

# Comparative Study of Degradation of *trans*-1,3,3,3-Trifluoropropene, 2,3,3,3-Tetrafluoropropene, Perfluoro-3-methylbutanone-2, and Sulfur Hexafluoride in Dielectric-Barrier Discharge

A. V. Tatarinov<sup>a</sup>, I. V. Bilera<sup>a</sup>, V. A. Shakhmatov<sup>a</sup>, S. V. Avtaeva<sup>b</sup>, P. V. Solomakhin<sup>c</sup>, R. Maladen<sup>d</sup>, C. Prévé<sup>d</sup>, and D. Piccoz<sup>e</sup>

<sup>a</sup> Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,  
Leninskii pr. 29, Moscow, 119991 Russia

e-mail: atat@ips.ac.ru

<sup>b</sup> Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia

<sup>c</sup> ZAO Schneider Electric, ul. Dvintsev 12-1, Moscow, 127018 Russia

<sup>d</sup> Schneider Electric Industries SAS, ZAC Champ St Ange, 38760, Varcès Allières et Risset, France

<sup>e</sup> Schneider Electric Industries SAS, Boulevard de la Résistance, BP 84019, Mâcon Cedex 9, France

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**Abstract**—Degradation of gaseous dielectrics after aging in barrier discharge has been experimentally studied and comparative analysis of their properties has been performed. The gases used as gaseous dielectrics have been *trans*-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)), 2,3,3,3-tetrafluoropropene (HFO-1234yf), perfluoro-3-methylbutanone-2  $\text{CF}_3\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ , and sulfur hexafluoride  $\text{SF}_6$ . The product composition of gas degradation before and after 5-h aging in the barrier discharge has been determined by gas chromatography–mass spectrometry and gas chromatography. According to the measurement data, 2,3,3,3-tetrafluoropropene is less prone to degradation and has the highest dielectric strength among the test carbon-containing gases.

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Sulfur hexafluoride  $\text{SF}_6$  is widely used in industry and research [1]. In particular, it is used as a gaseous insulator in high-voltage switches of various types. Although  $\text{SF}_6$  is one of the best gases in dielectric strength, a high voltage inevitably gives rise to partial discharges, which gradually lead to degradation of the gas and the occurrence of degradation products [2, 3]. Sulfur hexafluoride itself is nontoxic, but all the products of its electrical and thermal degradation including those in the presence of other molecules (such as  $\text{H}_2\text{O}$ ,  $\text{N}_2$ , air) are toxic and corrosive [1, 4]. The most toxic products found are  $\text{S}_2\text{F}_{10}$ ,  $\text{SF}_4$ ,  $\text{SO}_2\text{F}_2$ ,  $\text{SOF}_2$ ,  $\text{SOF}_4$ ,  $\text{S}_2\text{OF}_{10}$ ,  $\text{S}_2\text{O}_2\text{F}_{10}$  [2, 3],  $\text{F}_2$ , and HF [5]. This is a disadvantage, since damage of a high-voltage switch results in a release of these gases into the environment, causing its pollution by components hazardous to life.

It is also known that  $\text{SF}_6$  is one of the most dangerous greenhouse gases, its global warming potential for 100 years is  $\text{GWP}_{100} = 23900$  at atmospheric lifetime of 3200 years [6]. Greenhouse gas emissions are regulated by international agreements [7], and  $\text{SF}_6$  substitutes are being actively sought for now.

Currently, the most promising candidates that are acceptable from the environmental point of view

include commercially available hydrofluoroolefins (HFO), in particular, fluorinated propylenes (such as 2,3,3,3-tetrafluoropropene and *trans*-1,3,3,3-tetrafluoropropene) [8, 9]. Hydrofluoroolefins are used as refrigerants, propellants, etc. [9].

The second class of chemicals that meet environmental requirements is perfluoroketones ( $\text{C}_n\text{K}$ , where  $n$  is the number of carbon atoms in the molecule). Perfluoro-4-methylpentanone-3 is proposed for use as a flame retardant [10]. Its homologue perfluoro-3-methylbutanone-2 (abbreviated as C5K) is nontoxic and has low values of  $\text{GWP}_{100} = 1$  and ozone depletion potential  $\text{ODP} = 0$ . However, since the boiling point of C5K is as high as  $24^\circ\text{C}$ , its use as a dielectric gas is possible only in a mixture with  $\text{N}_2$  or  $\text{CO}_2$ . When a partial discharge is initiated in the insulating medium of high-voltage switches, high-frequency current pulses with a nanosecond to microsecond duration occur, aperiodically disappearing and appearing again. Revealing the effect of quite rare partial discharges on the properties of the gas takes months of continuous operation. To speed up the research process, gas-filled devices with different electrode configurations, but with the same characteristic electrical fields can be used. In the inter-

electrode gap of the gas-filled working chamber of dielectric barrier discharge (DBD), streamer microdischarges arise, having a structure and physical properties similar to those of partial corona discharges in high-voltage switches. Since a DBD streamer locally charges the anode insulator and thus locally reduces the electric field at breakdown, the new streamer cannot be generated between the same points on the cathode and anode surface. The streamers "run" in the interelectrode gap, uniformly penetrating the entire working volume of the gas [11]. This phenomenon gives a considerable gain in gas aging time compared with aging in high-voltage switches, in which the discharges break down the gas only in the vicinity of the electrodes and are unevenly distributed over the space of the working chamber.

