used today in the semiconductor industry, plasma chemistry and fire suppression [21]. While the addition of hydrogen increases toxicity, hydrofluorocarbons (HFCs) still generally have low toxicity. The main impurities of CF$_3$I (CH$_3$I, CH$_2$IH, CH$_2$$\equiv$H) are allowable for use in normally occupied areas [22]. In summary, the toxicity of decomposition of CF$_3$I we detected is relatively low and it is surely up to toxicity standards in equipment.

## 4. Discussion

The composition of CF$_3$I (Fig. 7) was calculated with the minimization of the Gibbs free energy method [23] to determining the chemical state of CF$_3$I gas. The specific calculation steps of the calculation were presented in previous literature [23, 24]. The so-called Newton-Raphson method was used to analyze the data of GC and MS experiments. The results reveal that C$_2$F$_6$, tetrafluoroethene (C$_4$F$_4$), octafluoropropane (C$_8$F$_8$), pentafluorothiylidide (C$_5$I), were the gaseous by-products of CF$_3$I under AC breakdown tests or the interruptions at current of 200 A. However, when the current increase to 400 A, more than 95% CF$_3$I was thoroughly decomposed. Thus C$_2$F$_6$, CF$_2$ became the primary products.

By analyzing the relative peak intensities, we can see the proportion change of by-products in different experimental conditions. As shown in Fig. 6, the content of C$_2$F$_6$, C$_2$F$_3$I, C$_2$F$_4$ and C$_2$F$_5$ keep increasing with AC breakdown times. The amounts of other components, including CH$_3$I, CH$_2$IH, CH$_2$$\equiv$H, C$_2$F$_6$ and H$_2$O, remain stable after AC breakdown tests. Thus, these gases could be thought as the inherent impurities rather than the decomposition products. The intensity of C$_2$F$_2$I was approximately equal for interruption at 200 A and AC breakdown tests. The amount of C$_2$F$_2$I increased slightly while the opposite happened to the amount of C$_2$F$_3$I, which is consistent with reference [14].

Under the conditions of high pressure, C$_2$F$_3$I produced during discharge after a certain period is converted to CF$_3$I and I$_2$. Although there are several kinds of by-products, the maximum content of these is about 3500 ppm while others are less than 1000 ppm. That is to say, decomposition amount of CF$_3$I in these situations is less than 1%. It is also a reflection of the insulation stability of CF$_3$I gas. But apparently, CF$_3$I gas could not fulfill the interruptions for 400 A in the load switch we used. Two distinct peaks of CF$_4$ and C$_2$F$_6$ with much larger peak area than that of CF$_3$I could be observed in the GC-MS analysis (Fig. 5). The abundance ratios of CF$_2$/CF$_3$I and C$_2$F$_6$/CF$_3$I are 8 and 9.5 respectively. In other words, more than 95% CF$_3$I was already decomposed.

## Table 1. GC-MS data of the by-products

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Retention time (min)</th>
<th>Data of GC-MS (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CF$_4$</td>
<td>1.94</td>
<td>88, M; 69, CF$_2$I; 50, CF$_2$I</td>
</tr>
<tr>
<td>2</td>
<td>C$_2$F$_4$</td>
<td>2.55</td>
<td>138, M; CF$_2$F$_2$; 69, CF$_2$I; 50, CF$_3$I</td>
</tr>
<tr>
<td>3</td>
<td>C$_2$F$_4$</td>
<td>2.97</td>
<td>100, M; 50, CF$_2$I</td>
</tr>
<tr>
<td>4</td>
<td>C$_2$F$_4$</td>
<td>5.28</td>
<td>160, CF$_2$F$_2$; 119, C$_2$F$_4$; 100, CF$_2$F$_2$; 69, F; 50, CF$_2$I; 31, FC</td>
</tr>
<tr>
<td>5</td>
<td>CF$_3$I</td>
<td>10.59</td>
<td>196, M, 127, I; 69, F, C</td>
</tr>
<tr>
<td>6</td>
<td>C$_2$F$_7$I</td>
<td>12.33</td>
<td>246, M, 227, CF$_2$F$_3$I; 127, I; 119, C$_2$F$_5$; 100, C$_2$F$_6$; 69, CF$_2$I; 50, CF$_2$I</td>
</tr>
</tbody>
</table>

