



# One potential source of the potent greenhouse gas SF<sub>5</sub>CF<sub>3</sub>: the reaction of SF<sub>6</sub> with fluorocarbon under discharge

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## Abstract

In this paper, we verified Sturges's speculation (Science, 2000) that SF<sub>5</sub>CF<sub>3</sub> might originate as a breakdown product of SF<sub>6</sub> in high-voltage equipment via the spark discharge reactions of SF<sub>6</sub> with a few fluorocarbons, such as CHF<sub>3</sub> and CH<sub>2</sub>F<sub>2</sub>. However, SF<sub>5</sub>CF<sub>3</sub> was unlikely to be formed from CF<sub>3</sub> group attacking SF<sub>5</sub> radical based on the results that no SF<sub>5</sub>CF<sub>3</sub> was detected in the reactions of SF<sub>6</sub> with CF<sub>4</sub> or CF<sub>3</sub>Br. The reactions of SF<sub>6</sub> with CHF<sub>3</sub> and CH<sub>2</sub>F<sub>2</sub> under spark discharge produced SF<sub>5</sub>CF<sub>3</sub> and the yields of SF<sub>5</sub>CF<sub>3</sub> were determined as a function of the initial fluorocarbon to SF<sub>6</sub> ratio, total gas pressure and discharge time. The reaction processes of SF<sub>6</sub> with CHF<sub>3</sub> and CH<sub>2</sub>F<sub>2</sub> were discussed briefly.

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## 1. Introduction

Extensive attention has been paid to trifluoromethyl sulfur pentafluoride (SF<sub>5</sub>CF<sub>3</sub>), the greenhouse gas with the strongest radiative force (0.59 W m<sup>-2</sup> ppbv<sup>-1</sup>) on a per molecule basis (Nielsen et al., 2002), all around the world soon after Sturges and his coworkers (Science, 2000) detected it from the Antarctic firm. In spite of many research works on SF<sub>5</sub>CF<sub>3</sub> properties and sinks undertaken (Chim et al., 2001; Kennedy and Mayhew, 2001; Sailer et al., 2002), little is known about the sources of SF<sub>5</sub>CF<sub>3</sub>. The only known source of SF<sub>5</sub>CF<sub>3</sub> so far, the release as a by-product during the manufacture of certain fluorochemicals (Santoro, 2000), contributes only a small portion to the approximately 3900 metric tons of SF<sub>5</sub>CF<sub>3</sub> in the atmosphere.

Due to the good agreement between the increasing trends of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> in the atmosphere over the past 30 years, Sturges et al. (Science, 2000) hypothesized that the source of SF<sub>5</sub>CF<sub>3</sub> was SF<sub>5</sub> radical, a breakdown product of SF<sub>6</sub>, attacking CF<sub>3</sub> groups from the surface of fluoropolymers in high-voltage equipment. Further studies on the spark discharge reactions of SF<sub>6</sub> with a series of fluorocarbons that fluoropolymers might produce were carried out in our laboratory. The studies had two goals. First, to provide an experimental check of the source of SF<sub>5</sub>CF<sub>3</sub> claimed by Sturges et al.; second, to achieve a better understanding of the formation mechanism of the thoroughly anthropogenic greenhouse gas SF<sub>5</sub>CF<sub>3</sub>.

In this article, CF<sub>4</sub>, CHF<sub>3</sub> and CH<sub>2</sub>F<sub>2</sub> were selected as the major reactants to study their detailed reactions with SF<sub>6</sub> under the spark discharge condition. Results were presented and discussed with respect to the literature data.

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## 2. Experimental

### 2.1. Experimental materials

The gases used in the experiments were as follows: SF<sub>6</sub> (at a purity of 99.9%) and CF<sub>2</sub>BrCl (purity of 99.5%) obtained from Shanghai Refrigerant Products Inc.; SF<sub>5</sub>CF<sub>3</sub> (purity of 98.0%) and CHF<sub>3</sub> (purity of 99.5%) from Wuxi Xinnan Chemical Gases Inc.; CF<sub>4</sub> (purity of 99.9%) from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences; CH<sub>4</sub> (purity of 99.9%) from Shanghai Pujiang Gas Supply Limited Co.; CF<sub>3</sub>Br (purity of 99.9%) from Shanghai Cangsong Chemical Engineering Products Service; CH<sub>2</sub>F<sub>2</sub> (purity of 99.5%) from Zhejiang Lantian Environmental Protection High-Tech Limited Co. All the gases were not further purified before use.

### 2.2. Experimental apparatus and methods

Sample handling was performed in a glass vacuum system with Teflon stopcocks (see Fig. 1). After the system was evacuated to 1.5 Pa, specific reactant gases were introduced into the cell and the pressure was measured using a membrane manometer with a precision of 13 Pa (0.1 Torr).

The reaction cell (2 cm in diameter and 14 cm long) with a Teflon stopcock was made of glass and equipped with two platinum electrodes with a distance of 1.5 cm. The self-designed spark discharge generator used in the experiment consists of a high-voltage transformer with an output voltage of 3 kV and an oscillating transmitter with a frequency of 2 MHz. Based on the consideration that SF<sub>5</sub>CF<sub>3</sub> was easily broken during discharge due to the low bond energy of F<sub>3</sub>S–CF<sub>3</sub> ( $4.06 \pm 0.45$  eV) (Chim et al., 2001), the intermittent discharge method (i.e. every discharge (1.83 J per spark) lasted 1.0 s followed by another 1.0 s of interval) was adopted to allow the produced SF<sub>5</sub>CF<sub>3</sub> to escape from the discharge area in

time. The interval time was not counted as far as the discharge time was mentioned.

A Nicolet Fourier transform infrared spectrum (FTIR) spectrometer (Nexus-470IR), operating at a spectral resolution of 1.0 cm<sup>-1</sup> over the range from 500 to 4000 cm<sup>-1</sup>, was employed to analyze the components of samples. Both sample spectra and background spectra were recorded using a gas vessel (3.8 cm in diameter and 10 cm long) equipped with a pair of KBr windows fixed with viton “O” ring. Sixty-four scans were co-added for each sample. The standard IR absorption peaks of SF<sub>5</sub>CF<sub>3</sub> are observed at 612, 755, 884, 889, 903, 1169, 1172, 1257 cm<sup>-1</sup> (Sturges et al., 2000; Nielsen et al., 2002). The absorption at 1257 and 903 cm<sup>-1</sup> obeyed the Beer–Lambert law in the 0–400 Pa pressure range. However, considering the strong absorption of SF<sub>6</sub> overlapping with that of SF<sub>5</sub>CF<sub>3</sub> at 1255 cm<sup>-1</sup>, only the absorption peak of 903 cm<sup>-1</sup> was suitable for quantifying the SF<sub>5</sub>CF<sub>3</sub> produced.

Gas chromatography–mass spectrometry (GC–MS) was also employed to confirm the existence of SF<sub>5</sub>CF<sub>3</sub>. In gas chromatography (Varian CP-3800), a 30 m × 0.32 mm Gas-Pro capillary column was applied to separate the components of the samples at 180 °C swept by helium. Mass spectra were measured by Varian Saturn 2000 mass spectrometer with an electron impact (EI) ionization source of 70 eV energy operating at 150 °C. The amount of SF<sub>5</sub>CF<sub>3</sub> formed in one experiment was too small to be detected and would reach a maximum value with the discharge prolonged so that the samples were harvested five times under the same condition for each datum to obtain a better signal/noise ratio. The gaseous products were filled into the collector through the inlet and condensed by a liquid nitrogen trap. After the sample was warmed to room temperature, it was injected into the chromatograph for analysis.

All the experiments were carried out at room temperature.