In this study, we investigated the degradation of *trans*-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)), 2,3,3,3-tetrafluoropropene (HFO-1234yf), and perfluoro-3-methylbutanone-2 in a dielectric-barrier discharge in comparison to that of SF<sub>6</sub>.

## EXPERIMENTAL

The DBD setup consisted of three blocks: the gas-vacuum system designed for prevacuation, admission of a test gas, and sampling after the test; the DBD working chamber; and an electric unit including the power supply and the measuring section. The working chamber was a glass tube (outer diameter, 19 mm; inner diameter, 15.9 mm) with a cylindrical steel electrode (13.5 mm in diameter and 350 mm in length) inside. The outer electrode was a fine-mesh brass net bearing against the outer surface of the tube. Microdischarges occurred in the space between the tube and the steel electrode surface. The end faces of the glass tube accommodated connections to a pumping line, a gas admission valve, and a pressure gauge. The glass tube simultaneously served as a dielectric barrier and made a closed space to be filled with a test gas.

After evacuating the discharge chamber to  $\sim 10^{-3}$  atm, a test gas was introduced into it. The working pressure was 1 atm. The discharge tube was connected in series with a measuring capacitor  $C_I$ . Alternating voltage was applied across the high-voltage electrode of the discharge tube and the ground  $C_I$  capacitor plate. The capacitance of  $C_I$  (180 nF) was chosen to be much higher than that of the entire electrode system of the discharge chamber (96 pF), so voltage  $U_I$  on capacitor  $C_I$  was negligible as compared with the voltage drop across the discharge tube [12]. The voltage on the high-voltage electrode was supplied from the high-voltage winding of a power transformer during the entire test-gas aging time. The amplitude of the voltage was controlled with a laboratory autotransformer that set the voltage on the primary winding of the transformer.

The power absorbed by DBD in each test was determined using voltage-charge Lissajous figures. Being proportional to the discharge current, the voltage on capacitor  $C_I$  was recorded at the X input of a GW Instek GDS-71102 oscilloscope. The DBD voltage was measured using a capacitive voltage divider  $C_1-C_2$  (33 nF-33 pF) connected in parallel to the discharge  $C_I$  portion of the circuit. The signal is taken from the midpoint of the divider and is sent to the Y input of the oscilloscope. The power absorbed by the DBD during the feed signal time was determined by measuring the area of the resulting Lissajous figure [12, 13].

Each of the test gases was aged for 5 h with three applied voltages of 2, 6, and 10 kV. The frequency of applied voltage was 50 Hz.

After aging, the gas from the working chamber was sampled using Tedlar bags and gas-tight Hamilton syringes.

