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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Decomposition of Pentafluoroallyl Fluorosulfate Oxide

N. V. Lebedev, V. V. Berenblit, P. E. Troichanskaya, and V. A. Gubanov

Lebedev Research Institute of Synthetic Rubber, Federal State Unitary Enterprise, St. Petersburg, Russia

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Abstract—Decomposition of pentafluoroallyl fluorosulfate oxide under nucleophilic catalysis is studied. The possible reaction mechanism is considered.

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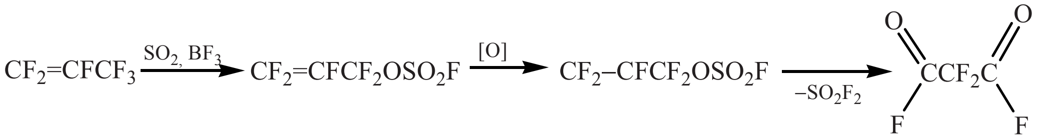
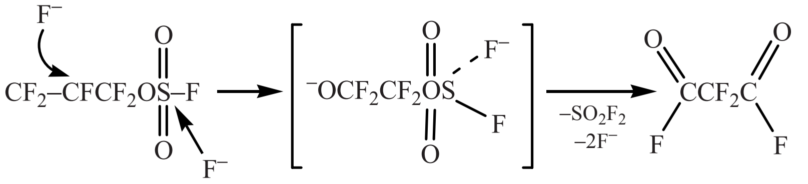
Decomposition of pentafluoroallyl fluorosulfate oxide (AFSO) under the action of cesium and potassium fluorides gives difluoromalonyl difluoride (MDF) in high yield [1]. The synthesis of MDF consists in addition of sulfur trioxide to hexafluoropropene (HFP) with the formation of pentafluoroallyl fluorosulfate (AFS) [2, 3], its liquid-phase oxidation to AFSO [4], and decomposition of AFSO under the action of fluoride ions with simultaneous elimination of sulfuryl fluoride:



HFP AFS AFSO MDF

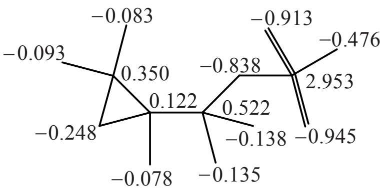
A study of the third step of the MDF synthesis showed that decomposition of AFSO under the action of nucleophilic agents yields a multicomponent mixture of products whose identification was not considered in the literature. It was necessary to find the conditions of AFSO decomposition (taking into account the effect of the nucleophilic agent, solvent, and temperature) that ensure the highest MDF yield and to identify the by-products.

As seen from the structure, the AFSO molecule has two electrophilic centers. Their attack by the fluoride anion results in isomerization of the oxirane ring and elimination of sulfuryl fluoride, with the formation of MDF molecule containing two acyl fluoride groups:

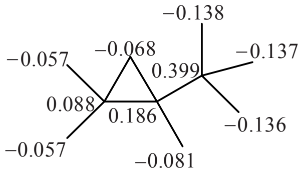


It is known that in hexafluoropropene oxide (HFPO) fluoride anion attacks the C^2 atom which has the higher positive charge density in the ring to form perfluoropropionyl fluoride [5]. Our quantum-chemical calculations (HyperCube 8.0.4 program, AM1 semiempirical method) revealed in AFSO and HFPO molecules the centers that are preferentially accessible to nucleophilic attack.

It follows from the charge density distribution that the fluoride ion should primarily attack the sulfur atom of the fluorosulfate group. Zapevalov [6] noted that the

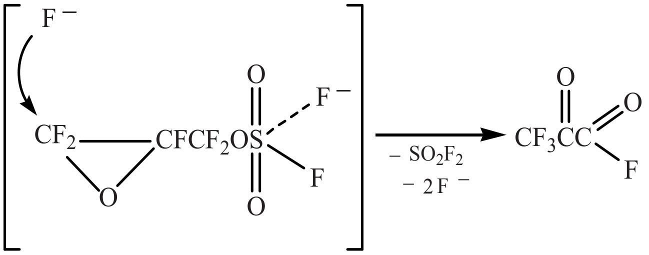


AFSO



HFPO

presence of an electrophilic fluorosulfate group in the β-position to the epoxy ring facilitates the nucleophilic attack of both functional groups, resulting in simultaneous ring opening and elimination of fluorosulfate in the form of sulfuryl difluoride. However, in the case of simultaneous attack of the fluoride anion, the isomerization of the oxirane ring should result in formation of trifluoropyruvyl fluoride rather than MDF:



This assumption contradicts the experimental data, as trifluoropyruvyl fluoride was not detected in AFSO decomposition products.

