FLUOROALIPHATIC ESTERS OF FLUOROSULFONIC ACID. 5. CONJUGATE RADICAL FLUOROSULFATOHALOGENATION OF HIGHER FLUOROOLEFINS

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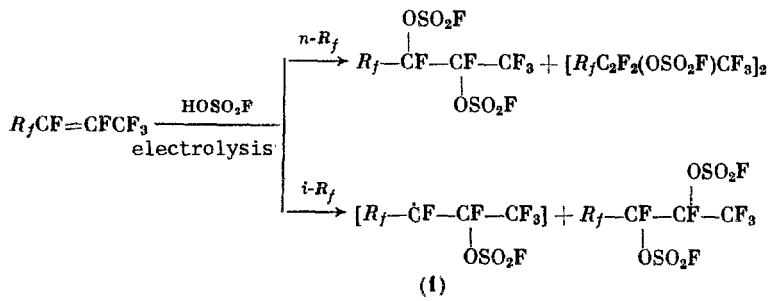
A study has been made of the electrochemical fluorosulfation of perfluoro-2-alkenes in the presence of halogens, leading to the formation of fluoroaliphatic vicinal fluorosulfatohalides. The reaction proceeds as a conjugate radical addition of peroxydisulfuryl difluoride and the halogen at the double bond of the olefin; the ratio of the resulting regioisomers is determined by steric factors.

Keywords: *electrolysis, fluorosulfatohalogenation, stable radical.*

According to [1], perfluoro-2-alkenes with a branched structure, under conditions of electrochemical fluorosulfation, form exclusively vicinal bis-fluorosulfates without any products of fluorosulfatodimerization, in contrast to the behavior of their linear analogs:



(1)

The difference in reactivity of linear and branched perfluoro-2-alkenes with electrochemically generated peroxydisulfuryl difluoride (PSD) is explained by the regiospecificity of addition of $FSO_3^{\cdot}$ to branched-chain fluoroolefins. In the radicals (**1**) that are formed in this reaction the radical center is positioned alongside the branched perfluoroalkyl group, so that the dimerization of these radicals is sterically hindered.

ESR registration of the stable radical **1** (R_f = i-C_3H_7) in the interaction of the PSD with a 15- to 20-fold molar excess of **2b** (Fig. 1) provides a certain degree of support for this hypothesis. The ESR spectra of the radical **1** at 20°C are characterized by hyperfine coupling (HFC) of the unpaired electron with the nuclei of the fluorine atoms: $a_{F\text{-}\alpha}$ (1F) = 6.45 Oe, $a_{F\text{-}\beta}$(2F) = 15.1 Oe, g = 2.0032. When the temperature is raised to 70°C with the aim of obtaining a high-resolution ESR spectrum, the radical **1** disappears rapidly. In order to determine the constants of HFC with the γ-fluorine atoms at high temperature, the radical **1** was obtained by photolysis of the bromide **11** in the presence of dicarboranylmercury [2] (found $a_{F\text{-}\gamma}$ = 2.4 Oe, $a_{F\text{-}\delta(FSO_2O)}$ = 1.2 Oe). However, a final answer to the question of how the direction of radical attack at the double bond of the olefin is influenced by the structure of the perfluoro-2-alkene can be obtained only by chemical fixation of the intermediate α-fluorosulfatoperfluoroalkyl radicals. To this end, we investigated the interaction of PSD, under conditions of its electrochemical generation, with **2b** and perfluoro-2-hexene (**2a**) in the presence of Cl_2, and also the reaction with **2b** and perfluoro-2-methyl-2-pentene (**4**) in the presence of Br_2.

The interaction of **2a** and **2b** with electrochemically generated PSD in the presence of Cl_2 led to the formation of a mixture of isomeric fluorosulfatochlorides **(5a, b-6a, b)**, bis-fluorosulfates **(7a, b)**, and dichlorides **(8a, b)**:

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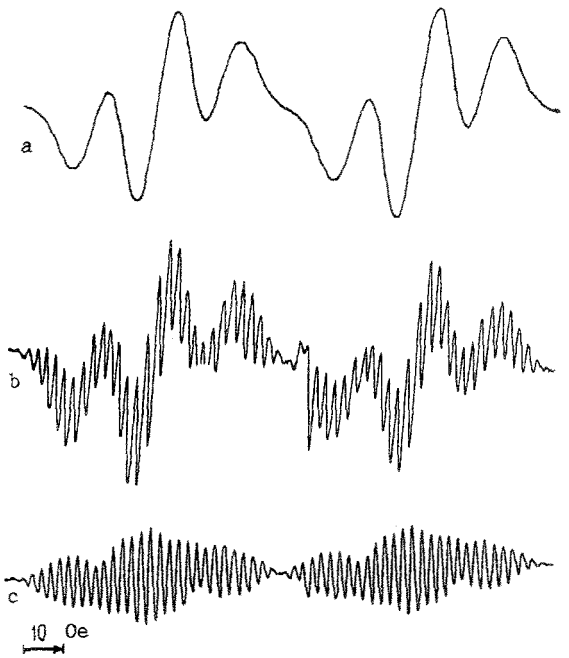


Fig. 1. a) ESR spectrum of radical **1** at 20°C (**1:2b** = 1:20); b) spectrum of solution of **1** in olefin **2b**, 5 min after saturating with Cl_2 (indicating superposition of spectra of radical **1** and radical-adduct of Cl atoms with **2b**); c) spectrum of radical-adduct of chlorine atoms with **2b**, 10 min after saturating solution of **1** in **2b**.

$$R_fCF{=}CFCF_3 \xrightarrow[\text{electrolysis}]{HSO_3F,\ Cl_2} \underset{(2a,\ b)}{}$$

$$\longrightarrow \underset{(5a,\ b)}{R_fCFCl{-}CFCF_3} + \underset{(6a,\ b)}{R_fCF(OSO_2F){-}CClCF_3} + \underset{(7a,\ b)}{R_fCF(OSO_2F){-}CFCF_3} + \underset{(8a,\ b)}{R_fCFCl{-}CFClCF_3}$$

$R_f = C_3F_7$ (**a**); $R_f = i\text{-}C_3F_7$ (**b**).

The ratio of isomers **5:6** is highly dependent on the constitution of the olefins: The ratio is 1:1 for **5a,6a**, but 4:1 for **5b:6b**. In analyzing the results, we cannot ignore the possibility of generating FSO_3Cl (**9**) in the course of electrolysis (regarding the formation of **9** by the reaction of PSD with Cl_2, see [3]), with the formation of a mixture of isomeric fluorosulfatochlorides in a ratio **5a:6a** = 3:1 or **5b:6b** = 2:3. Comparing the results of the present work with those of [4], we can conclude that the different distribution of the regioisomers **5** and **6** that are obtained is due to the different character of their formation — not the addition of **9** to the fluoroolefin, but conjugate radical addition of PSD and Cl_2 at the multiple bond:

$$\text{>C=C<} \xrightarrow{FSO_2O^{\cdot}} \text{>C(OSO}_2\text{F)}\text{–C<} \xrightarrow[-Cl^{\cdot}]{Cl_2} \text{>C(OSO}_2\text{F)}\text{–Cl}$$

The high content of the isomer **5b** points out the decisive role of the steric factor in the addition of $FSO_3^{\cdot}$ to **2b**.

We should note particularly the formation of the dichloride **8b** in the electrolysis of HSO_3F in the presence of PSD and Cl_2. It was shown in a separate experiment that under the same conditions as those of the electrolysis (same temperature and reaction time), but without the application of any current no **8b** whatever was formed. It is evident that the PSD catalyzes the chlorination of **2b**, and hence, the conjugate radical addition of Cl_2 and PSD to **2b**, the first act of which is the addition of $Cl^{\cdot}$ to **2b**, also in position 2, can be regarded as one of the possible paths of synthesis of the isomer **6b**:

$$\mathbf{2b} \xrightarrow{PSD} \underset{(1)}{(CF_3)_2CF{-}\dot{C}F{-}CF(OSO_2F){-}CF_3} \xrightarrow{Cl_2} \mathbf{5b} + Cl^{\cdot}$$

$$\mathbf{2b} \xrightarrow{Cl^{\cdot}} (CF_3)_2CF-\dot{C}F-CFCl-CF_3 \xrightarrow{Cl_2} \mathbf{8b}$$
(10)

This view is supported by ESR data obtained upon chlorination of a solution of the radical **1** in **2b**: The signal of **1** disappears, and the signal of the radical **10** is registered in the spectrum (see Fig. 1).

