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ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

Development of Technology of Perfluoroethyl Isopropyl Ketone Production

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Abstract—Synthesis of perfluoroethyl isopropyl ketone by an interaction of hexafluoropropene with perfluoropropionic acid fluoride or hexafluoropropene oxide was examined. Interchangeability of perfluoropropionic acid fluoride and hexafluoropropene oxide was demonstrated. The features of perfluoroethyl isopropyl ketone synthesis were studied in polar aprotic solvents on catalysts: alkali metal fluoride. A method for obtaining perfluoroethyl isopropyl ketone by direct catalytic reaction in a tubular reactor without use of solvents was suggested and investigated. The mechanism of interaction was considered. The main impurities resulting in obtaining perfluoroethyl isopropyl ketone were determined. The methods of cleaning perfluoroethyl isopropyl ketone were worked out.

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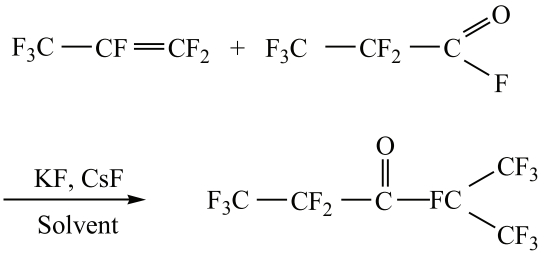
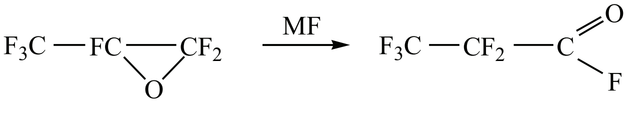
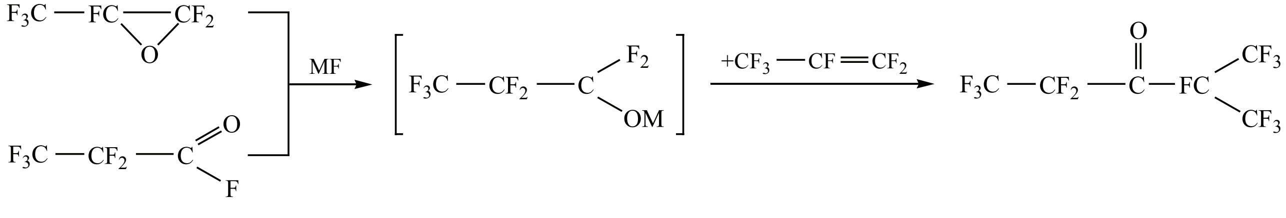
Perfluoroethyl isopropyl ketone C_2F_5–C(O)–*i*-C_3F_7 (hereinafter ketone) in recent years is of heightened interest in connection with its fire extinguishing agent properties [1]. In addition, it is a valuable intermediate product for obtaining a number of organofluorine compounds and also effective solvent [2]. An interaction of hexafluoropropene (HFP) with perfluoropropionic acid fluoride (PFAF) catalyzed by alkali metal fluoride in aprotic polar solvents, diglyme or acetonitrile, is the main method for the ketone synthesis [3–5]:



The process was carried out in an autoclave at a temperature form 20 using CsF to 85°C when using KF as a catalyst. Yield of ketone was 58–63.5%. Primarily, an issue of raw materials should be solved in developing the method suitable for a technology of the ketone production. Pentafluoropropionic acid fluoride in our country is not produced, but it is relatively easy can be obtained by isomerization of hexafluoropropene oxide (HFPO) [6–8]:



For this process as well as for the ketone obtaining the alkali metal fluorides KF and CsF are used as catalysts. Moreover, HFPO isomerization and ketone synthesis occur under the same conditions. In the case of PFAF and HFPO alkali metal perfluoropropionate is formed first [5], which then reacts with HFP:



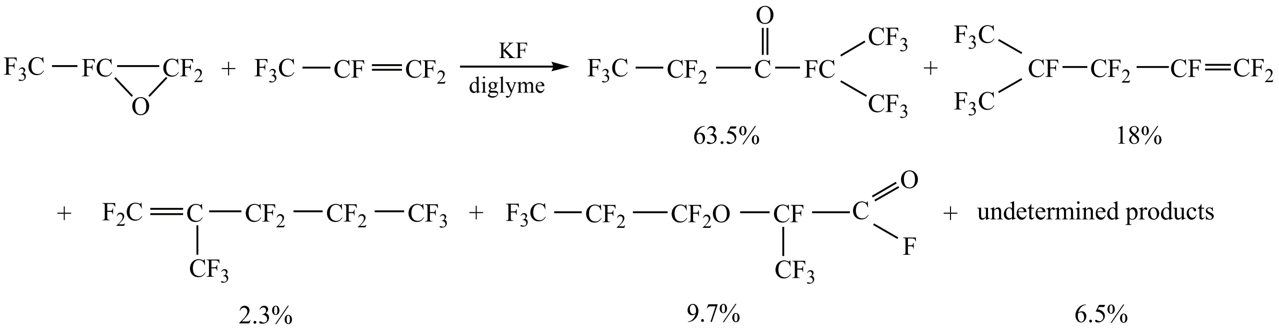
Therewith presumably, the rate of perfluoropropionate formation is much higher in both cases than that of interaction of perfluoropropionate with HFP. Ketone synthesis of HFPO and PFAF occurs without visible differences in the process rate, composition, and ratio of the products: this fact is a unique case of interchangeability of raw materials. Further this made it possible to combine the isomerization of HFPO and ketone synthesis [9].

In the study of the ketone synthesis it was found that its output depended strongly on the water content in the solvent. The dependence of the ketone output on the water content in acetonitrile (water content in CsF, KF $c \leq 0.001$ wt%) is shown below:

Water content in the solvent, wt%	0.01	0.02	0.04	0.06	0.09	0.16	0.18	>0.18
Yield of perfluoroethyl isopropyl ketone , wt%	63.5	61.5	60.2	54.3	45.0	34.0	28.5	22

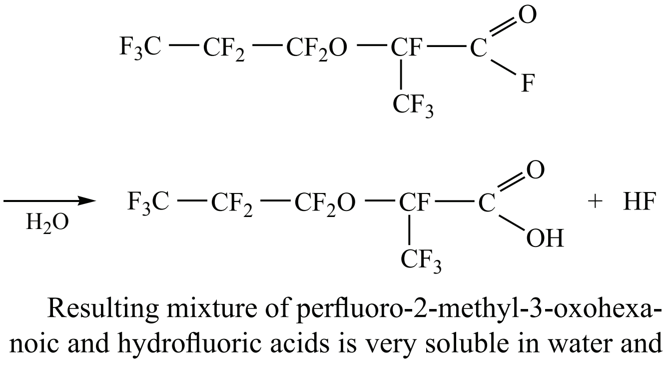
The output reducing is explained by a formation of an MF·HF complex, which has no catalytic activity. This complex was formed in the interaction of PFAF with water as can be seen from the data.

The process of ketone obtaining is accompanied by the formation of by-products, mainly, 2-perfluoromethylpentene (HFP dimer) and perfluoro-2-methyl-3-oxahexanol fluoride (HFPO dimer). Their total content in the crude can reach 30%. Synthesis of HFP and HFPO dimers was carried out in conditions similar to those for the ketone [10]. Along with them, 6.5% of high-boiling compounds were formed. The discharged catalyst were of yellow-brown color, its dissolving in water gets resinous film. These compounds encapsulate crystals of metal fluoride reducing its catalytic activity by 30–50% that makes necessary to use a freshly prepared catalyst in each synthesis:



The ketone isolation by distillation is ineffective since boiling point of the ketone, HFP, and HFPO dimmers are 48.5, 46–51, and 56°C, respectively.

The HFPO dimer as well as all fluorides of perfluorocarboxylic acid reacts vigorously with water and can be easily removed from the reaction mixture by hydrolysis [11]:



Resulting mixture of perfluoro-2-methyl-3-oxohexanoic and hydrofluoric acids is very soluble in water and separated from the crude ketone, practically insoluble in water. It should be noted that aqueous solution of these acids is highly corrosive. This fact should be accounted for in the process designing. Alkaline solutions can be applied for reducing the corrosivity, e.g., solutions of soda (or baking soda), but hydrolysis of the most ketone becomes notable in alkaline environment:

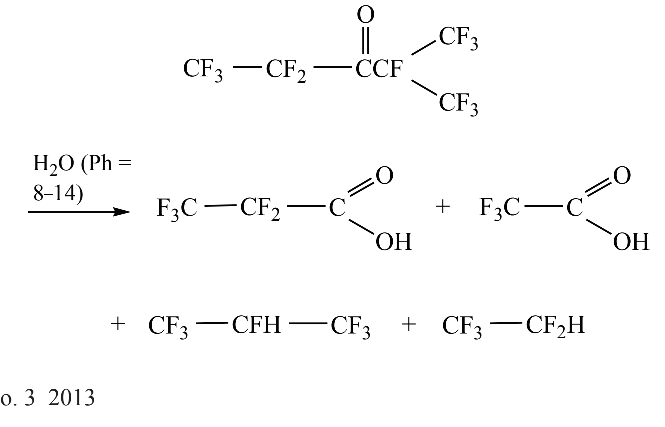
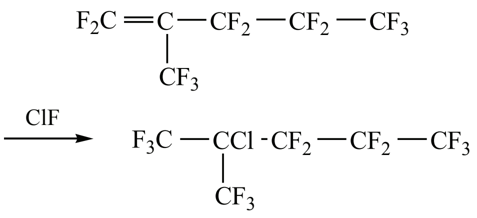
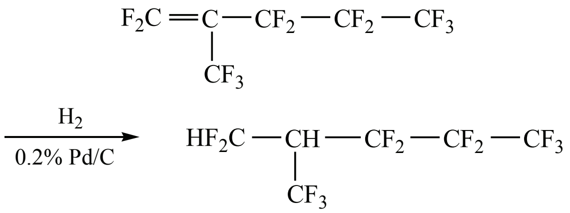


Figure 1 shows results of the ketone hydrolysis study in aqueous solutions of different acidity.

For the separation of the ketone from HFP dimer [11], the latter can be turned into high-boiling compounds, e.g., into 2-perfluoromethyl-2-chloroperfluoropentane (bp 83°C) by reaction with monofluorochlorine or into 1,2-dihydro-2-perfluoromethylpentane (bp 71°C) by hydrogenation on palladium catalyst:



$$F_2C{=}\underset{\substack{|\\ CF_3}}{C}{-}CF_2{-}CF_2{-}CF_3 \xrightarrow{ClF} F_3C{-}\underset{\substack{|\\ CF_3}}{CCl}{\cdot}CF_2{-}CF_2{-}CF_3$$



$$F_2C{=}\underset{\substack{|\\ CF_3}}{C}{-}CF_2{-}CF_2{-}CF_3 \xrightarrow[0.2\%\ Pd/C]{H_2} HF_2C{-}\underset{\substack{|\\ CF_3}}{CH}{-}CF_2{-}CF_2{-}CF_3$$

These compounds are relatively easily separated from the ketone by distillation. Both reactions proceed quantitatively at 20°C and the ketone remains practically unchanged. In view of the high aggressiveness of monofluorochlorine and the need for creation of its preparation unit we selected hydrogenation of HFP dimer. Hydrogenation was carried out in a vertical reactor filled with activated carbon SKT-6 coated with a palladium.

On the basis of the research a pilot plant of ketone production with output of 5 kg day^{-1} was constructed with the target product purity 99.6–99.95%. The plant included the following stages: preparation of the starting mixture, the catalyst and solvent charging, the ketone synthesis, hydrolysis of HFPO dimer, drying, hydrogenation of HFP dimer on a palladium catalyst, and distillation of the crude.

Although the method for the ketone synthesis in aprotic polar solvents and developed ways of its cleaning allow obtaining the ketone of 99.9% purity there exist significant shortcomings that impede implementation of this method on an industrial scale:

– The need for drying solvents to a residual water content of less than 0.08 wt%;

– The fresh catalyst and solvent are required in each synthesis;

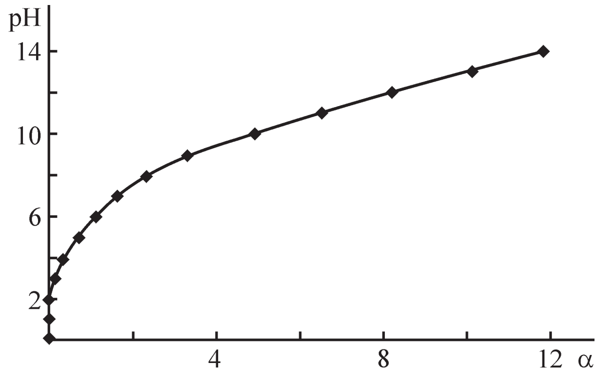


Fig. 1. Hydrolysis of the ketone at 20°C. The volume ratio of ketone : solution = 1 : 5, stirring speed 350 rpm. (α) degree of hydrolysis of PFEIK (%).