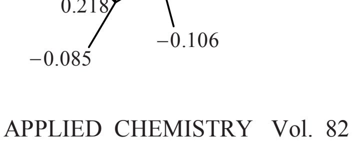
The structure of AFSO suggests the possible occurrence of a series of undesirable processes. In particular, the reaction of intermediate alkoxides with the epoxy group of AFSO may result in its oligomerization with the formation of a series of polyoxyalkyl sulfates. Furthermore, the fluorosulfate group can be replaced by an alkoxy group with the formation of another series of oligomers. Replacement of fluorosulfate groups by fluoride ion with the formation of trifluoromethyl derivatives is also possible. At elevated temperatures, the oxirane ring can undergo thermolysis with the elimination of difluorocarbene.

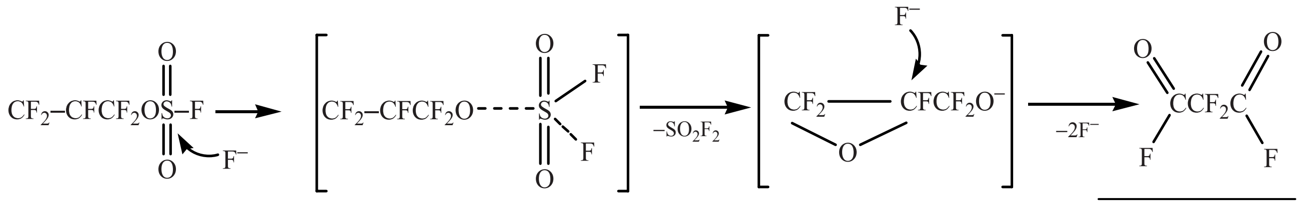
As in isomerization of HFPO to perfluoropropionyl fluoride, we tested as nucleophilic catalysts Lewis bases such as tertiary amines, alkali metal fluorides as sources of ionic fluorine, and the complex of hydrogen fluoride with triethylamine. The experimental data on the decomposition of AFSO are given in Table 1.

We failed to prepare MDF following the protocol from [1], with CsF as catalyst, because of the predominant occurrence of side oligomerization processes (run no. 18). Potassium fluoride in the presence of activators [dioxane, diglyme, tetraglyme, ethylene glycol, PEG oligomers (M = 400–1500)] and the complex $Et_3N{\cdot}3HF$ in acetonitrile appeared to be more effective nucleophilic agents from the viewpoint of MDF formation. Addition of solvents capable of specific solvation of cations in the KF–acetonitrile system increased the MDF yield and decreased the formation of by-products. Tertiary amines appeared to be chemically unstable under the reaction conditions (run nos. 11, 13) because of the reaction with the fluorosulfate group in accordance with [7]. Addition of onium salts led to an increase in the overall reaction rate, but the amount of MDF in the reaction products decreased and that of the oligomers increased (run no. 17). In DMSO on KF, the reaction was accompanied by considerable oligomerization and tarring (run no. 14). On KF without solvent and in nonpolar aprotic solvents (toluene, benzene, hexane), there was no reaction at all, which indicates that the catalytic species is the dissolved fluoride (run nos. 1, 2, 12).

With NaF as catalyst, only slow evolution of small amounts of carbonyl difluoride and sulfuryl difluoride was observed (run no. 15). Addition of KF led only to an increase in the intensity of their evolution and to tarring of the reaction mixture.