The composition of the products of electrolysis of HSO_3F in the presence of **2b** and Br_2 and their current yield (CY) are determined to a large degree by the order of adding the bromine to the reaction mass. If the Br_2 is added gradually to the electrolyte during the course of electrolysis, the main reaction product is the fluorosulfatobromide **11** (ratio **11:12** = 95:5, total CY 65.6%); in contrast, if a reaction mass originally containing the entire quantity of bromine is subjected to electrolysis, the regioselectivity of the process is considerably lower, with a ratio **11:12** = 60:40, and the CY drops to 21%:

$$\mathbf{2b} \xrightarrow[\text{electrolysis}]{HOSO_2F;\ Br_2} (CF_3)_2CF-\underset{\displaystyle OSO_2F}{\underset{|}{CF}}-CFBrCF_3 + (CF_3)_2CF-\underset{\displaystyle OSO_2F}{\underset{|}{CF}}-CFBrCF_3 + \mathbf{7b}.$$
(11) (12)

In view of the possibility of forming FSO_3Br (**13**) in the process of electrolysis,* we investigated the interaction of **13** (obtained by the reaction of PSD with Br_2 and HSO_3F) with **2b** in an HSO_3F medium; we found that a mixture of **11** and **12** is formed with very nearly equal amounts of the two components (55:45).

Our results suggest that in the absence of excess Br_2, the fluorosulfatobromination of **2b** is accomplished primarily through a type of conjugate radical addition. The first act of this reaction is the addition of $FSO_3\cdot$ at the double bond, the direction of which is determined exclusively by steric factors and is accomplished regiospecifically in position 2 of the olefin. The formation of the isomer **12** should apparently be attributed to addition, to the **2b**, of the bromine fluorosulfate **13** obtained by electrochemical oxidation of Br_2, not the interaction of PSD with bromine. According to [6], the oxidation potential of Br_2 is considerably lower than that of HSO_3F, with the electrochemical oxidation of bromine representing an essentially reversible process. Thus, the electrolysis of a mixture of HSO_3F and Br_2 comes down essentially to a redox reaction of bromine, and this is responsible for a lower CY of **11** and **12** when the electrolysis is carried out in the presence of excess Br_2:

$$Br_2 \underset{\text{cathode; } +e^-}{\overset{\text{anode; } -e^-}{\rightleftharpoons}} 2Br^+ \xrightarrow{HSO_3F} FSO_3Br \xrightarrow{\mathbf{2b}} \mathbf{11} + \mathbf{12}.$$
(13)

Under the action of CsF, **11** is readily converted to the bromoketone **14** with a high yield:

$$\mathbf{11} \xrightarrow[-SO_2F_2]{[CsF]} (CF_3)_2CF-CFBr-\overset{\displaystyle O}{\overset{\|}{C}}-CF_3.$$
(14)

By electrolysis of a mixture of HSO_3F and **4** with gradual addition of Br_2, the fluorosulfatobromides (**15** and **16**) and the bis-fluorosulfate (**17**) were obtained in a 1:0.12:1.2 ratio. The high regioselectivity of this reaction can also be explained from the standpoint of a conjugate radical addition, in the course of which $FSO_3\cdot$ preferentially attacks the monosubstituted vinyl carbon atom in **4**, giving the tertiary radical **18**. The assumption of intermediate formation of the radical **18** also provides an explanation for the higher content of the bis-fluorosulfate **17** in the reaction products: The van der Waals radius of oxygen is considerably smaller than the van der Waals radius of bromine (1.40 and 1.95 Å, respectively [7]), and this makes it possible for the $FSO_3\cdot$ to compete successfully with bromine in the reaction with **18**, in spite of the lower instantaneous concentrations of PSD in comparison with Br_2:

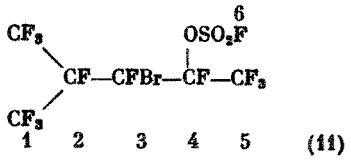
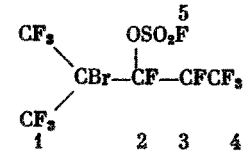
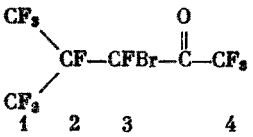
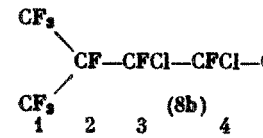
$$(CF_3)_2C=CFC_2F_5 \xrightarrow[(4)]{PSD} [(CF_3)_2C^{\cdot}-\underset{\displaystyle OSO_2F}{\underset{|}{CFC_2F_5}} + (CF_3)_2C-\underset{\displaystyle FSO_2O}{\underset{|}{C^{\cdot}FC_2F_5}}] \xrightarrow[(18)]{}$$

$$\xrightarrow{Br_2} (CF_3)_2CBr-\underset{\displaystyle OSO_2F}{\underset{|}{CFC_2F_5}} + (CF_3)_2C-\underset{\displaystyle FSO_2O}{\underset{|}{CFBrC_2F_5}}$$
(15) (16)

$$\xrightarrow{PSD} (CF_3)_2C-\underset{\displaystyle OSO_2F}{\underset{|}{CFC_2F_5}}$$
FSO_2O (17)

*Regarding the interaction of PSD with Br_2, see [5].

TABLE 1. ^{19}F NMR Spectra

Compound	δ, ppm
 (11)	Mixture of erythro and threo isomers: −9.3; −8.9; −8.5 (12F¹), 91.7; 92.0 (2F²), 43.9; 49.0 55.1; 56.0 (2F³ + 2F⁴), −5.0; −4.7 (6F⁵), −129.3; −129.2 (2F⁶)
 (15)	−14.5; −13.9 (6F¹), 39.1 (F²), 38.1 (2F³) 1.4 (3F⁴), −131.1 (F⁵)
 (14)	−5.4 (6F¹), 98.7 (F²), 64.4 (F³), −3.6; −3.4 (3F⁴)
 (8b)	Mixture of erythro and threo isomers: −9.4; −9.1; −8.6 (12F¹), 91.4; 91.6 (2F²), 44.9; 46.6; 51.7 (2F³ + + 2F⁴), −4.1; −3.7 (6F⁵)

However, in view of the fact that **13** adds smoothly to **4**, giving **15** as the main reaction product, it is impossible, on the basis of the available data, to draw any final conclusion on the electrophilic or radical character of the fluorosulfatobromination of **4**.

EXPERIMENTAL

^{19}F NMR spectra were taken in a Perkin—Elmer R-32 NMR spectrometer (90 MHz for ^{1}H, and 84.6 MHz for ^{19}F). The chemical shifts are given in ppm relative to the external standards TMS and CF_3COOH (these are listed in Table 1). Mass spectra were taken in a YGMS 7070E spectrometer with a 70-eV ionization voltage; in the following material, values of *m/z* are listed, with the relative intensity (%) in parentheses.

Electrolysis of HSO_3F in the Presence of 2b and Cl_2. In a diaphragmless electrolyzer (anode and cathode SU-2000 glassy carbon), were placed 30 ml of HSO_3F and 2.1 g of $NaSO_3F$. The electrolysis was continued for a 6-h period with a current of 0.5 A while bubbling in Cl_2 (12-15 ml/min) and gradually adding 20 g (66 mmoles) of **2b**; the reaction mass was then poured onto ice; the organic layer was separated, obtaining 18.1 g of a mixture containing (GLC) 46.5% **5b** [3], 11% **6b** [3], 25.5% **7b** [8], and 17% **8b**. By fractional distillation, an analytical sample of **8b** was isolated, bp 110-111°C. Mass spectrum of **8b**: 351 $[M - F]^+$ (0.06), 301 $[M - CF_3]^+$ (0.29), 263 $[C_5F_7Cl_2]^+$ (1.27), 235 $[C_4F_8Cl]^+$ (37.04), 201 $[M - C_3F_7]^+$ (3.28), 185 $[C_3F_6Cl]^+$ (3.16), 147 $[C_3F_4Cl]^+$ (11.69), 135 $[C_2F_4Cl]^+$ (17.19), 93 $[C_3F_3]^+$ (5.08), 85 $[CF_2Cl]^+$ (54.92), 69 $[CF_3]^+$ (100.00).