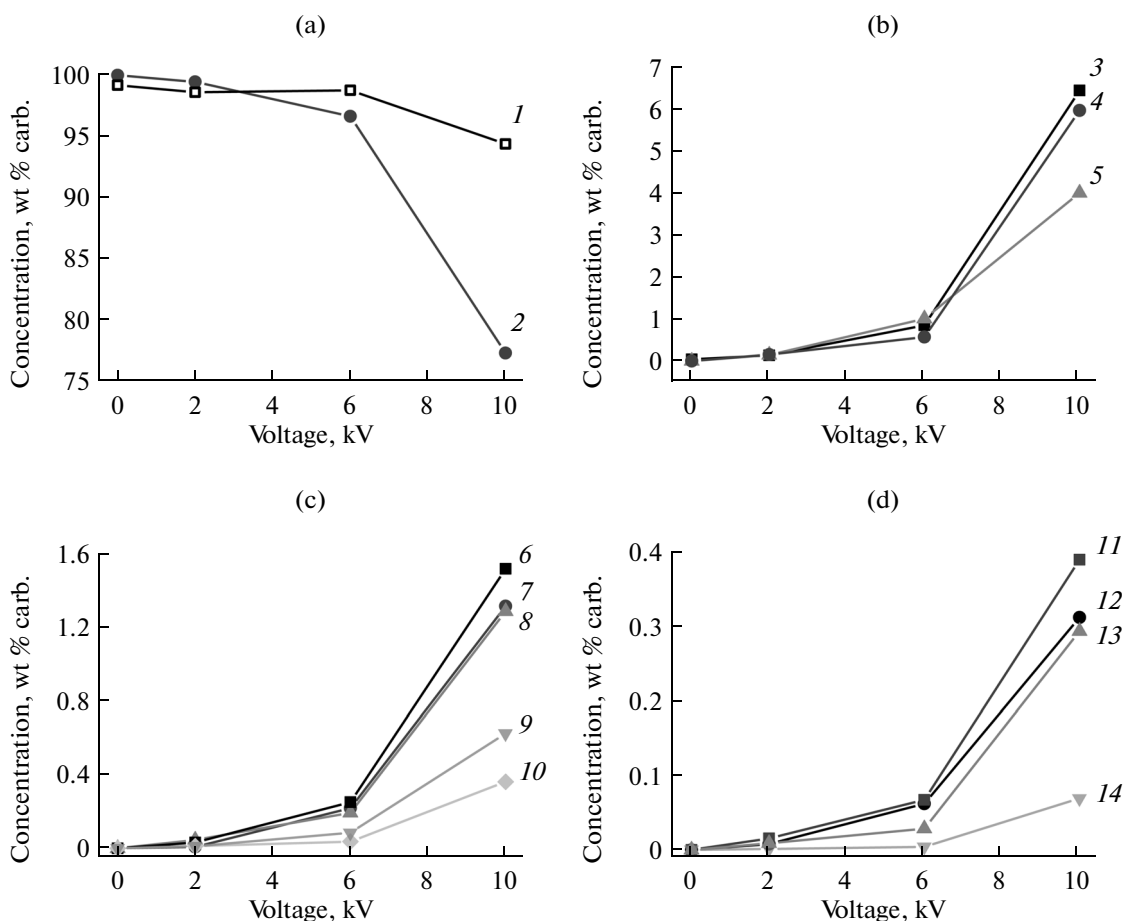
The chemicals used in the study were *trans*-1,3,3,3-tetrafluoropropene (*trans*-CF<sub>3</sub>CH=CHF) (of 99.96% purity), 2,3,3,3-tetrafluoropropene (CF<sub>3</sub>CF=CH<sub>2</sub>) (99.0%), perfluoro-3-methylbutanone-2 (CF<sub>3</sub>C(O)CF(CF<sub>3</sub>)<sub>2</sub>) (98.7%), and SF<sub>6</sub> (99.9%).

Analyses were performed on a Chrompack CP9000 gas chromatograph. Fluorinated organic compounds were separated on a CP-PoraBOND Q 25 m × 0.53 mm capillary column using a flame ionization detector. The composition of the reactant gases and the products of discharge in SF<sub>6</sub> were determined using a thermal conductivity detector (HayeSep Q 80/100 packed column, 3 m × 2 mm). The permanent gases H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, and CO<sub>2</sub> were separated on a 3 m × 2 mm CarboSieve S-II 80/100 column.

Gas sample components were identified by gas chromatography-mass spectrometry (GC-MS). In operation with fluoroolefins, a Shimadzu analytical instrument (two-dimensional chromatograph) was used. The sample was sequentially separated on Poraplot Q and Supercowax-10 columns and detected in a mass spectrometer. The products of discharge in SF<sub>6</sub> were determined on a Agilent 6890N instrument with a quadrupole mass spectrometer, using a 10 m × 0.53 mm poly(trimethylsilylpropyne)-coated analytical column (made at the Topchiev Institute [14]).

## RESULTS AND DISCUSSION

Prior to aging in DBD, the composition of the starting materials was examined. The main impurity in *trans*-CF<sub>3</sub>CH=CHF was its *cis*-isomer ( $\sim 0.04$  wt %), and the amount of other components was at the level of 0.001 wt %. Impurities in CF<sub>3</sub>CF=CH<sub>2</sub> were C<sub>2</sub>F<sub>4</sub> (0.17 wt %), trifluoromethylacetylene CF<sub>3</sub>C≡CH (0.004 wt %), pentafluoropropane CF<sub>3</sub>CF<sub>2</sub>CH<sub>3</sub> (0.72 wt %), and an unidentified component (0.10 wt %).