AFSO starts to decompose at 60–65°C, which coincides with the decomposition temperatures of perfluoroalkyl fluorosulfates [8]. Attempts to perform an isomerization of AFSO (by analogy with HFPO) at low temperatures on various catalysts failed. Presumably, the first step of AFSO decomposition by the ionic mechanism is formation of a transition complex by the attack of the fluoride anion at the





sulfur atom bearing the largest positive charge in the molecule. Decomposition of the complex with the elimination of SO_2F_2 results in redistribution of the charge density in intermediate potassium 2,3-epoxyperfluoropropylate, and the fluoride anion causes isomerization of the oxirane with the formation of MDF:

The best results in decomposition of 15 g (0.065 mol) of AFSO, with an MDF yield of up to 60 mol %, were obtained under laboratory conditions in a glass apparatus at the weight ratio acetonitrile (solvent) : KF (catalyst) : ethylene glycol (process activator) = 12 : 1.5 : 0.07 at the boiling point of the solvent (run no. 8),

Table 1. Yield of MDF in decomposition of 15 g of AFSO under various conditions

Run no.	Medium, ml	Catalyst, g	Activator	T, °C	Amount of crude product in trap, g	MDF yield[a]		Bottom residue, g
						wt %	mol %	
1	–	KF, 1	Diglyme, 0.15 ml	64	–	–	–	15[b]
2	–	AS-14[c], 1	Diglyme, 2 ml	64	0.5	12	1	14.5[b]
3	CH_3CN, 15	KF, 2	Dioxane, 1 ml	81	11	38	48	4
4	CH_3CN, 15	KF, 2	Tetraglyme, 1 ml	81	10	37	42	4
5	CH_3CN, 15	KF, 2	Diglyme, 1 ml	81	11	39	49	3
6	CH_3CN, 15	KF, 1.7	PEG-400, 1 ml	81	10.5	32	38.5	4.5
7	CH_3CN, 15	KF, 1.6	18-Crown-6-6, 0.5 g	81	10	34	39	5
8	CH_3CN, 15	KF, 1.5	Ethylene glycol, 0.07 g	81	12.5	42	60	2.5
9	CH_3CN, 15	KF, 2	PEG-1500, 1 g	81	8.5	29	28	5.5
10	CH_3CN, 15	KF(sd)[d], 1.6	–	81	10	34	39	5
11	CH_3CN, 15	KF, 2; Et_3N, 0.2 ml	Dioxane, 1 ml	81	10	36	41	5
12	Benzene, 15	KF, 2	Dioxane, 1 ml	80	–	–	–	15[b]
13	Toluene, 15	*N,N*-Dimethylaniline, 0.3	–	85	1.5	17	3	12[b]
14	CH_3CN, 7.5; DMSO, 7.5	KF, 1	Ethylene glycol, 0.07 g	81	2	4	1	12
15	CH_3CN, 15	NaF, 3; KF, 1	Ethylene glycol, 0.07 g	81	–	–	–	15[b]
16	CH_3CN, 10	KF, 1	Ethylene glycol, 0.07 g	81	7	5	4	7
17	CH_3CN, 15	KF, 0.4	$[Bu_4P]Br$, 0.15 g	81	6.5	24	18	8.5
18	CH_3CN, 15	CsF, 0.6	–	81	3.5	19	7.5	11.5
19	CH_3CN, 30	KF(sd), 0.05 g	Ethylene glycol, 0.07 g	81	2	35	8	13[b]
20	CH_3CN, 30	$Et_3N \cdot 3HF$, 2 g	–	81	13.5	41	63	2.5

[a] According to GLC data.

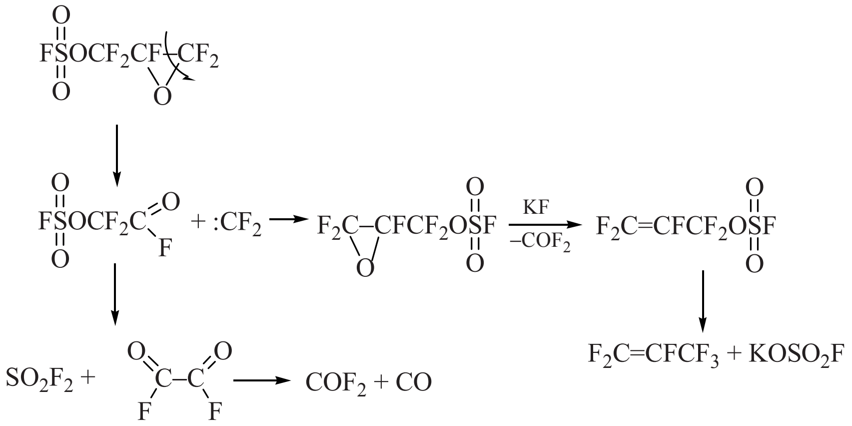
[b] Unchanged AFSO.