## 3. Results and discussion

### 3.1. Spark discharge of pure SF<sub>6</sub>

In the preliminary experiment,  $1.3 \times 10^4$  Pa SF<sub>6</sub> without any additive gas was exposed to discharge. After a spark discharge of 10 min, the main products discerned by the IR spectrum (see Fig. 2) were SOF<sub>2</sub> (747, 808, 1330, 1340 cm<sup>-1</sup>), SO<sub>2</sub>F<sub>2</sub> (848, 885, 1269, 1500 cm<sup>-1</sup>), SiF<sub>4</sub> (1028 cm<sup>-1</sup>). SF<sub>4</sub> was not detected because of the overlap of its absorption peak at 747 cm<sup>-1</sup> with that of SOF<sub>2</sub>.

The previous researcher (Chu, 1986) had already confirmed the formation of SF<sub>5</sub> radical by spark discharge. Thus, the main reactions that occurred in the initial stage of spark discharge of SF<sub>6</sub> were as

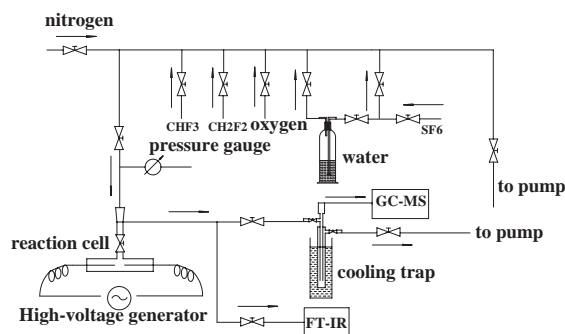


Fig. 1. Schematic diagram of the experimental system used in this research work.

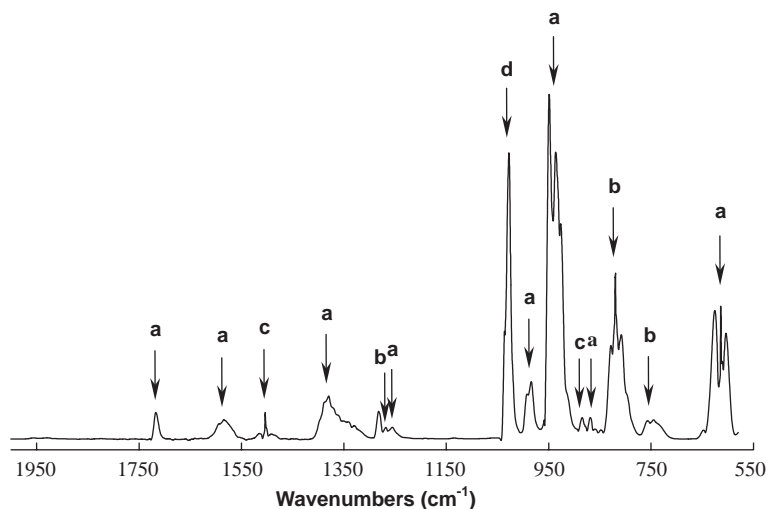
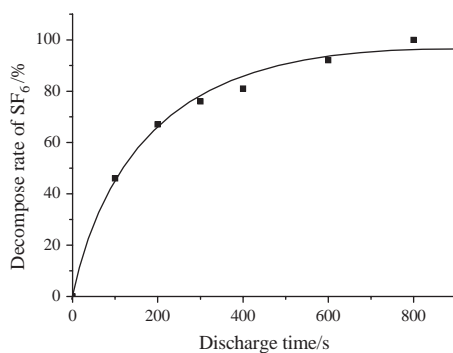


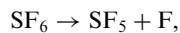
Fig. 2. IR spectrum of discharge products of  $2.0 \times 10^4$  kPa  $\text{SF}_6$  for 300 s (a)  $\text{SF}_6$  (b)  $\text{SOF}_2$  (c)  $\text{SO}_2\text{F}_2$  (d)  $\text{SiF}_4$ .



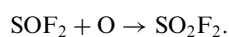
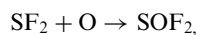
Where, decompose rate of  $\text{SF}_6$ (%) was defined as:  $\frac{\text{the amount of } \text{SF}_6 \text{ decomposed}}{\text{the amount of } \text{SF}_6 \text{ before discharge}} \cdot 100\%$

Fig. 3. Effect of discharge time on the dissociation rate of  $\text{SF}_6$  under discharge.

follows:



Then the free fluorine atom reacted with  $\text{SiO}_2$ , the major component of glass (Liu et al., 1996):



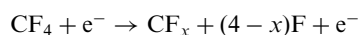
These reactions could be verified by the etch-figure on the glass wall of the reaction cell.  $\text{SF}_6$  continued to be decomposed as the discharge time prolonged till no  $\text{SF}_6$  was left, as shown in Fig. 3. The reaction rate constant and the influence of additive gases were reported in detail in our previous work (Zhang et al., 2004).

### 3.2. Reactions of $\text{SF}_6$ with $\text{CF}_4$ , $\text{CF}_3\text{Br}$ , $\text{CF}_2\text{ClBr}$ or $\text{CH}_4$

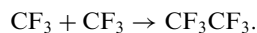
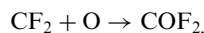
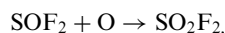
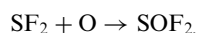
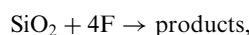
#### 3.2.1. Reaction of $\text{SF}_6$ and $\text{CF}_4$

$\text{CF}_4$ , a  $\text{CF}_3$  group donor under discharge condition and a commonly used gas in electrical installations, was selected to react with  $\text{SF}_6$  under spark discharge conditions.  $6.7 \times 10^3$  Pa  $\text{CF}_4$  and  $6.7 \times 10^3$  Pa  $\text{SF}_6$ , the

ratio in domain in high-voltage equipment nowadays, were introduced into the reaction cell and then discharged for 600 s. From the IR spectrum, the discernable gaseous products were COF<sub>2</sub>, SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub>, CF<sub>3</sub>CF<sub>3</sub>, CS<sub>2</sub> and SiF<sub>4</sub>. No SF<sub>5</sub>CF<sub>3</sub> could be detected in the products under this condition or under the other combination conditions between different discharge times (100, 200, 300, 500, 900 and 1200 s) and CF<sub>4</sub>-to-SF<sub>6</sub> ratios (1:5, 1:2, 1:1, 4:1, 10:1). The presence of COF<sub>2</sub> and CF<sub>3</sub>CF<sub>3</sub> verified the dissociation of CF<sub>4</sub> by electron impact and their formation followed the equations



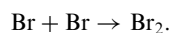
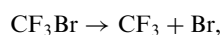
(Pradayrol et al., 1997),



Due to the thermodynamic and kinetic advantage of the recombination of SF<sub>6</sub> and CF<sub>4</sub> decomposition products with fluorine atom, the recombination of fluorine atom and CF<sub>3</sub> radical occurred simultaneously in the system. The CF<sub>4</sub> molecule somewhat behaved as a source of fluorine atoms that could combine with SF<sub>5</sub> radical to regenerate SF<sub>6</sub> (Pradayrol et al., 1997).

### 3.2.2. Reaction of SF<sub>6</sub> and CF<sub>3</sub>Br

Our previous research has already shown that CF<sub>3</sub>Br is capable of giving a great deal of CF<sub>3</sub> during discharge (Yu et al., 1997) and provide CF<sub>3</sub> much more easily because of the relatively low bond energy of F<sub>3</sub>C–Br (as Table 1 shown). In view of these analyses, CF<sub>3</sub>Br was selected to replace CF<sub>4</sub> in the further experiment. We tried different combinations between the discharge times (100, 200, 300, 500, 900 and 1200 s) and CF<sub>3</sub>Br-to-SF<sub>6</sub> ratios (1:5, 1:2, 1:1, 4:1, 10:1). However, the gaseous products were the same as those found in the SF<sub>6</sub>–CF<sub>4</sub> system except for an additional occurrence of Br<sub>2</sub> and again no SF<sub>5</sub>CF<sub>3</sub> was detected. The possible formation channel for Br<sub>2</sub> was



From the above experiments, it therefore seemed that SF<sub>5</sub>CF<sub>3</sub> was unlikely to be formed via SF<sub>5</sub>'s combination with CF<sub>3</sub> directly.