– A relatively low output of ketone: less than 63.5%;

– A large number of impurities of HFPO and HFP dimers: up to 30 wt%, necessitates including hydrolysis and hydrogenation units, respectively, for their separation;

– Cyclicity of the process and the need to operate under the pressure of 0.5–0.7 MPa;

– The need for disposal of large quantities of waste, including, possibly, toxic.

New alternative ways of the ketone synthesis should be developed due to the difficulties, which complicate and make the process expensive, and first the solvents should be eliminated. Thus, it should be created a highly selective catalyst, which would eliminate or at least significantly reduce the content of impurities, especially HFPO and HFP dimers possessing similar boiling points. A number of fluorine-containing compounds, as well as activated carbons and compositions based on them were tested as catalysts. The results are listed in Table 1.

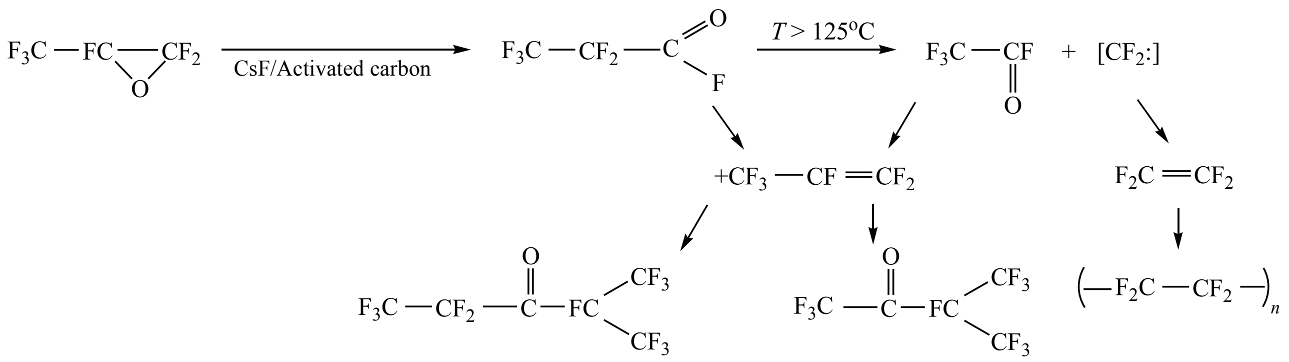
As can be seen from Table 1 catalyst CsF supported on activated carbon BAU-2, K-3, SKT-6 and prepared at 200°C demonstrates the best results. As the production of carbon AG-3 and SKT-6 is currently suspended and carbon BAU-2 is widely used and relatively cheap product, further research has conducted on activated carbon BAU-2. This catalyst significantly reduced the formation of by-products, especially HFPO and HFP dimers and allowed carrying out the process at 130°C with the output of up to 92% [12]. Use of a catalyst KF together with CsF, deposited on activated carbon, may reduce the concentration of expensive CsF and increases the ketone content in the raw material [13].

At the same temperature, the isomerization of HFPO into PFAF occurs.