**Fig. 1.** Products of *trans*-CF<sub>3</sub>CH=CHF degradation by aging in DBD at different voltages on the electrodes: (a) residual amounts of (1) *trans*-CF<sub>3</sub>CH=CHF and (2) CF<sub>3</sub>CF=CH<sub>2</sub> (given for comparison); (b) (3) *cis*-CF<sub>3</sub>CH=CHF, (4) unidentified products, (5) CF<sub>3</sub>C≡CH; (c) (6) C<sub>2</sub>F<sub>4</sub>, (7) CF<sub>4</sub>, (8) C<sub>2</sub>F<sub>6</sub>, (9) CF<sub>3</sub>CF=CH<sub>2</sub>, (10) C<sub>2</sub>HF<sub>5</sub>; and (d) (11) CF<sub>2</sub>=CHF, (12) CF<sub>2</sub>=CH<sub>2</sub>, (13) C<sub>3</sub>F<sub>8</sub>, (14) C<sub>3</sub>F<sub>6</sub>.

During aging in DBD, fluoroolefins undergo degradation and condensation and gaseous products and polymer films are built up. The main gaseous products of *trans*-CF<sub>3</sub>CH=CHF degradation under these conditions are the olefin isomer *cis*-CF<sub>3</sub>CH=CHF and trifluoromethylacetylene CF<sub>3</sub>C≡CH (Fig. 1b). All quantities in Figs. 1–3 are given in weight percent based on only one element carbon (wt % carb.). The main gaseous products of the CF<sub>3</sub>CF=CH<sub>2</sub> decomposition in DBD are *trans*-CF<sub>3</sub>CH=CHF and CF<sub>3</sub>C≡CH (Fig. 2).

According to the analysis data, the yield of *trans*-CF<sub>3</sub>CH=CHF and CF<sub>3</sub>CF=CH<sub>2</sub> degradation products significantly increases with an increase in voltage across the DBD electrodes from 2 to 6 and further to 10 kV. The only exception is the formation of *cyclo*-C<sub>4</sub>F<sub>8</sub> at *U* = 2 kV for CF<sub>3</sub>CF=CH<sub>2</sub>. At a voltage of 10 kV, the number of products is significantly greater, with the decay and destruction processes to form the perfluoroalkanes CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>F<sub>8</sub>; tetrafluoroethylene C<sub>2</sub>F<sub>4</sub>; and other fluoroolefins becoming more intense. According to the results of GC–MS analysis

in the selected ion monitoring (SIM) mode, there was no perfluoroisobutene in the products of both test gases.

Determining on the CarboSieve S-II chromatographic column the products of degradation of both of the initial hydrofluoroolefins under severe conditions (*U* = 10 kV), we found that they contained H<sub>2</sub> (~0.5 vol %), CO (~1.7 vol %), and CO<sub>2</sub> (0.7–0.8 vol %).

During the aging of both hydrofluoroolefins, a pressure drop in the reactor by ~250 torr was detected. The pressure dropped proportionally to the time. This behavior is obviously due to film deposition on the inner surfaces of the reactor. The formation of fluorocarbon films from fluorinated compounds with a high C/F ratio during gas-phase etching is known from the literature [6].

Elemental analysis of samples of the films deposited during *trans*-CF<sub>3</sub>CH=CHF degradation in DBD was performed using the dynamic flash combustion method involving the subsequent gas chromatographic