Table 1  
The bond energy of some important fluorocarbon studied in this paper

Reagent		Bond-energy (eV)
CF <sub>4</sub> <sup>a</sup>	C–F	5.56
CF <sub>3</sub> Br <sup>a</sup>	F <sub>3</sub> C–Br	3.06
	F <sub>2</sub> BrC–F	5.60
CF <sub>2</sub> ClBr <sup>a</sup>	F <sub>2</sub> ClC–Br	2.80
	F <sub>2</sub> BrC–Cl	3.10
	ClBrFC–F	5.30
CHF <sub>3</sub>	CF <sub>3</sub> –H <sup>b,c</sup>	4.61
	CHF <sub>2</sub> –F <sup>c</sup>	5.57
CH <sub>2</sub> F <sub>2</sub> <sup>d</sup>	CF <sub>2</sub> H–H	4.34

<sup>a</sup>From Lide (2001–2002).

<sup>b</sup>From Amphlett et al. (1966).

<sup>c</sup>From Okamoto and Tomonari (2000).

<sup>d</sup>From Pritchard and Perona (1969).

### 3.2.3. Reaction of SF<sub>6</sub> and CF<sub>2</sub>ClBr

Considering the following postulations, we chose CF<sub>2</sub>ClBr to react with SF<sub>6</sub> under discharge conditions: (1) Compared with the ClBrFC–F bond, F<sub>2</sub>ClC–Br bond and F<sub>2</sub>BrC–Cl bond can be broken much more easily (see Table 1) and provide CF<sub>2</sub>; (2) SF<sub>5</sub>CF<sub>3</sub> might be the rearrangement form of SF<sub>6</sub>CF<sub>2</sub>, one of the possible products of CF<sub>2</sub> being attacked by SF<sub>6</sub>. The reactions were performed under the same discharge conditions with the discharge time ranging from 100 to 1200 s and the ratio of CF<sub>2</sub>BrCl to SF<sub>6</sub> from 10:1 to 1:5. Again, no SF<sub>5</sub>CF<sub>3</sub> could be detected in the IR spectrum in this reaction system.

### 3.2.4. Reaction of SF<sub>6</sub> and CH<sub>4</sub>

CH<sub>4</sub> and SF<sub>6</sub> were subjected to the discharge condition on the assumption that SF<sub>5</sub>CF<sub>3</sub> might be formed via the dehydrofluorination reaction between SF<sub>5</sub>CH<sub>3</sub> and fluorine atom. Despite the fact that the experiments were performed under the combination conditions with various discharge times (from 100 to 1200 s) and CH<sub>4</sub>-to-SF<sub>6</sub> ratios (from 10:1 to 1:5), no SF<sub>5</sub>CF<sub>3</sub> could be detected in the products.

### 3.3. Spark discharge reactions producing SF<sub>5</sub>CF<sub>3</sub>

The hydrofluorocarbons (HFCs), such as trifluoromethane (CHF<sub>3</sub>) and difluoromethane (CH<sub>2</sub>F<sub>2</sub>), which were used in place of CF<sub>4</sub>, were also chosen to test. It was detected that SF<sub>5</sub>CF<sub>3</sub> was produced in both discharge systems (SF<sub>6</sub> + CHF<sub>3</sub> and SF<sub>6</sub> + CH<sub>2</sub>F<sub>2</sub>). The typical absorption peaks of SF<sub>5</sub>CF<sub>3</sub> at 903, 889 and

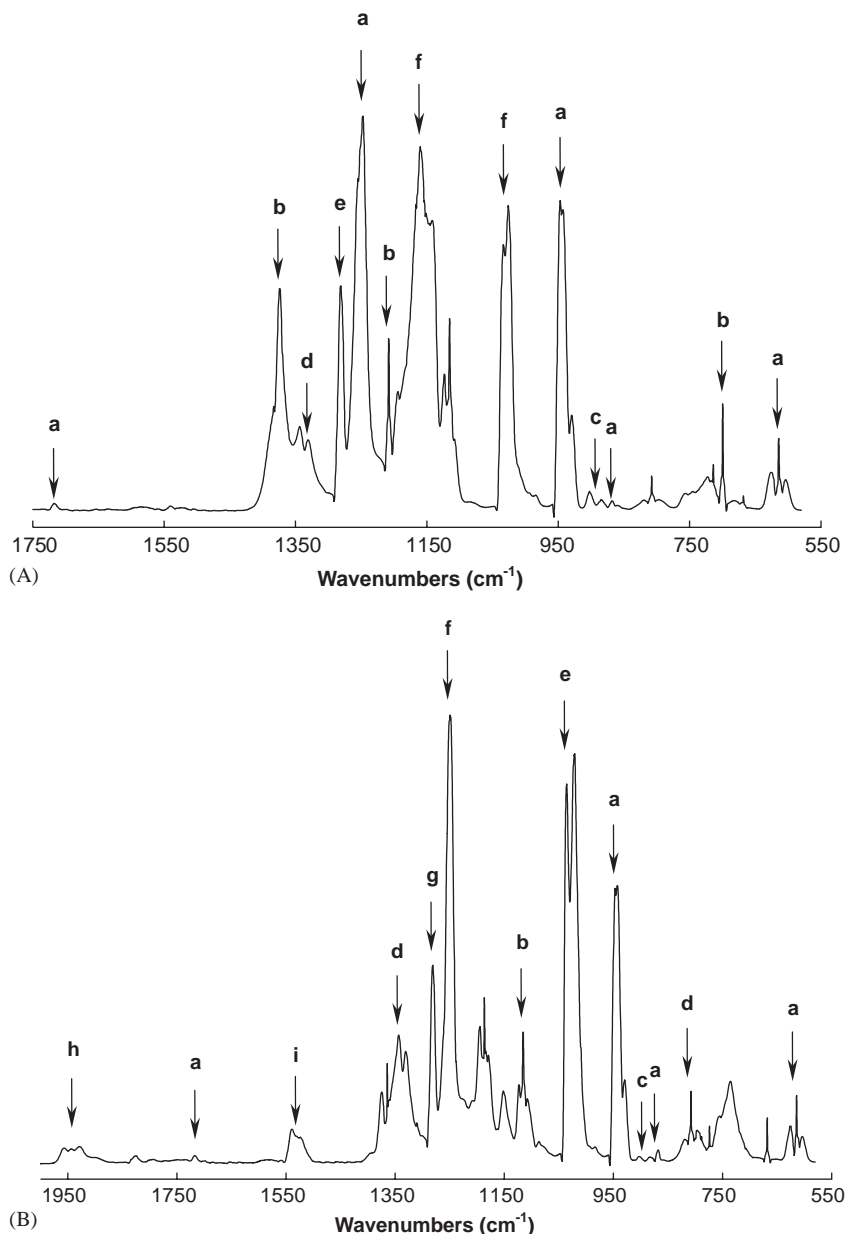


Fig. 4. (A) IR spectrum of products from  $2.0 \times 10^4$  kPa  $\text{SF}_6$  and  $1.6 \times 10^4$  kPa  $\text{CHF}_3$  after discharged for 300 s, (a)  $\text{SF}_6$  (b)  $\text{CHF}_3$  (c)  $\text{SF}_5\text{CF}_3$  (d)  $\text{SOF}_2$  (e)  $\text{CF}_4$  (f)  $\text{SiF}_4$ . (B) IR spectrum of products from  $2.0 \times 10^4$  kPa  $\text{SF}_6$  and  $6.7 \times 10^4$  kPa  $\text{CH}_2\text{F}_2$  discharged for 300 s, the inset shows the amplified peaks of 903, 889,  $884\text{ cm}^{-1}$  (a)  $\text{SF}_6$  (b)  $\text{CH}_2\text{F}_2$  (c)  $\text{SF}_5\text{CF}_3$  (d)  $\text{SOF}_2$  (e)  $\text{SiF}_4$  (f)  $\text{CF}_3\text{CF}_3$  (g)  $\text{CF}_4$  (h)  $\text{CF}_2\text{O}$  (i)  $\text{CS}_2$ .