Table 1. Catalytaic methofd of perfluoroethyl isopropyl ketone symthesis

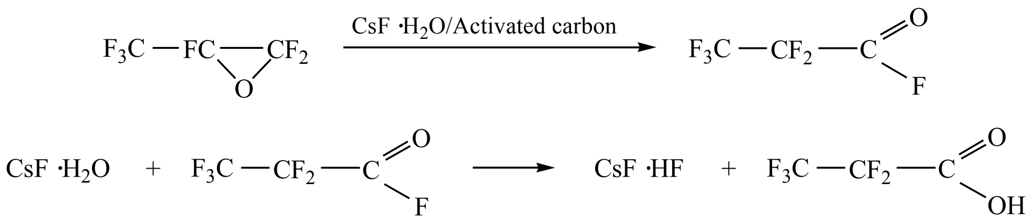
Catalyst	T, °C	Impurities content, wt%			Content of the ketone in the raw material	Ketone yield
		low-boiling acidic	perfluoro-2-methyl-3-oxahexanol fluoride	2-perfluoro methyl pentene	wt%	
CsF	130	14.8	0.19	0.05	85.0	12.4
	180	30.29	0.21	0.1	69.4	13.8
CaF_2 + NaF + KF	130	20.8	0.64	0.06	78.5	21.6
CaF_2 + NaF + CsF	130	10.3	0.6	0.1	89.0	77.6
Activated carbon BAU-2	130	5.6	15.8	5.1	73.5	64.0
	160	19.0	16.5	5.9	58.6	52.0
Activated carbon SKT-6	130	5.6	15.7	5.0	73.7	64.2
KF on activated carbon BAU-2	130	25.5	1.2	0.8	72.5	62.0
	160	28.0	1.2	0.2	70.6	60.3
KF on activated carbon BAU-2	130	24.1	1.2	0.2	74.5	62.6
2% CsF on activated carbon BAU-2	130	5.9	0.5	0.1	93.5	91.1
5–20% CsF on activated carbon BAU-2	130	5.8	0.1	0.05	94.0	92.0
	160	13.9	0.1	0.05	86.0	83.0
5–20% CsF on activated carbon SKT-6	130	5.6	0.1	0.05	94.3	92.2
KF + CsF (10% KF + 10% CsF) on activated carbon BAU-2	120	0.15	0.47	0.08	99.3	92.0

However, further study showed, that at this temperature degradation and polymerization are accelerated and an efficiency of the catalyst and, thus, the ketone yield decrease:



The resulting polymer (PTFE) blocks the nucleophilic sites of the carbon surface of the catalyst and significantly lowers (by 40–55%) its catalytic activity. Such catalyst allows operation up to 200 hours.

The catalyst structure was studied by electron probe microanalysis. It was found that the catalyst prepared at 200°C contains a complex $CsF \cdot H_2O$, which in the course of isomerization of HFPO into PFAF turns into complex $CsF \cdot HF$ possessing no catalytic activity:



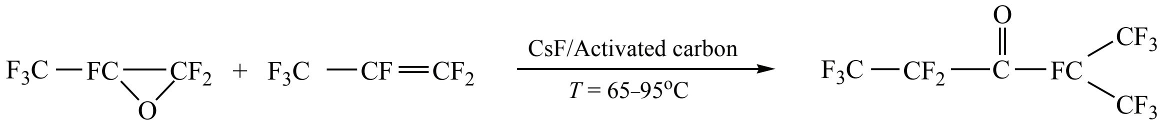
Further investigation was required for developing a catalyst effective at low temperatures, providing conversion 99% or more, and maintaining activity for more than 200 hours. The catalyst activated at 320–350°C under vacuum with periodic nitrogen purging, does not contain this complex since it is decomposed:

$$CsF \cdot HF \xrightarrow{T = 320\text{–}350^{\circ}C} CsF + HF\uparrow$$

Results of X-ray microanalysis are shown in Table 2.

In addition, an alternation of nitrogen purge of the catalyst with evacuation at 320–350°C contributes to dispersing CsF crystals to less than 100 nm, and submit the catalyst to the surface of the active sites of activated carbon that significantly increases its catalytic efficiency. A technique of activation of the catalyst was developed. Obtained catalyst retains catalytic activity for 800 hours of operation, reduces the temperature of the ketone synthesis (from 130 to 65–95°C) and isomerization of HFPO into acid fluoride (from 120–130 to 45–60°C), also the formation of by-products is reduced.

Micrographs of CsF catalyst samples prepared at different temperatures and supported on activated carbon BAU-2 are shown in Fig. 2. Figure 2 demonstrates that in the catalyst obtained at 350°C CsF crystals are placed on the catalyst surface and not inside as in sample no. 1. The high efficiency of CsF catalyst on activated carbon enables conducting the ketone synthesis by interaction of HFPO with HFP in the tubular reactor at sufficiently high rates of the process at 65–95°C with the yield of upto 95%:



Experimental data are listed in Table 3.

In examination of macrokinetics of the interaction of HFP with HFPO or PFAF it was found that a calculated activation energy was 7.683 and 7.185 kJ mol^{-1} K^{-1}, respectively. Its value is consistent with the ordinary values of heats of adsorption of substances on porous catalysts. This indicates that the reaction is controlled by the adsorption step of the initial reagents. The proximity of the

Table 2. Results of X-ray microanalysis

Activation temperature, °C	Content, wt%					Cs/F	Formula[a]
	S	K	Ca	Cs	F		
200	0.2	0.3	0.7	5.2	1.5	3.5	CsF·HF
320–350	0.1	0.4	0.5	6.3	0.9	7.0	CsF

[a] Correspond to the obtained stoichiometric ratio.