[c] AS-14 is an anion-exchange resin.

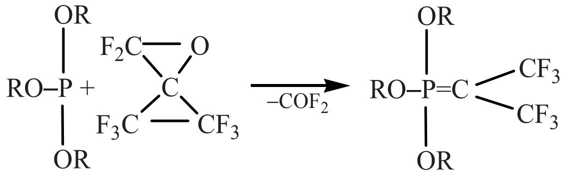
[d] KF(sd) denotes KF dried by vacuum spraying.

and also in the presence of the complex $Et_3N{\cdot}3HF$ in acetonitrile (run no. 20).

In the course of the experiment, the AFSO decomposition products, including MDF and sulfuryl difluoride, were removed from the reactor and condensed in a cooled trap. Among the reaction products we identified by ^{19}F NMR carbonyl difluoride (up to 15 mol %), oxalyl difluoride (up to 5 mol %), and, unexpectedly, HFP whose yield in some experiments reached 10 mol %. Apparently, specific catalytic decomposition of AFSO with the formation of carbene (see below) occurs concurrently with the catalytic decomposition of AFSO by the ionic mechanism via nucleophilic attack of fluoride anion with the formation of MDF:



The HFP formation can be accounted for by insertion of difluorocarbene with the formation of AFS and eliination of carbonyl difluoride, followed by replacement of the fluorosulfate group of AFS by fluoride anion. This mechanism can be confirmed by an unusual reaction of highly electrophilic fluorinated epoxides with trialkyl phosphites, occurring at room temperature and yielding trialkoxyphosphorylides [9]:



The capability of AFS for substitution of the fluorosulfate group by nucleophilic fluoride anion under the action of alkali metal fluorides was demonstrated in [10].

It could be assumed that HFP is formed via successive addition of carbene $:CF_2$ with intermediate formation of tetrafluoroethylene; in this case, however, the product mixture should contain both tetrafluoroethylene and hexafluorocyclopropane [11, 12] whose signals were absent from the ^{19}F NMR spectra.

As for the kinetics of by-product formation, with the progress of AFSO decomposition the content of HFP and COF_2 in the product mixture increases (see figure), which contradicts the above scheme, because fluoride ion is present in catalytic amounts. Apparently, HFP can be formed not only by substitution of the fluorosulfate group in AFS by fluoride anion, but also by elimination of SO_3. For example, Hass et al. [13] showed that FSO_2CF_2COF is unstable in the presence of CsF, with one of the decomposition pathways yielding sulfur dioxide and trifluoroacetyl fluoride. Krespan and England point to possible elimination of sulfur trioxide and demonstrate the reversibility of AFS synthesis from HFP and sulfur trioxide [2].

It should be noted that only with $Et_3N{\cdot}3HF$ used as the catalyst the MDF : HFP ratio remained constant in the course of the reaction. Apparently, with KF as catalyst, with the progress of the concurrent substitution of the fluorosulfate group by fluorine, the catalyst surface becomes covered with potassium fluorosulfate, which is less soluble in acetonitrile. As this product is accumulated in the system, the reaction direction shifts toward carbene decomposition, which is apparently responsible for the observed decrease in the MDF yield and increase in the yield of by-products of AFSO decomposition, including HFP.

Somewhat larger content of carbonyl fluoride according to the results of analysis may be due to decomposition of oxalyl difluoride because of its instability under the reaction conditions.