$884\text{ cm}^{-1}$  were observed in the IR spectra of both systems after discharge reactions (see Fig. 4), though the yields of  $\text{SF}_5\text{CF}_3$  were rather small.

The GC-MS spectrum of the products of discharge reaction between  $\text{SF}_6$  and  $\text{CHF}_3$ , as shown in Fig. 5, also verified the formation of  $\text{SF}_5\text{CF}_3$ . Fig. 5c demonstrated the mass spectrum of the elute of 5.756 min in Fig. 5b, which was well consistent with the standard mass

spectrum of  $\text{SF}_5\text{CF}_3$  (Fig. 5a). It was observed that the  $\text{SF}_5\text{CF}_3$  yield was much more in the  $\text{SF}_6$ - $\text{CHF}_3$  system than that in the  $\text{SF}_6$ - $\text{CH}_2\text{F}_2$  system under the same reaction condition. The formation mechanism of  $\text{SF}_5\text{CF}_3$  would be discussed in the subsequent section.

Discharge time,  $X$ -to- $\text{SF}_6$  ( $X$  presented  $\text{CHF}_3$  and  $\text{CH}_2\text{F}_2$ ) ratio and total gas pressure were found to exert influence on the yield of  $\text{SF}_5\text{CF}_3$ .

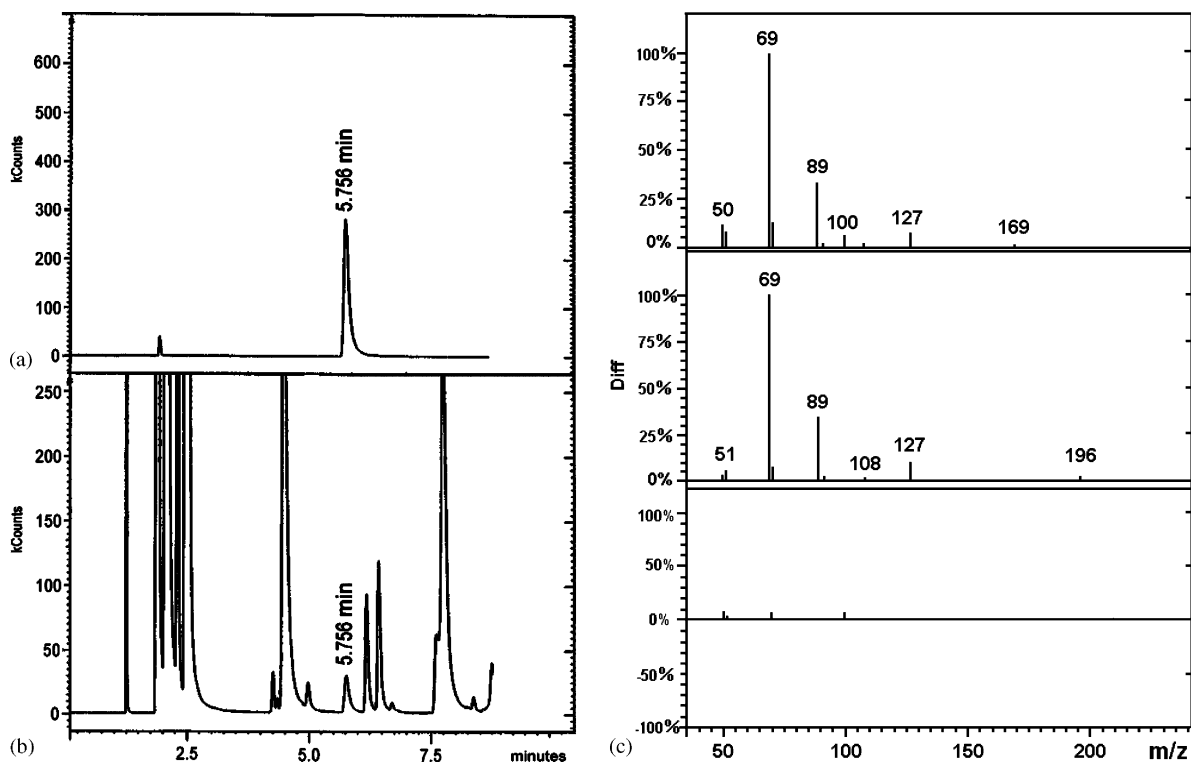
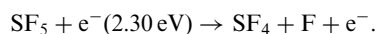
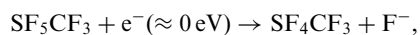
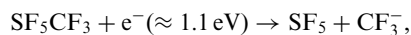
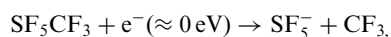


Fig. 5. (a) Gas chromatogram plot of sample  $\text{SF}_5\text{CF}_3$  (from Xinnan Corporation, Wuxi, China). (b) Gas chromatogram plot of the products from the reaction of  $\text{SF}_6$  and  $\text{CHF}_3$ . Comparing with plot (a),  $\text{SF}_5\text{CF}_3$  peak with the retention time of 5.756 min was found. (c) Upper: mass spectrum of  $\text{SF}_5\text{CF}_3$  peak in gas chromatogram plot (a). Middle: standard mass spectrum of  $\text{SF}_5\text{CF}_3$ . Bottom: Difference between upper and middle.

### 3.3.1. The yield of $\text{SF}_5\text{CF}_3$ vs. discharge time

The dependence of the yield of  $\text{SF}_5\text{CF}_3$  upon the discharge time was shown in Figs. 6a and 7a. In both systems, the  $\text{SF}_5\text{CF}_3$  yields reached peak values at specific discharge time points; this might be caused by a further decomposition of  $\text{SF}_5\text{CF}_3$  by electron impact as the discharge time prolonged, which had been studied in the previous work (Sailer et al., 2002):



where, the values in brackets are the energies of the electrons needed in the reaction.

The decomposition reaction of  $\text{SF}_5\text{CF}_3$  and the formation reaction of  $\text{SF}_5\text{CF}_3$  by  $\text{SF}_6$  and  $X$  ( $X$  represented  $\text{CHF}_3$  and  $\text{CH}_2\text{F}_2$ ) under spark discharge

were competitive reactions and both of them contributed to the apparent yield of  $\text{SF}_5\text{CF}_3$ .

It could also be noted that at the beginning of discharge, the quantity of active groups and excited molecules increased with time. However, as the discharge time prolonged, the reactant molecules would be dissociated into constituent atoms and rare free radicals and excited molecules were able to stay stable in the system, which inhibited the formation of  $\text{SF}_5\text{CF}_3$ .

### 3.3.2. The yield of $\text{SF}_5\text{CF}_3$ vs. the initial ratio of $\text{SF}_6$ -to- $X$

The influence of initial  $\text{CHF}_3/\text{SF}_6$  ratio on the quantity of  $\text{SF}_5\text{CF}_3$  produced was determined with a discharge time of 300 s and a total gas pressure of 18 kPa for the  $\text{SF}_6$ - $\text{CHF}_3$  system, the condition under which we achieved the largest  $\text{SF}_5\text{CF}_3$  yield in Section 3.3.1. The results presented in Fig. 6b showed that enhancing the initial ratio of  $\text{CHF}_3$ -to- $\text{SF}_6$  would increase the yield of  $\text{SF}_5\text{CF}_3$  over the whole range studied in the  $\text{SF}_6$ - $\text{CHF}_3$  system.