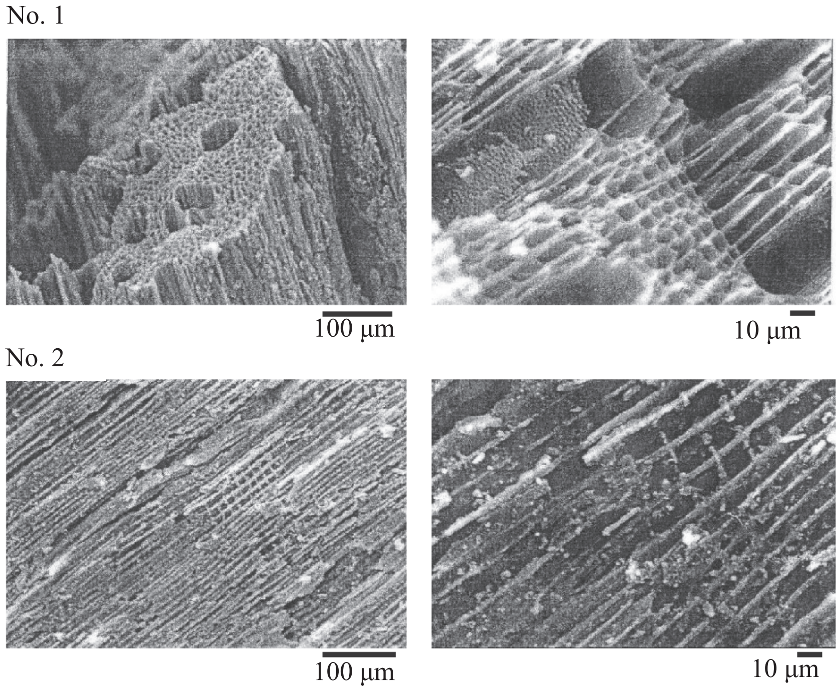


Fig. 2. Micrographs of catalyst samples prepared at 200°C (no. 1), 350°C (no. 2).

activation energy of interaction of hexafluoropropene with both HFPO and PFAF confirms that both processes are interchangeable and proceed in the same conditions (temperature, contact time, conversion, and composition of raw material).

A mechanism of interaction proceeding through the formation of intermediate complex (cesium perfluoropropionate), which then reacts with HFP forming the ketone, was suggested based on the studies.

According to the results of kinetic studies a design and specific performance of the reactor for the ketone production were calculated that allowed designing and constructing an industrial reactor for the product obtaining at the pilot plant of FSUE RSC “Applied Chemistry.”

Since the process proceeds with a decrease in a specific volume it is technologically appropriate to reduce a reaction volume in the course of the reaction: in this case vortex flows are reduced and side processes decreases [14]. Implementation of the device, which automatically reduces the volume upon the reaction course, is possible when the process occurs in a flow conical reactor, whose area of an inlet cross section is about twice the outlet.

Implementation of the advantages of the conical reactor under industrial conditions was not possible: a straight flow-through device was used in the development of the technology, however, it was successfully used to study the kinetics of the reaction [15, 16].

Measurements showed that the isomerization of HFPO into PFAF proceeds with heat release (65.8 kJ mol^{-1}). In order to maintain the required temperature an isomerization reactor was constructed, which was a pipe filled with a catalyst. Inside this reactor there was a heat

Table 3. Synthesis of perfluoroethyl isopropyl ketone on the developed catalyst CsF/activated carbon

Parameter of the process		The amount of impurities, wt %				Ketone content	Ketone yield
T, °C	*P*, MPa	low-boiling	HFP dimer	HFPO dimer	high-boiling	wt%	
65–95	0.2–0.3	1.91	–	0.06	0.03	98	95
>95	0.2–0.3	5.9	–	0.06	0.05	94	91

exchanger for removing from the reaction zone the heat released.

On the basis of the research on the experimental plant of FSUE RSC "Applied Chemistry" the pilot plant of the ketone synthesis was constructed, comprising the following steps: preparing a mixture of HFPO–HFP, isomerization and synthesis of ketone, washing of raw material with water, and rectification. The methods of the ketone synthesis were patented [9, 12, 13, 16].