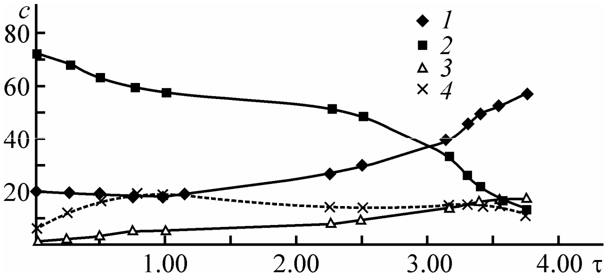
It is necessary to give some comments on the role of specific catalysis of carbene decomposition of the oxirane ring. This is a low-temperature (70–80°C) solution process that distinguishes it from the thermal process (for HFPO, the threshold temperature of thermal decomposition with the formation of difluorocarbene is 150°C [14]). Carbenes generated in solution, and especially in the presence of metals, appear to be more or less bound in a complex with the solvent and/or metal, which affects the lifetime, effective volume, selectivity, and electrophilic properties of the carbene [15]. The surface of crystalline fluoride or fluorosulfonate of potassium or another metal can act as catalyst. For example, the use of a magnetic stirrer made of a ferromagnetic alloy without protective glass shell led to a dramatic increase in the yield of the reaction by-products. Attempts to implement the process in a stainless steel apparatus led to a decrease in the MDF yield to 20 mol % because of an increase in the yield of the low-boiling components. Apparently, specific catalysis on the metal surface led to redistribution of chemical mechanisms in favor of the carbene decomposition.

The presence of high-boiling oligomers in the bottom residue (20–30 wt % based on converted AFSO) suggests the occurrence of both side processes of AFSO oligomerization and oxidative reaction of sulfur trioxide with the solvent.

EXPERIMENTAL

AFSO decomposition products were analyzed chromatographically on an LKhM-8MD instrument [model 5, thermal conductivity detector, programmed heating from 30 to 200°C at a rate of 6 deg min^{-1}, 3 mm × 3 m columns, Silokhrom-80 support (fraction 0.25–0.35 mm, packing density 0.30±0.01 g cm^{-3}), stationary phase PEF (15 wt %), carrier gas helium (40 ml min^{-1})].

The ^{19}F NMR spectra were taken on an AM-500 Bruker Spectrospin spectrometer at 470.572 MHz against internal hexafluorobenzene ($\delta = -162.9$ ppm). Acetone-d_6 was used as solvent. The fluorine chemical shifts were converted to the δ scale relative to CCl_3F.

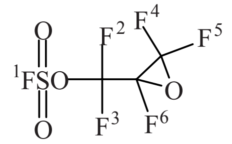
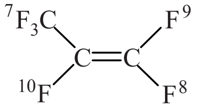


Composition of gaseous products of AFSO decomposition, according to GLC data. (*c*) Relative content of compound and (τ) time. (*1*) COF_2, (*2*) SO_2F_2, (*3*) HFP, and (*4*) MDF.

Pentafluoroallyl fluorosulfate oxide (bp 64°C) was prepared according to [2, 4] (yield 60%) and was no less than 98% pure. Acetonitrile was dried by distillation from phosphorus pentoxide. Benzene, toluene, and hexane were distilled from sodium. Dimethyl sulfoxide and triethylamine were dried with calcium hydride and distilled. Calcined and dried potassium fluoride was additionally dried in a vacuum at 300°C.

AFSO decomposition. A 100-ml three-necked flask equipped with a magnetic stirrer, a thermometer, a dropping funnel with pressure compensation, and a reflux condenser connected by a polyethylene tube to a glass trap with the outlet protected by calcium chloride tube was charged in succession in a dry nitrogen stream with 1 g (0.017 mol) of KF, 0.07 g (0.001 mol) of ethylene glycol, and 15 ml of acetonitrile. The funnel was charged with 10 ml (15 g, 0.06 mol) of AFSO. The heating and stirring were switched on, and the trap was cooled with an isopropanol–liquid nitrogen mixture to a temperature from –80 to –90°C. At 75°C, slow dropwise addition of AFSO was started. The mixture warmed up and started to boil (81°C). The evolved decomposition products were condensed in the trap. The gas phase composition in the course of the process was monitored by TLC by taking 1-ml samples of the gas phase with a syringe through a rubber tube connecting the top of the reflux condenser with the polyethylene tube. AFSO was added over a period of 90–100 min, after which the mixture was heated for an additional 30 min. The trap contents (12.5 g) were finally analyzed by GLC by taking liquid samples. A sample of decomposition products in a methylene chloride solution was sealed in a glass insert and analyzed by ^{19}F NMR. Composition of the condensate in the trap (mol %, ^{19}F NMR data): SO_2F_2 52 (bp –52°C), $(COF)_2$ 2 (bp 0°C), COF_2 13.5 (bp –84°C), CF_3COF

Table 2. ^{19}F NMR spectra of identified compounds in AFSO decomposition products