In parallel, the influence of the  $\text{CH}_2\text{F}_2/\text{SF}_6$  ratio was determined at a total pressure of 27 kPa discharged for

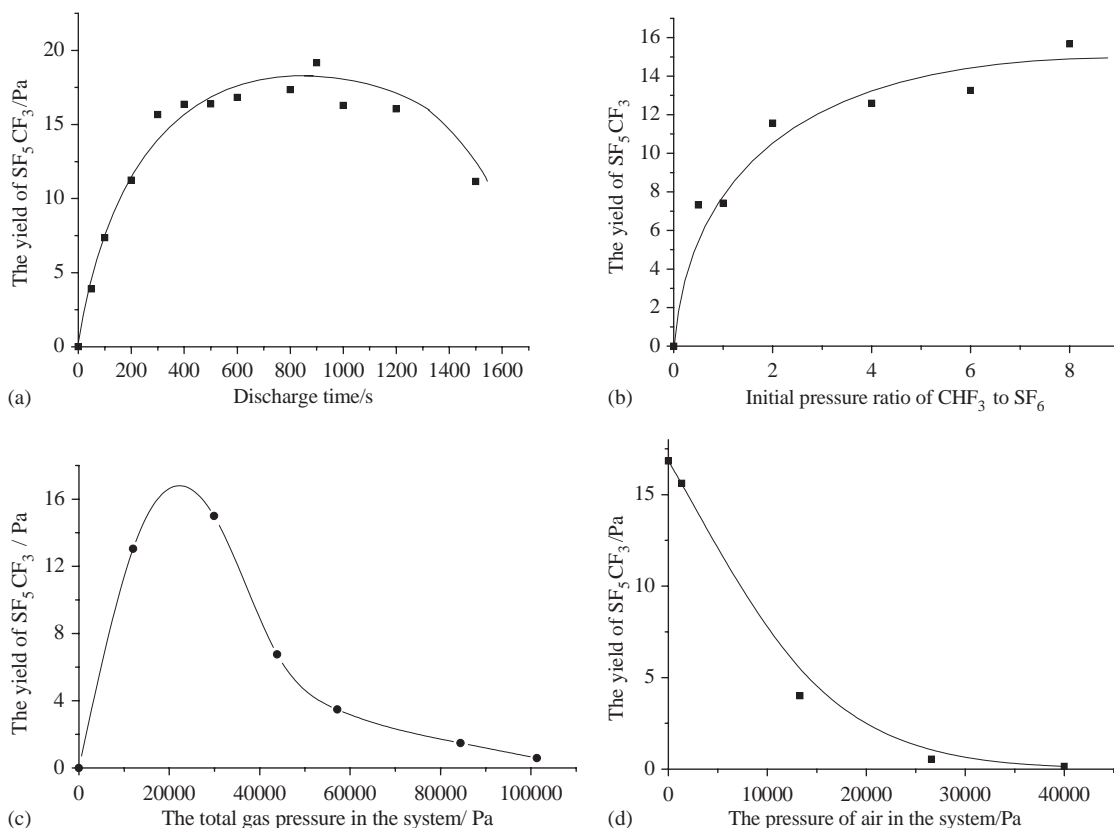


Fig. 6. The yield potential with discharge time, initial CHF<sub>3</sub>-to-SF<sub>6</sub> ratio, total pressure in SF<sub>6</sub>-CHF<sub>3</sub> system. (a) Influence of discharge time on the formation of SF<sub>5</sub>CF<sub>3</sub> under discharge ( $P_{\text{SF}_6} = 2 \text{ kPa}$ ;  $P_{\text{CHF}_3} = 16 \text{ kPa}$ ). (b) Influence of initial CHF<sub>3</sub>-to-SF<sub>6</sub> ratio on the formation of SF<sub>5</sub>CF<sub>3</sub> under discharge (discharge time: 300 s; total gas pressure: 18 kPa). (c) Influence of total gas pressure on the formation of SF<sub>5</sub>CF<sub>3</sub> under discharge (discharge time: 300 s;  $P_{\text{CHF}_3}/P_{\text{SF}_6} = 1:8$ ). (d) Influence of additive air on the formation of SF<sub>5</sub>CF<sub>3</sub> under discharge (discharge time: 300 s;  $P_{\text{SF}_6} = 2 \text{ kPa}$ ;  $P_{\text{CHF}_3} = 16 \text{ kPa}$ ).

600 s, under which condition we achieved the peak yield of SF<sub>5</sub>CF<sub>3</sub> in Section 3.3.1. This trend of the yield of SF<sub>5</sub>CF<sub>3</sub> went against that of the SF<sub>6</sub>-CHF<sub>3</sub> system. The quantity of SF<sub>5</sub>CF<sub>3</sub> produced reached a maximum value when the ratio of CH<sub>2</sub>F<sub>2</sub> to SF<sub>6</sub> was 1:3 over the whole range studied, i.e. 1:5–5:1, as Fig. 7b showed. This phenomenon would be explained in Section 4.3.

### 3.3.3. The yield of SF<sub>5</sub>CF<sub>3</sub> vs. total gaseous pressure

Figs. 6c and 7c demonstrated the similar trends of the influence of total gas pressure on the yields of SF<sub>5</sub>CF<sub>3</sub> (total gas pressure value varying from 0–100 kPa). The yield of SF<sub>5</sub>CF<sub>3</sub> increased rapidly with  $P_{\text{total}}$  over the range from 0 to 25 kPa and then decreased with increasing  $P_{\text{total}}$  until it reached 60 kPa. The amount of SF<sub>5</sub>CF<sub>3</sub> produced in the SF<sub>6</sub>-CH<sub>2</sub>F<sub>2</sub> system remained constant when the pressure increased from 60 kPa to 100 kPa, while the yield of SF<sub>5</sub>CF<sub>3</sub> in the SF<sub>6</sub>-CHF<sub>3</sub> system declined gradually.

When at low total pressure, active groups could barely interact with each other and therefore the quantity of SF<sub>5</sub>CF<sub>3</sub> produced was rather small.

The number of ions, radicals and excited molecules produced by direct impact of electron was constrained by the certain electron density under the spark discharge system. Though high concentrations of reactants made the total amount of molecules attacked increased at high pressure, the total proportion of molecules attacked by electrons lowered. Hence, the increase of the concentration of active species, such as radicals and ions, inside the spark channel encouraged the collision process as well. The ions, radicals, electrons and excited molecules were partially quenched by the unexcited ones, which caused the low yield of SF<sub>5</sub>CF<sub>3</sub>.

### 3.3.4. The yield of SF<sub>5</sub>CF<sub>3</sub> vs. electron energy

The longer the distance between electrodes, the lower the mean electron energy is if other conditions