Electrolysis of HSO_3F in the Presence of 2a and Cl_2. Analogously, from 15 g (50 mmoles) of **2a**, over a period of 3 h, 14.8 g of a mixture was obtained, containing (GLC): 7.8% **5a** [3], 8.9% **6a** [3], 3.6% **7a** [7], and 79.7% **8a**. By fractional distillation of the mixture, an analytical sample of **8a** was isolated, bp 112-113°C. Mass spectrum of **8a**: 335 $[M - Cl]^+$ (0.12), 301 $[M - CF_3]^+$ (0.27), 263 $[C_5F_7Cl_2]^+$ (0.81), 235 $[C_4F_8Cl]^+$ (38.56), 201 $[C_3F_7]^+$ (11.36), 185 $[C_3F_6Cl]^+$ (5.49), 169 $[C_3F_7]^+$ (15.69), 147 $[C_3F_4Cl]^+$ (21.51), 135 $[C_2F_4Cl]^+$ (34.80), 131 $[C_3F_5]^+$ (9.47) $[C_2F_5]^+$ (19.02), 85 $[CF_2Cl]^+$ (35.59), 69 $[CF_3]^+$ (100).

Electrolysis of HSO_3F in the Presence of 2b and Br_2. A. In an electrolyzer (SU-2000 glassy carbon anode, 8Kh13 steel cathode), were placed 15 ml of HSO_3F and 1.1 g of $NaSO_3F$, along with 14.8 g (49 mmoles) of **2b**. The electrolysis was performed with a 0.1-A current for a period of 14 h, while gradually adding 4.3 g (27 mmoles) of Br_2. The mixture was poured over ice, and the organic layer was separated, washed with water, and dried with $MgSO_4$. By distillation, obtained 17 g of a mixture containing (GLC): 92.5% **11**, 3.6% **12**, and 3.9% **8b**. Total CY (**11** + **12**) 65.6%. By fractionation of the mixture, an analytical sample of **11** was isolated, bp 55-56°C (20 mm). Found, %: C 14.85; F 51.50; Br 16.03. $C_6F_{13}BrO_3S$. Calculated,

%: C 15.04; F 51.56; Br 16.68. Mass spectrum of **11**: 409 $[M - CF_3]^+$ (0.56), 291 $[C_5F_8Br]^+$ (2.34), 279 $[C_4F_8Br]^+$ (4.58), 231 $[C_5F_9]^+$ (4.01), 199 $[C_2F_4OSO_2F]^+$ (54.43), 191 $[C_3F_4Br]^+$ (3.92), 129 $[Cf_2Br]^+$ (12.49), 97 $[C_2F_3O]^+$ (26.91), 83 $[SO_2F]^+$ (44.82), 69 $[CF_3]^+$ (100.0), 67 $[SOF]^+$ (4.25); (**12**): 379 $[M - OSO_2F]^+$ (2.07), 329 $[C_5F_{10}Br]^+$ (1.38), 299 $[C_4F_8OSO_2F]^+$ (57.08), 231 $[C_5F_9]^+$ (9.83), 197 $[C_4F_7O]^+$ (40.77), 179 $[C_2F_4Br]^+$ (15.80), 169 $[C_3F_7]^+$ (31.02), 149 $[CF_2OSO_2F]^+$ (6.66), 131 $[C_3F_5]^+$ (10.96), 129 $[CF_2Br]^+$ (9.61), 119 $[C_2F_5]^+$ (11.61), 83 $[SO_2F]^+$ (76.45), 69 $[CF_3]^+$ (100.0).

B. A mixture of 15 ml of HSO_3F, 1.1 g of $NaSO_3F$, 14.8 g (49 mmoles) of **2b**, and 4.3 g (27 mmoles) of Br_2 was subjected to electrolysis with a 0.1-A current for 14 h. After working up the reaction mass obtained 16 g of a mixture, by distillation of which 10.7 g of the original olefin was recovered, along with 5.2 g of a mixture containing (GLC): 62% **11**, 38% **12**. Yield of (**11** + **12**) 79% relative to olefin reacted, conversion 25%, CY 21%.

Interaction of 2b with PSD and Br_2. A mixture of 1 g (5 mmoles) of PSD with 1.6 g (10 mmoles) of Br_2 and 3 ml of HSO_3F was stirred for 30 min. Then 3 g (10 mmoles) of **2b** was added dropwise, and the mixture was stirred for an additional 30 min. The reaction mixture was poured into water, and the organic layer was separated, washed with water, and dried with $MgSO_4$. By distillation, obtained 2.5 g (52%) of a mixture containing (GLC): 45.4% **11**, 54.6% **12**.