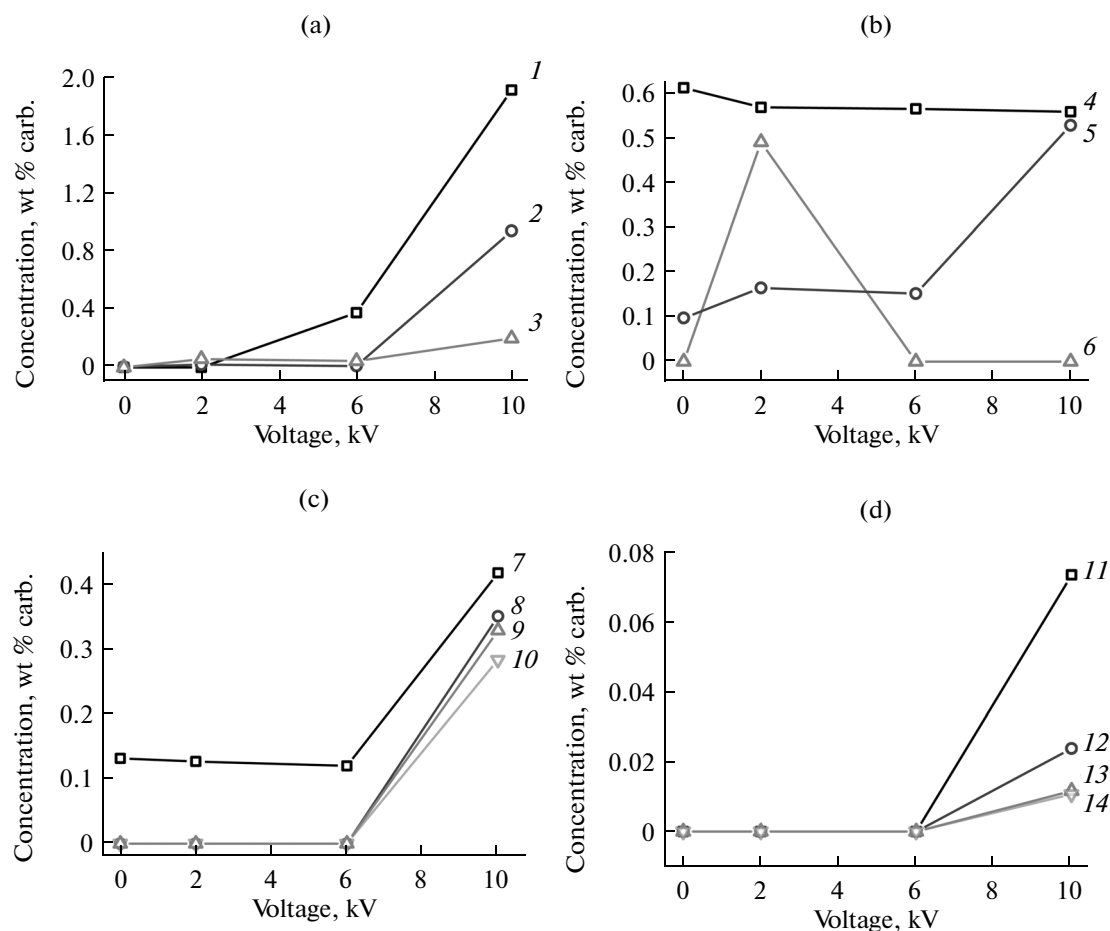


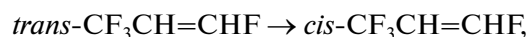
Fig. 2. Products of  $\text{CF}_3\text{CF}=\text{CH}_2$  degradation by aging in DBD at different voltages on the electrodes: (a) (1)  $\text{trans-CF}_3\text{CH}=\text{CHF}$ , (2)  $\text{CF}_3\text{C}=\text{CH}$ , (3)  $\text{cis-CF}_3\text{CH}=\text{CHF}$ ; (b) (4)  $\text{CF}_3\text{CF}_2\text{CH}_3$ , (5) unidentified products, (6)  $\text{cyclo-C}_4\text{F}_8$ ; (c) (7)  $\text{C}_2\text{F}_4$ , (8)  $\text{CF}_4$ , (9)  $\text{CF}_2=\text{CH}_2$ , (10)  $\text{C}_2\text{F}_6$ ; and (d) (11)  $\text{CF}_2=\text{CHF}$ , (12)  $\text{C}_3\text{F}_8$ , (13)  $\text{C}_2\text{HF}_5$ , (14)  $\text{C}_3\text{F}_6$ .

determination. The results of the study are presented in Table 1. It is seen that analytically undetectable elements make about 60%. Assuming that they are mainly represented by fluorine, the chemical element that is part of the starting hydrofluoroolefin, we find that the film has the  $\text{C}_2\text{HF}_2$  composition. Such a composition suggests the presence of two types of carbon structures in the polymer, the chain ( $\text{CX}_2-\text{CX}_2$ ) or ( $\text{CX}_2-\text{CX}(\text{CX}_3)$ ) structure and the planar ( $\text{CX}=\text{CX}$ ) structure in approximately equal amounts, where  $\text{X} = \text{H}$  or  $\text{F}$ .

The data in Fig. 1a show that at voltages of 6 and 10 kV, the residual amount of  $\text{trans-CF}_3\text{CH}=\text{CHF}$  is noticeably smaller than that of  $\text{CF}_3\text{CF}=\text{CH}_2$ . At the

same drop in pressure of the starting hydrofluoroolefin in the reactor, this means that the degree of conversion of  $\text{trans-CF}_3\text{CH}=\text{CHF}$  is higher under comparable conditions.