| Fig. 6. The intensity of by-products as a function of the times of AC breakdown tests. Additional data points are the by-products under interruption CO$_2$, CF$_3$I and five tiny peaks for CHF$_3$, C$_2$H$_3$I, H$_2$O, C$_4$F$_8$, and C$_3$H$_3$F$_3$. However, N$_2$ and CO$_2$ were detected because a few amount of air mixed in sample gas during sample introduction process. Moreover, it should be noted the kind of chromatogram column used in our GC-MS experiments could not catch oxygen signal. Other components were the known impurity during CF$_3$I producing process [18, 19]. Compared with initial gas as reference, the results reveal that C$_2$F$_6$, tetrafluoroethene (C$_4$F$_4$), octafluoropropane (C$_8$F$_8$), pentafluorothiylidide (C$_5$I), were the gaseous by-products of CF$_3$I under AC breakdown tests or the interruptions at current of 200 A. However, when the current increase to 400 A, more than 95% CF$_3$I was thoroughly decomposed. Thus C$_2$F$_6$, CF$_2$ became the primary products.

By analyzing the relative peak intensities, we can see the proportion change of by-products in different experimental conditions. As shown in Fig. 6, the content of C$_2$F$_6$, C$_2$F$_3$I, C$_2$F$_4$ and C$_2$F$_5$I keep increasing with AC breakdown times. The amounts of other components, including CHF$_3$, CH$_2$IH, CH$_2$$\equiv$H, C$_2$F$_6$ and H$_2$O, remain stable after AC breakdown tests. Thus, these gases could be thought as the inherent impurities rather than the decomposition products. The intensity of C$_2$F$_2$I was approximately equal for interruption at 200 A and AC breakdown tests. The amount of C$_2$F$_2$I increased slightly while the opposite happened to the amount of C$_2$F$_3$I, which is consistent with reference [14].

## Table 2. Species in the calculation of the compositions of the CF$_3$I gas

<table>
<thead>
<tr>
<th>Classification</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral molecules</td>
<td>CF$_3$I; C$_2$F$_4$I; C$_2$F$_3$I; C$_2$F$_2$I; C$_2$F$_4$; C$_2$F$_5$I; CF$_2$I; BF; BF$_2$; CF; C$_2$; C$_3$; F; F$_2$; F$_3$</td>
</tr>
<tr>
<td>Radical</td>
<td>C, F, I, CF$_3$, CF$_2$, CF, C$_2$F$_2$</td>
</tr>
<tr>
<td>Ions</td>
<td>CF$^+$, CF$^3$, C$^+$, C$^6$, C$^2$, C$^3$, F$^+$, F$^2$, F$^3$, F$^+$, I$^+$, I$^–$</td>
</tr>
<tr>
<td>Electron</td>
<td>e</td>
</tr>
</tbody>
</table>
According to the experimental results, CF$_3$I gas can remain stable after ac breakdown test and interruption of load current at 200 A. However, when the given energy is large enough (interruption of load current at 400 A), CF$_3$I gas will decompose completely.

5. Conclusion

The dissociation behaviors of CF$_3$I gas under load current interruption were studied with a commercial SF$_6$-filled arc quenching load switch. And the by-products of CF$_3$I after several hundred times of AC breakdown discharges in the self-made cavity were also detected as a reference.

The decomposition properties of CF$_3$I were dramatically different under different load current interruption. It concretely embodies in the components and contents of by-products. Under AC discharges and successful arc extinguishment at a current of 200 A, less than 1% CF$_3$I is decomposed. The dominant by-product is C$_2$F$_6$ and a small amount of C$_3$F$_8$, C$_2$F$_6$ and C$_3$F$_8$I, which is the same as by-products after the AC breakdown discharges. The maximum content of these gases is about 3500 ppm while others are less than 1000 ppm. However, under the interruption at a current of 400 A, almost 95% CF$_3$I gas is decomposed. The primary decomposition products are C$_3$F$_8$ and CF$_4$. All of the detected products are weakly toxic.

We also discuss the mechanism of the decomposition process though the calculation of equilibrium CF$_3$I arc plasma. CF$_3$I gas can hardly recover once the decomposition process occurred. However, further investigations on the temperature profile of the formed plasma and its relationship with the energy should be carried out.

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References

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