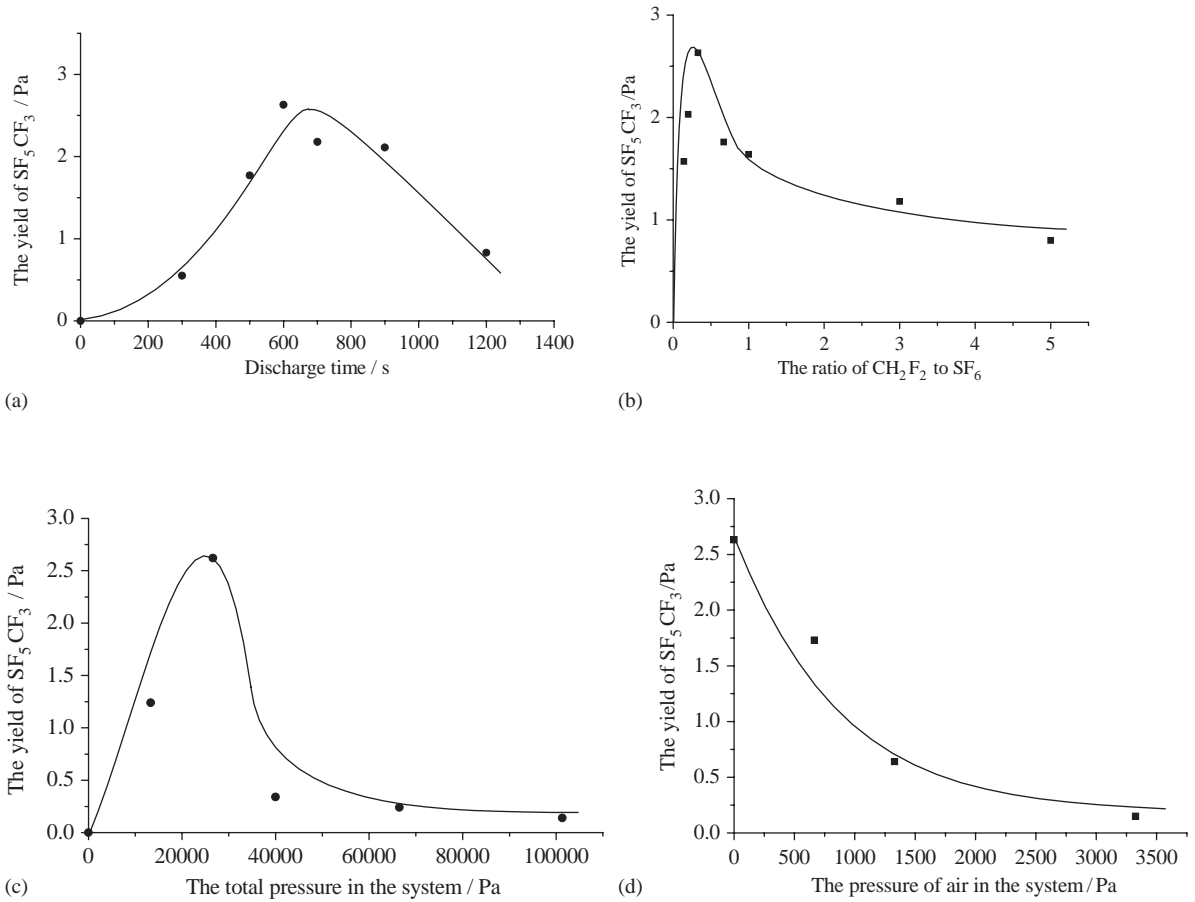


Fig. 7. The yield potential with discharge time, initial CH<sub>2</sub>F<sub>2</sub>-to-SF<sub>6</sub> ratio, total pressure in SF<sub>6</sub>-CH<sub>2</sub>F<sub>2</sub> system. (a) Influence of discharge time on the formation of SF<sub>5</sub>CF<sub>3</sub> under discharge ( $P_{\text{SF}_6} = 20 \text{ kPa}$ ;  $P_{\text{CH}_2\text{F}_2} = 6.7 \text{ kPa}$ ). (b) Influence of initial CH<sub>2</sub>F<sub>2</sub>-to-SF<sub>6</sub> ratio on the formation of SF<sub>5</sub>CF<sub>3</sub> under discharge (discharge time: 600 s; total gas pressure: 27 kPa). (c) Influence of total gas pressure on the formation of SF<sub>5</sub>CF<sub>3</sub> under discharge (discharge time: 600 s;  $P_{\text{CH}_2\text{F}_2}/P_{\text{SF}_6} = 1 : 3$ ). (d) Influence of additive air on the formation of SF<sub>5</sub>CF<sub>3</sub> under discharge (discharge time: 600 s;  $P_{\text{SF}_6} = 20 \text{ kPa}$ ;  $P_{\text{CH}_2\text{F}_2} = 6.7 \text{ kPa}$ ).

Table 2

The influence of electrode distance on the yield of SF<sub>5</sub>CF<sub>3</sub>

SF <sub>6</sub> -CHF <sub>3</sub> system		SF <sub>6</sub> -CH <sub>2</sub> F <sub>2</sub> system			
$P_{\text{SF}_6} = 2 \text{ kPa}$ ; $P_{\text{CHF}_3} = 16 \text{ kPa}$		$P_{\text{SF}_6} = 20 \text{ kPa}$ ; $P_{\text{CH}_2\text{F}_2} = 6.7 \text{ kPa}$			
Discharge time (s)	The yield of SF <sub>5</sub> CF <sub>3</sub> (Pa)		Discharge time (s)	The yield of SF <sub>5</sub> CF <sub>3</sub> (Pa)	
	Electrode distance: 1.5 cm	Electrode distance: 0.5 cm		Electrode distance: 1.5 cm	Electrode distance: 0.5 cm
0	0	0	0	0	0
300	15.7	2.98	300	0.55	2.03
600	16.8	13.0	600	2.63	3.72
700	19.2	14.5	900	2.11	4.01

are all the same (Xu and Zhu, 1996). The different mean electron energies were achieved by changing the electrode distance. The influence of electrode

distance on the yield of SF<sub>5</sub>CF<sub>3</sub> was presented in Table 2. No matter the discharge time, decreasing the distance between two electrodes would have an

adverse effect on the formation of SF<sub>5</sub>CF<sub>3</sub> in SF<sub>6</sub>–CHF<sub>3</sub> system.

A shorter distance between electrodes brought about a higher electron energy and therefore generated more free radicals in the system. The phenomenon that a shorter electrode distance would have a negative effect on the yield of SF<sub>5</sub>CF<sub>3</sub> in SF<sub>6</sub>–CHF<sub>3</sub> system indicated that the reaction of SF<sub>6</sub> with CHF<sub>3</sub> was not dominated by free radical processes.

As to the SF<sub>6</sub>–CH<sub>2</sub>F<sub>2</sub>, however, we arrived at just the opposite result, in other words, the quantity of SF<sub>5</sub>CF<sub>3</sub> produced with an electrode gap of 0.5 cm was larger than that with an electrode gap of 1.5 cm. This result to some extent indicated a slightly different formation mechanism of SF<sub>5</sub>CF<sub>3</sub> in SF<sub>6</sub>–CHF<sub>3</sub> system from that in SF<sub>6</sub>–CH<sub>2</sub>F<sub>2</sub> system.

#### 4. Formation mechanism of SF<sub>5</sub>CF<sub>3</sub>

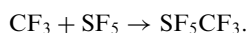
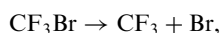
The studies on the reaction between several fluorocarbons (CF<sub>4</sub>, CF<sub>3</sub>Br, CHF<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>) and pure SF<sub>6</sub> under spark discharge condition brought about the following points:

- (1) In agreement with the literature (Chu, 1986), the spark discharge of pure SF<sub>6</sub> supplied SF<sub>5</sub> radical. However, based on the results of the spark discharge reaction of SF<sub>6</sub> with CF<sub>4</sub> or CF<sub>3</sub>Br, most attainable CF<sub>3</sub> radical donors, SF<sub>5</sub>CF<sub>3</sub> was unlikely to be formed from CF<sub>3</sub> groups attacking SF<sub>5</sub> radical directly. Otherwise, CF<sub>4</sub> and CF<sub>3</sub>Br would have formed SF<sub>5</sub>CF<sub>3</sub> on interaction with SF<sub>6</sub> under discharge condition.
- (2) It was obvious that only HFCs, CHF<sub>3</sub> in particular, could produce SF<sub>5</sub>CF<sub>3</sub> through reaction with SF<sub>6</sub> under discharge condition. The phenomenon that the amount of SF<sub>5</sub>CF<sub>3</sub> produced varied with the compound structure was explained in relation to molecular structure theory.