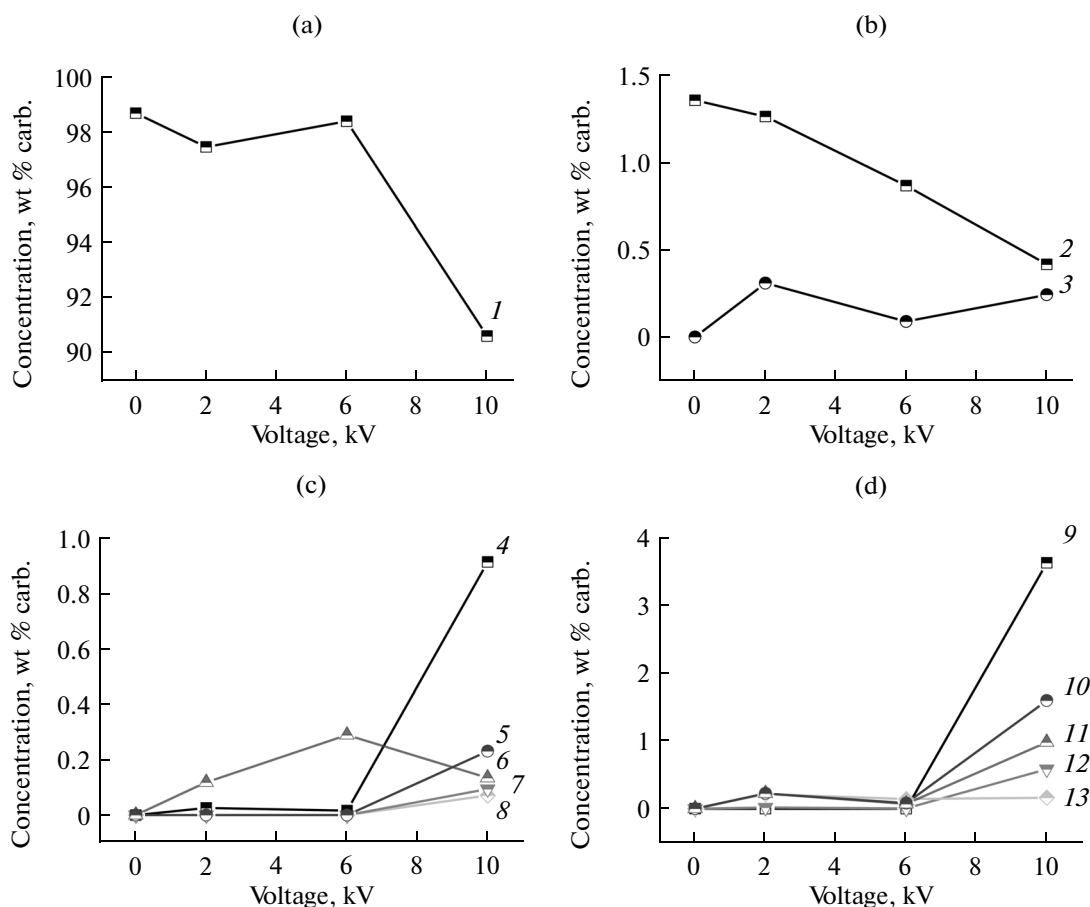
The main channels of  $\text{trans-CF}_3\text{CH}=\text{CHF}$  conversion in a barrier discharge is isomerization to  $\text{cis-CF}_3\text{CH}=\text{CHF}$  and 1,2-dehydrofluorination:



It is known that the geometric isomerization of hydrofluoroolefins occurs at a high rate; for example, the pre-exponential factor of the rate constant for the  $\text{trans-cis}$  isomerization of 1,2-difluoroethylene

Table 1. Results of elemental analysis of the polymer produced in DBD treatment of HFO-1234ze(E)

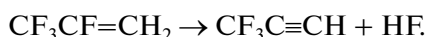
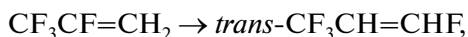
Sample name	Element determined and measurement units			
	Nitrogen, %	Carbon, %	Hydrogen, %	Sulfur, %
Condensate from discharge	0.11	38.9	1.58	0.60



**Fig. 3.** Products of C5K degradation by aging in DBD at different voltages on the electrodes: (a) (1) C5K; (b) (2) CF<sub>3</sub>COOCH<sub>3</sub>, (3) CF<sub>3</sub>COOCF<sub>3</sub>; (c) (4) C<sub>3</sub>F<sub>6</sub>, (5) C<sub>3</sub>F<sub>8</sub>, (6) CF<sub>2</sub>=CF-CHF<sub>2</sub>, (7) C<sub>2</sub>F<sub>6</sub>, (8) CF<sub>4</sub>; and (d) (9, 12) C<sub>4</sub>F<sub>10</sub>, (10, 11) C<sub>6</sub>F<sub>14</sub>, (12) C<sub>4</sub>HF<sub>5</sub>, (13) C<sub>5</sub>F<sub>12</sub>.

CHF=CHF is  $\log A = 12.98$  and the activation energy is  $E_a = 60.1$  kcal/mol [15].