δ, ppm	Multiplet	$J_{\mathrm{F}^*\text{–}\mathrm{F}^*}$, Hz	Number of F atoms	Structure	References[a]
50.45	t	^{1}F–$^{2;3}$F, 8.3	1		[2]
–79.3	d.t	^{2}F–^{3}F, 145 ^{2}F–$^{1;4}$F, 10	1		
–80.7	d.t	^{3}F–^{2}F, 145 ^{3}F–$^{1;4}$F, 7.6	1		
–109.4	d.d.t	^{4}F–^{5}F, 40.6 ^{4}F–^{6}F, 20.3 ^{4}F–$^{2;3}$F, 10	1		
–112.1	d.d	^{5}F–^{4}F, 40.7 ^{5}F–^{6}F, 16.5	1		
–155.4	t	^{6}F–$^{4;5}$F, 17.8	1		
–69.0	d.d.d	^{7}F–^{9}F, 20.3 ^{7}F–^{10}F, 12.7 ^{7}F–^{8}F, 7.6	3		[17]
–91.75	d.d.q	^{8}F–^{9}F, 53.4 ^{8}F–^{10}F, 38.2 ^{8}F–^{7}F, 7.6	1		
–105.8	d.d.q	^{9}F–^{10}F, 117 ^{9}F–^{8}F, 53.4 ^{9}F–^{7}F, 20.3	1		
–192.9	d.d.q	^{10}F–^{9}F, 117 ^{10}F–^{8}F, 38.1 ^{10}F–^{7}F, 12.7	1		
21.6	t	^{11}F–^{12}F, 10.5	2	$C^{12}F_2(CO^{11}F)_2$	[18]
–111.5	t	^{12}F–^{11}F, 10.2	2		
21.5	t	^{13}F–^{15}F, 8.9	1	$C^{14}F_3C^{15}F_2CO^{13}F$	[19]
–83.6	s		3		
–123.1	s		2		
16.7	q	^{16}F–^{17}F, 6.5	1	$C^{17}F_3CO^{16}F$	[20]
–74.9	d	^{17}F–^{16}F, 6.0	3		
–20.9	s		2	$CO^{18}F_2$	[21]
23.5	s		2	$^{19}FOC\text{–}CO^{19}F$	[22]
33.8	s		2	$SO_2^{20}F_2$	[23]
50.2	t	^{21}F–^{23}F, 7.6	1	$^{22}FOCC^{23}F_2OSO_2F^{21}$	
15.8	t	^{22}F–^{23}F, 2.5	1		
–76.4	d.d	^{23}F–^{21}F, 7.6 ^{23}F–^{22}F, 2.5	2		

[a] The spectra are in agreement with the published data.

0.5 (bp –59°C), CF_3CF_2COF 1 (bp –23°C), HFP 5, MDF 22 (bp –9°C), $FOCCF_2OSO_2F$ 0.5, AFSO 1, and unidentified impurities 2.5. The MDF yield and spectra of the identified compounds are given in Tables 1 and 2. The bottoms were also analyzed by GLC. The bottoms (2.5 g) after filtering off the salts and distilling off acetonitrile were a dark red mixture of high-boiling AFSO oligomers.

CONCLUSIONS

(1) Decomposition of pentafluoroallyl fluorosulfate oxide under the action of nucleophilic catalysts yields a multicomponent mixture of products, which suggests the reaction occurrence along several concurrent pathways.

(2) Difluoromalonyl difluoride is formed in the maximal yield (up to 60 mol %) in acetonitrile in the presence of catalytic amounts of KF and ethylene glycol, or of the complex $Et_3N{\cdot}3HF$.

(3) A scheme of formation of the identified by-products of pentafluoroallyl fluorosulfate oxide decomposition by the carbene mechanism was suggested.

(4) In the course of decomposition of pentafluoroallyl fluorosulfate oxide in the steady-state supply mode on potassium fluoride, the composition of the reaction products changes toward an increase in the yield of carbene decomposition products (hexafluoropropene and carbonyl difluoride), owing to specific catalysis on the surface of the forming potassium fluorosulfate.

(5) Decomposition of pentafluoroallyl fluorosulfate oxide by the carbene mechanism is strongly influenced by the heterogeneous catalytic effect of the metal surface.

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