In the discharge volume, interaction between accelerated charged particles (i.e., electrons and ions) and other chemical species (i.e., atoms, molecules and radicals) take place simultaneously (Eliasson and Kogelschatz, 1991). There are three primary processes that have the possibility to run concurrently in discharge situation.

##### 4.1. Free radical (including active atoms) reaction

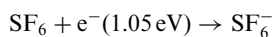
According to Sturge's speculation, the free radical reactions correspond to the following equations:



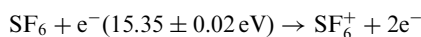
SF<sub>5</sub> and CF<sub>3</sub> radicals have strong electron affinity due to the fluorine atom, the atom possessing the strongest electronegativity (4.0 according to Pauling electronegativity) (Sharpe, 1992). The behaviors of the two radicals, however, are totally different. The trifluoromethyl radical has the priority to pyramidal configuration (Nonhebel and Walton, 1974; Endo et al., 1982), which is proportional to further reactions because fluorine atoms and carbon atom have more chances to connect with other active groups. Whereas, according to Irikura's (1995) study, when SF<sub>6</sub> loses one fluorine atom to form SF<sub>5</sub> group, its geometric structure changes from O<sub>h</sub> ( $r = 1.593$ ) to C<sub>4v</sub> ( $r_1 = 1.577, r_2 = 1.623, \theta_{12} = 91.4, \theta_{22} = 90.0$ ). This change augments the steric hindrance effect. Besides, both the sulfur atom of SF<sub>5</sub> and the carbon atom of CF<sub>3</sub> possess strong electropositivity attributing to the strong electronegativity of the fluorine atom. As a result, the intensive repulsion hinders the combination of SF<sub>5</sub> with CF<sub>3</sub>. These may be the reasons why SF<sub>5</sub>CF<sub>3</sub> has barely been formed in both the SF<sub>6</sub>–CF<sub>4</sub> and SF<sub>6</sub>–CF<sub>3</sub>Br systems.

##### 4.2. Ionization reaction

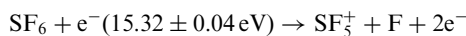
Several cations and anions may be produced from gaseous molecules losing or capturing electron in electric field. SF<sub>6</sub>, for instance, can be broken into SF<sub>6</sub><sup>-</sup>, SF<sub>6</sub><sup>+</sup>, SF<sub>5</sub><sup>+</sup>. Once attacked by electron, the SF<sub>6</sub>, CHF<sub>3</sub> and CH<sub>2</sub>F<sub>2</sub> molecules will dissociate corresponding to the following equations:



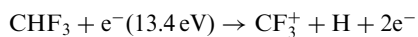
(Grimsrud et al., 1985),



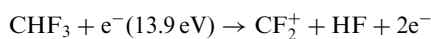
(Frost et al., 1967),



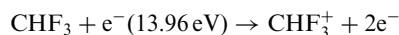
(Mitsuke et al., 1990),



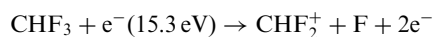
(Furuya et al., 2002),



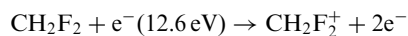
(Furuya et al., 2002),



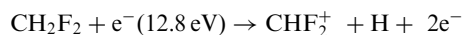
(Furuya et al., 2002),



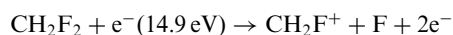
(Furuya et al., 2002),



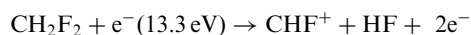
(Torres et al., 2000),



(Torres et al., 2000),



(Torres et al., 2000),



(Torres et al., 2000).

where, the values in brackets are the energies of the electrons needed in the reaction.

During spark discharge, a plasma column is formed at the center and a shock wave originates from the hot column. The shock carries away the energy from the center of the column and ionizes the gases in the core of the column. Thus, the whole discharge column can be divided into two regions: (a) plasma in thermal equilibrium ( $T > 1.0 \times 10^4 \text{ K}$ ), in which the mean electron energy was 1.3–2.6 eV; (b) plasma in nonequilibrium, in which the electron energy varies from 0 to 10 eV (Eliasson and Kogelschatz, 1991). So only  $\text{SF}_6^-$  could be formed with ease because of the low electron energy in this system. As far as the low ion concentration was concerned, the formation reactions of  $\text{SF}_5\text{CF}_3$  involving ions could be neglected in this system.

#### 4.3. Excited state molecule reaction

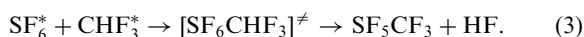
The part of the electrons at specific energy state accorded well with the Maxwell distribution function (Zhao, 1993):

$$f(\varepsilon) = 2.07(\bar{\varepsilon})^{-3/2} \cdot \varepsilon^{1/2} \exp(-1.5\varepsilon/\bar{\varepsilon}),$$

where  $f(\varepsilon)$  is the part of the electrons at specific energy state,  $\bar{\varepsilon}$  is the mean energy that the electrons in the system possess, and  $\varepsilon$  is the energy that a specific electron possesses.

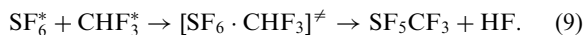
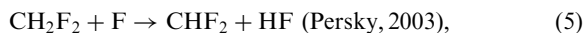
Less than 8.69% of electrons possessing energy higher than 4.34 eV (the bond energy of  $\text{CF}_2\text{H-H}$ ) could be offered as an explanation for the fact that most of the active particles existing in the system were not free

radicals but excited molecules. So, the reaction involving excited molecules was favored to produce  $\text{SF}_5\text{CF}_3$ . As for the formation of  $\text{SF}_5\text{CF}_3$  in the reactions of  $\text{SF}_6$  with  $\text{CHF}_3$  in the excited state molecules, we proposed one possible process as follows.  $\text{SF}_6^*$  and  $\text{CHF}_3^*$ , produced from  $\text{SF}_6$  and  $\text{CHF}_3$ , respectively, while capturing energy from the electrons under discharge, attached together to form the transient  $[\text{SF}_6 \cdot \text{CHF}_3]^\ddagger$ . Then,  $[\text{SF}_6 \cdot \text{CHF}_3]^\ddagger$  converted to steady  $\text{SF}_5\text{CF}_3$  molecule after eliminating HF. Once produced in the process, HF would collide with the cell wall to form  $\text{SiF}_4$ , which leads to failure detection of HF in the products. The conversion channels could be expressed as follows:



The weaker electronegativity of hydrogen atom (2.1 according to Pauling electronegativity) (Sharpe, 1992) than that of fluorine atom leads to a longer bond length of C–H than that of C–F. Thus, when at excited state,  $\text{CHF}_3^*$  will attack  $\text{SF}_6^*$  to form the transient  $[\text{SF}_6 \cdot \text{CHF}_3]^\ddagger$  and then convert to a stable  $\text{SF}_5\text{CF}_3$  molecule via elimination of HF with respect to the relative low bond energy of C–H in  $\text{CHF}_3$  molecule (Okamoto and Tomonari, 2000).