In contrast to *trans*-CF<sub>3</sub>CH=CHF, geometric isomerism is not inherent in CF<sub>3</sub>CF=CH<sub>2</sub> and, hence, there is no *trans*-*cis* isomerization reaction, a property that is beneficial to the stability of the molecule (Fig. 1a). The main channels of CF<sub>3</sub>CF=CH<sub>2</sub> conversion in barrier discharge are isomerization into *trans*-CF<sub>3</sub>CH=CHF and 1,2-dehydrofluorination:



The 1,2-dehydrofluorination of fluoroolefins (fluoroethylene and 1,1-difluoroethylene) typically requires approximately 80 kcal/mol [16–19]. The dehydrofluorination of either hydrofluoroolefin results in the formation of one HF molecule per molecule of trifluoroacetylene CF<sub>3</sub>C=CH. Using IR spectrometry, we failed to detect HF traces in the hydrofluoroolefin degradation products. Most likely, HF had reacted with the glass walls of the discharge tube or the IR optical cell as early as the aging process in DBD or gas sampling, respectively. The interaction

of HF with trifluoroacetylene would give different hydrofluoroolefins. For example, the DBD in CF<sub>3</sub>CF=CH<sub>2</sub> will result in both CF<sub>3</sub>CH=CHF isomers (*trans*- and *cis*- in a 9–10/1 ratio).

In the case of aging of hydrofluoroolefins in DBD under severe conditions, carbon oxides CO and CO<sub>2</sub> were detected in the product mixture. The oxygen required for their formation could be produced in the discharge by reacting HF with the glass walls of the barrier discharge tube.

Initial perfluoro-3-methylbutanone-2 (C5K) contained methyl trifluoroacetate CF<sub>3</sub>COOCH<sub>3</sub> (~1.3 wt %) and a very small amount of water vapor H<sub>2</sub>O (~0.05 wt %) as impurities.

According to the analysis data, the main products of the process are hexafluoropropene C<sub>3</sub>F<sub>6</sub>, 1,1,2,3,3-pentafluoropropene CF<sub>2</sub>=CF-CHF<sub>2</sub>, perfluorobutane C<sub>4</sub>F<sub>10</sub>, and perfluoro(methyl acetate) CF<sub>3</sub>COOCF<sub>3</sub> (Fig. 3).

The pressure drop in the working chamber at an applied voltage of 6 or 10 kV was a few torr, which is considerably lower than in the case of hydrofluoroole-

**Table 2.** Results of GC and GC--MS analysis of toxic degradation products of test gases (vol. %)

Mixture after aging in DBD	Voltage across DBD electrodes		
	2 kV	6 kV	10 kV
HFO-1234ze(E)			CO (1.68), C <sub>3</sub> F <sub>6</sub> (0.02), CF <sub>3</sub> CCH (0.86)
HFO-1234yf			CO (1.73), C <sub>3</sub> F <sub>6</sub> (0.11), CF <sub>3</sub> CCH (2.58)
C5K	C <sub>3</sub> F <sub>6</sub> (0.03)	C <sub>3</sub> F <sub>6</sub> (0.01)	C <sub>3</sub> F <sub>6</sub> (0.89), CO (4.96)
SF <sub>6</sub>		S <sub>2</sub> F <sub>10</sub> +S <sub>2</sub> OF <sub>10</sub> (1.7)	SF <sub>4</sub> (0.07), S <sub>2</sub> F <sub>10</sub> + S <sub>2</sub> OF <sub>10</sub> (21.2)

**Table 3.** Degradation products of SF<sub>6</sub> after aging in DBD at different voltages on the electrodes

U, kV	O <sub>2</sub> /N <sub>2</sub> /Ar/CO	SF <sub>4</sub>	CO <sub>2</sub>	SF <sub>6</sub> + SO <sub>2</sub> F <sub>2</sub>	S <sub>2</sub> F <sub>10</sub> + S <sub>2</sub> OF <sub>10</sub>	H <sub>2</sub> O	Unidentified product	Total
0	0.05	0.00	0.00	99.94	0.00	0.014	0.00	100.00
6	0.05	0.00	0.04	96.89	2.88	0.14	0.00	100.00
10	0.05	0.05	0.39	66.17	32.9	0.33	0.10	100.00

ins. Nonetheless, there was also film deposition on the electrode and the glass tube.

The initial sample of sulfur hexafluoride SF<sub>6</sub> (99.986 wt %) contained a small amount of water vapor H<sub>2</sub>O (0.014 wt %). According to GC--MS data, there were no impurities in SF<sub>6</sub>, other than water vapor.

The barrier discharge in SF<sub>6</sub> is ignited at 3.7 kV. Table 3 shows changes in the product composition of the test gas before and after testing at voltages of 6 and 10 kV. Note that the proportion of oxygen-containing compounds, such as CO<sub>2</sub> and H<sub>2</sub>O, increases.