Synthesis of 3-Bromoperfluoro-4-methylpentan-2-one (14). A mixture of 13.4 g (28 mmoles) of **11** and 0.5 g (3.2 mmoles) of dry CsF was stirred for 1.5 h at 60°C; the reaction products were vacuum-distilled into a trap (—78°C) and then redistilled. Obtained 8.7 g (82%) of **14**, bp 96-98°C. Found, %: C 19.07; F 54.88; Br 21.23. $C_8F_{11}BrO$. Calculated, %: C 19.11; F 55.44; Br 21.19. Mass spectrum of **14**: $[M]^+$ (0.03), 357 $[M - F]^+$ (0.08), 307 $[M - CF_3]^+$ (0.20), 279 $[M - C_2F_3O]^+$ (8.72), 260 $[M - C_2F_4O]^+$ (16.26), 228 $[M - CF_3Br]^+$ (5.53), 181 $[C_4F_7]^+$ (6.51), 159 $[C_4F_5O]^+$ (18.66), 129 $[CF_2Br]^+$ (10.81), 97 $[C_2F_3O]^+$ (55.16), 93 $[C_3F_3]^+$ (5.93), 69 $[CF_3]^+$ (100.0), 31 $[CF]^+$ (5.45). IR spectrum of **14** (ν, cm^{-1}): 1783 (C=O), 1487 (OSO_2).

Interaction of 4 with PSD and Br_2. A mixture of 1.3 g (6.8 mmoles) of PSD with 2.2 g (13.6 mmoles) of bromine and 5 ml of HSO_3F was stirred for 30 min; then, 4.1 g (13.6 mmoles) of **4** was added gradually, and stirring was continued for 30 min. The mixture was poured into water, and the organic layer was separated, washed with water, dried with $MgSO_4$, and distilled. Obtained 5.2 g (80%) of **15**, bp 63-65°C (25 mm). Found, %: C 15.03; F 51.10; Br 16.34. $C_6F_{13}BrO_3S$. Calculated, %: C 15.04; F 51.56; Br 16.68. Mass spectrum of **15**: 459 $[M - F]^+$ (0.07), 379 $[M - OSO_2F]^+$ (5.84), 359 $[M - C_2F_5]^+$ (2.40), 292 $[C_5F_8Br]^+$ (4.22), 249 $[C_3F_7O_3S]^+$ (59.64), 229 $[C_3F_6Br]^+$ (13.95), 169 $[C_3F_7]^+$ (12.49), 147 $[C_3F_5O]^+$ (13.99), 119 $[C_2F_5]^+$ (58.81), 83 $[SO_2F]^+$ (83.38), 69 $[CF_3]^+$ (100.0). The structure of **15** was confirmed by converting it to the bromoketone $(CF_3)_2C(Br)COC_2F_5$ by the action of dry CsF (identified by GLC comparison with a known sample [9]).

Electrolysis of HSO_3F in the Presence of 4 and Br_2. Under the conditions of experiment **A**, a mixture of 30 ml of HSO_3F and 2.1 g of $NaSO_3F$ was electrolyzed in the presence of 30 g (100 mmoles) of **4** with a 0.6-A current for 8 h, while gradually adding 8 g (50 mmoles) of bromine. After working up and distilling the reaction mass, obtained 31 g of a mixture with bp 63-65°C (25 mm), containing (GLC): 51.9% **17** [1], 42.9% **15**, and 5.2% **16**. Mass spectrum of **16**: 359 $[M - C_2F_5]^+$ (1.37), 281 $[C_6F_{11}]^+$ (3.31), 249 $[C_3F_6OSO_2F]^+$ (7.74), 229 $[C_3F_6Br]^+$ (39.19), 181 $[C_4F_7]^+$ (15.24), 169 $[C_3F_7]^+$ (5.73), 147 $[C_3F_5O]^+$ (13.39), 129 $[CF_2Br]^+$ (14.35), 119 $[C_2F_5]^+$ (8.31), 97 $[C_2F_3O]^+$ (9.11), 93 $[C_3F_3]^+$ (5.48), 83 $[SO_2F]^+$ (21.53), 69 $[CF_3]^+$ (100.0).

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