The production mechanism of  $\text{SF}_5\text{CF}_3$  in the reaction system of  $\text{SF}_6$  and  $\text{CH}_2\text{F}_2$  was rather complicated in contrast with that of  $\text{SF}_6$  with  $\text{CHF}_3$ . Firstly,  $\text{CH}_2\text{F}_2$  should be converted to  $\text{CHF}_3$ . Then,  $\text{CHF}_3$  reacted with  $\text{SF}_6$  to form  $\text{SF}_5\text{CF}_3$  following the same process mentioned above. The conversion channels were supposed to be consistent with the following mechanism:



The existence of reactions (4)–(6) was the reason for the visible yield decrease of  $\text{SF}_5\text{CF}_3$  in the reaction of  $\text{CH}_2\text{F}_2$  with  $\text{SF}_6$  compared with the reaction of  $\text{CHF}_3$  with  $\text{SF}_6$ . As far as the dissociation of certain  $\text{SF}_6$  into F was concerned, it was reasonable that the maximum yield of  $\text{SF}_5\text{CF}_3$  was achieved when the ratio of  $\text{CH}_2\text{F}_2$  to  $\text{SF}_6$  was 1:3. Only with the aid of fluorine atom produced from  $\text{SF}_6$  attached by high-energy electrons can  $\text{CH}_2\text{F}_2$  be converted to  $\text{CHF}_3$  successfully. Thus,

raising the mean electron energy increased the yield of SF<sub>5</sub>CF<sub>3</sub> in the SF<sub>6</sub>–CH<sub>2</sub>F<sub>2</sub> system to some extent, verifying that SF<sub>5</sub>CF<sub>3</sub> could be produced via the efficiency conversion of CH<sub>2</sub>F<sub>2</sub> to CHF<sub>3</sub> by interacting with fluorine atom.

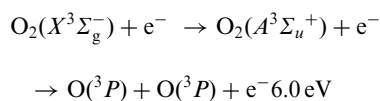
In both SF<sub>6</sub>–CHF<sub>3</sub> and SF<sub>6</sub>–CH<sub>2</sub>F<sub>2</sub> systems, the process of loss of HF is the key step in producing the SF<sub>5</sub>CF<sub>3</sub> molecule.

In brief, we could arrive at the conclusion that each of the reactions mentioned above may contribute to the formation of SF<sub>5</sub>CF<sub>3</sub>, but the reactions among excited molecules may play a key role to the production of SF<sub>5</sub>CF<sub>3</sub>.

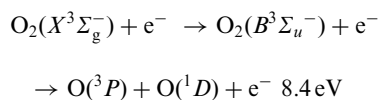
## 5. Atmospheric implications

### 5.1. The influence of air and water on the production of SF<sub>5</sub>CF<sub>3</sub>

Due to the impurity of SF<sub>6</sub>, air and water are common gases participating in real high-voltage equipment. We also studied the formation of SF<sub>5</sub>CF<sub>3</sub> in the SF<sub>6</sub>–CHF<sub>3</sub> and SF<sub>6</sub>–CH<sub>2</sub>F<sub>2</sub> systems under discharge in the presence of air and water. The addition of air definitely led to, both in SF<sub>6</sub>–CHF<sub>3</sub> and SF<sub>6</sub>–CH<sub>2</sub>F<sub>2</sub> systems, a lower production of SF<sub>5</sub>CF<sub>3</sub>, as shown in Figs. 6d and 7d. The influence of air on the yield of SF<sub>5</sub>CF<sub>3</sub> was realized by means of its major compositions, nitrogen and oxygen. Combination of excited molecules to form SF<sub>5</sub>CF<sub>3</sub> in reactant mixtures would be therefore diminished when SF<sub>6</sub> and CHF<sub>3</sub>/CH<sub>2</sub>F<sub>2</sub> were diluted by air. Because the bond energy of N<sub>2</sub> was 9.764 eV (Gaydon, 1950), rare N<sub>2</sub> could happen to dissociate when attacked by electrons, the mean energy of which varied from 0 to 10 eV. Most of N<sub>2</sub> would act simply as a quencher of excited state molecules. On the other hand, oxygen was a diatomic molecule with bond energy of 5.1 eV and could be excited, dissociated or ionized when attacked by electrons:



(Eliasson and Kogelschatz, 1991),



(Eliasson and Kogelschatz, 1991).

The atomic oxygen produced could react with the decomposition fragment of SF<sub>6</sub> under discharge condition, which was proved by the occurrence of SOF<sub>2</sub>,

SO<sub>2</sub>F<sub>2</sub> and COF<sub>2</sub> in the products. So the possibility of the interaction between SF<sub>6</sub> and CHF<sub>3</sub>/CH<sub>2</sub>F<sub>2</sub> became less. This was an explanation for the fact that the presence of air in SF<sub>6</sub>–CHF<sub>3</sub> and SF<sub>6</sub>–CH<sub>2</sub>F<sub>2</sub> systems decreased the productive level of SF<sub>5</sub>CF<sub>3</sub>. The SF<sub>5</sub>CF<sub>3</sub> produced was 16.83 Pa when relative humidity was 0% and 20.11 Pa when relative humidity was 2.0%, respectively, in SF<sub>6</sub>–CHF<sub>3</sub> system. The increased production of SF<sub>5</sub>CF<sub>3</sub> with relative humidity might be due to the H–OH bond of H<sub>2</sub>O molecule whose bond energy was 5.1 eV attacked by high-energy electrons to produce H atom, which accelerated the decomposition of SF<sub>6</sub> by dehydrofluorine reaction.

### 5.2. Atmospheric implication and strategies

The main results obtained on the spark-induced formation of SF<sub>5</sub>CF<sub>3</sub> can be summarized as follows: SF<sub>5</sub>CF<sub>3</sub> is unlikely to be produced from the reaction of SF<sub>6</sub> with perfluorinated carbon compounds (PFCs) but from the reaction of SF<sub>6</sub> with HFCs under discharge. Despite the fact that the power supply was a little lower and unable to simulate the real condition in high-voltage equipment, the mechanism of the reactions under spark discharge is basically the same. If HFCs can be produced from the solid insulator under discharge, the formation in high-voltage discharges can be one promising source of SF<sub>5</sub>CF<sub>3</sub> in the atmosphere when the large amount of SF<sub>6</sub> consumed in high-voltage equipment is considered. The remarkable result in this work has reduced the possible approaches to form SF<sub>5</sub>CF<sub>3</sub> and made its control possible.

Global warming is one of the most serious environmental issues under discussion. The 100-year mass-normalized global warming potential of SF<sub>5</sub>CF<sub>3</sub>, relative to CO<sub>2</sub> is 19,000. The contribution of SF<sub>5</sub>CF<sub>3</sub> to global warming is rather small at the current concentration nevertheless its impact would become more significant in the future at its fast growing rate, equivalent to 0.008 ppt year<sup>-1</sup> (Sturges et al., 2000). Leaving the definite source of SF<sub>5</sub>CF<sub>3</sub> unknown, any policy designed for decreasing its emission can mean nothing and the burden of reducing it would absolutely rely on its natural elimination processes, such as lightning, ionization and so on.

Once emitted into the atmosphere, SF<sub>5</sub>CF<sub>3</sub> would be removed exceedingly slowly in the order of 1000 year (Chim et al., 2003; Miller et al., 2002). SF<sub>6</sub> is an extremely stable gas with unique physical and chemical characteristics such as inert, nontoxic and nonflammable, which make it ideal for gas-insulated equipment. HFCs are considered as appropriate candidates to substitute the chlorofluorocarbons (CFCs), which were once widely used as solvents, refrigerants, foaming agents and propellants and phased out for their

significant impact on stratospheric ozone depletion and global climate. The fact that SF<sub>5</sub>CF<sub>3</sub> might originate from the reaction of SF<sub>6</sub> with HFCs highlights our attention on the melioration of high-voltage equipment. Since SF<sub>6</sub> is one kind of potent greenhouse gases, it is time to seek substitutes for it in high-voltage equipment. Before the ideal substitutes are found, we set up these ways to restrain the formation of SF<sub>5</sub>CF<sub>3</sub>:

- (1) Whenever technically possible, use SF<sub>6</sub> with low-risk gases such as N<sub>2</sub> and other inert gases to lower the amount of SF<sub>6</sub> consumed.
- (2) Avoid the use of solid insulators (such as fluoropolymers), which might provide HFCs under discharge in high-voltage equipment to go against the formation of SF<sub>5</sub>CF<sub>3</sub>.
- (3) Try to purify SF<sub>6</sub> and CF<sub>4</sub> in the production process to avoid the presence of HFCs in high-voltage equipment.

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