Toxicity of the mixtures after aging in DBD is an important issue in the assessment of the properties of the test gases. The chemical analysis of the degradation products of the test gases showed that the C5K ketone degradation products contain the toxic component C<sub>3</sub>F<sub>6</sub> even at a voltage of 2 kV. At 10 kV, the amount of CO in the degradation products of this gas is three times that in the degradation products of the olefins (Table 2). This difference is obviously due to the fact that oxygen is not inherently a part of the olefins, but it is the product of HF reaction with glass of the discharge tube. However, a significant amount of CF<sub>3</sub>C≡CH was found in the olefins after DBD treatment at 10 kV and, therefore, the hydrofluoroolefins HFO-1234yf and HFO-1234ze(E) cannot be recommended as a gas dielectric at high operating voltages. The toxic components in sulfur hexafluoride SF<sub>6</sub> were found to appear after DBD treatment at voltages of 6 and 10 kV.

Absorbed discharge power in the DBD of a test gas characterizes the dielectric strength of the gas. The higher the absorbed power, the easier the breakdown at a given applied voltage and the lower the dielectric strength of the gas. As can be seen from Table 4, sulfur

**Table 4.** Power absorbed by DBD in test gases at different aging voltages

Reactant	DBD-absorbed power, W		
	U = 2 kV	U = 6 kV	U = 10 kV
HFO-1234ze	0.03	0.7	2
HFO-1234yf	0.01	0.2	0.6
C5K	0.02	0.5	3
SF <sub>6</sub>	—	0.01	0.08

hexafluoride SF<sub>6</sub> has the best dielectric strength. 2,3,3,3-tetrafluoropropene HFO-1234yf is two to three times stronger than perfluoro-3-methylbutanone-2, and C5K is three to four times stronger than *trans*-1,3,3,3-tetrafluoropropene HFO-1234ze(E).

## REFERENCES

1. Tsai, W.T., *J. Fluorine Chem.*, 2007, vol. 128, no. 11, p. 1345.
2. Pradayrol, C., Casanovas, A.M., Hernoune, A., and Casanovas, J., *J. Phys. D: Appl. Phys.*, 1996, vol. 29, no 7, p. 1941.
3. Pradayrol, C., Casanovas, A.M., Aventin, C., and Casanovas, J., *J. Phys. D: Appl. Phys.*, 1997, vol. 30, no. 9, p. 1356.
4. Wang, Y.F., Shih, M., Tsai, C.H., and Tsai, P.J., *Chemosphere*, 2006, vol. 62, no. 10, p. 1681.
5. Tsai, C.H. and Shao, J.M., *J. Hazard. Mater.*, 2008, vol. 157, no. 1, p. 201.
6. Chang, M.B. and Chang, J.S., *Ind. Eng. Chem. Res.*, 2006, vol. 45, no. 12, p. 4101.
7. Hodnebrog, O., Etminan, M., Fuglestedt, J.S., Marston, G., Myhre, G., Nielsen, C.J., Shine, K.P., and

- Wallington, T.J., *Rev. Geophys.*, 2013, vol. 51, no. 2, p. 300.
8. Brown, J.S., *ASHRAE J*, 2008, vol. 51, no. 8, p. 22.
9. Wallington, T.J., Sulbaek Andersen, M.P., and Nielsen, O.J., *Chemosphere*, 2015, vol. 129, p. 135, doi:10.1016/j.chemosphere.2014.06.092
10. Taniguchi, N., Wallington, T.J., Hurley, M.D., Guschin, A.G., Molina, L.T., and Molina, M.J., *J. Phys. Chem. A*, 2003, vol. 107, no. 15, p. 2674.
11. Kogelschatz, U., Eliasson, B., and Egli, W., *J. Phys. IV*, 1997, vol. 7, no. C4, p. 47.
12. Pekárek, S., *J. Phys. D: Appl. Phys.*, 2012, vol. 45, no. 7, p. 075201.
13. Kogelschatz, U., *Plasma Chem. Plasma Process.*, 2003, vol. 23, no. 1, p. 1.
14. Berezkin, V.G., Korolev, A.A., and Khotimskii, V.S., *Dokl. Phys. Chem.*, 2000, vol. 370, nos. 1–3, p. 1.
15. Jeffers, P.M. and Shaub, W., *J. Am. Chem. Soc.*, 1969, vol. 91, no. 27, p. 7706.
16. Cadman, P. and Engelbrecht, W.J., *Chem. Commun.*, 1970, no. 7, p. 453.
17. Simmie, J.M., Quiring, W.J., and Tschuikow-Roux, E., *J. Phys. Chem.*, 1970, vol. 74, no. 5, p. 992.
18. Simmie, J.M. and Tschuikow-Roux, E., *Chem. Commun.*, 1970, no. 12, p. 773.
19. Simmie, J.M. and Tschuikow-Roux, E., *J. Phys. Chem.*, 1970, vol. 74, no. 23, p. 4075.

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