EXPERIMENTAL

Analysis of the product, intermediates was carried out by GLC on a Crystal 2000M chromatograph with a thermal conductivity detector, column silohrom + 20% α,α,α-trisbetacyanethoxyacetophenone, l = 2 m. IR spectra were recorded on an infrared spectrophotometer IRPrestige-21 (Shimadzu), the spectral range of 4000–400 cm^{-1}, the ^{19}F NMR spectra, on Spektrospin AM 500 (Bruker).

Hexafluoropropene oxide produced by JSC "Galopolimer," target product content 99%, content of HFP 0.4%. Hexafluoropropene produced by "HaloPolymer," target product content 99.9 wt% and more.

CsF and KF of analytical purity were dried in a platinum crucible at 500°C for 6 h, cooled in a desiccator, ground, and finally dried in vacuum at 250°C to a residual moisture content of 0.001 wt% or less. Solvents (diglyme, acetonitrile) were dried by calcined zeolite of CaA grade to a residual water content of 0.01 wt% or more.

Synthesis of perfluoroethyl isopropyl ketone in polar aprotic solvents. In a 18 L cylindrical reactor made of steel 12Kh18N10T equipped with a Gopher valve, manometer, magnetic stirrer, loading bubbler, and electrical heater, 5.3 L of acetonitrile or diglyme was charged and then 250 g of dry KF was added. Afterwards the stirrer was switched on and 85.52 g of HFPO was fed to the reactor from a cylinder (catalyst activation).

The feed of HFPO was monitored by the cylinder weight. After HFPO feeding completion the reactor content was stirred for 2 h without heating.

The reactor was evacuated to a residual pressure of 50 mm and then heated to 65–80°C and the mixture of HFP and HFPO was fed with constant stirring in a molar ratio of 1.03 : 1 for 6 hours avoiding an increased pressure above 0.7 MPa. After addition of the mixture in an amount of 8.3 kg the reactor content was stirred for 2 hours. Then reactor was cooled, pressure was reset, the reaction products were settled and separated into two layers. The bottom layer, crude ketone and fine potassium fluoride, was directed to filtration from the catalyst, followed by removal of impurities of HFPO dimer. The top layer, diglyme, was collected in the receiver and in the course of its accumulation its recovery (distillation) was performed: purified diglyme was for re-use.

Purification of perfluoroethyl isopropyl ketone from impurities of perfluoro-2-methyl-3-oxahexanol fluoride. *Alkaline hydrolysis.* The reaction mass (8.2 kg) was placed in a plastic container of 12 L and it was filled with 25% caustic solution at a ratio of 1 : 2 and stirred for 2 hours. Purifying ketone from impurities of HFPO dimer was carried out at room temperature. Gases formed were released. The reaction monitoring was carried out by chromatography. Weight of the reaction mixture after hydrolysis was 6.64 kg, the composition was: ketone 66.8%, HFPO dimer not present , dimer HFP 23.1%, high-boiling impurities 10.1%.

Crude perfluoroethyl isopropyl ketone purified from HFPO dimer was separated on a funnel, weighed, and analyzed, and then sent to the purification step from the HFP dimer.

Acidic hydrolysis. In a reactor with stirrer made of Teflon 4, the reaction mass (8.2 kg) after a synthesis step and water were charged in a ratio of 1 : 5. In the hydrolysis the reaction medium becomes acidic to pH 2–3. The process was carried out with constant stirring for 6 h. The reaction mixture weight after hydrolysis was 7.3 kg, the composition was: PFEIK 71.7%, HFPO dimer not present, HFP dimer 19.2%, high-boiling impurities 9.1%. Raw ketone was separated from the water and directed to the removal of impurities of HFP dimer.

Purifiaction of perfluoroethyl isopropyl ketone from impurities of 2-perfluoromethyl pentene. *Chloro-fluoridation.* In the reactor (a vertical column of a 0.75 m length and 0.03 m diameter equipped with a cooling jacket and filled with nickel Raschig rings) the raw ketone containing 19.2 wt% of HFP dimer was dosed by a measuring tank-metering at a rate of 400–530 g h^{-1}. Simultaneously to the bottom of the column ClF (97 wt% purity) obtained by the method described in [17] was fed at a rate of 5–6.5 L h^{-1} at a temperature in the jacket –5…–10°C. The raw ketone effluent from the column was collected in a receiver. The reaction was monitored by chromatography. The composition of the reaction mixture after chloro-fluoridation and washing with baking soda was:

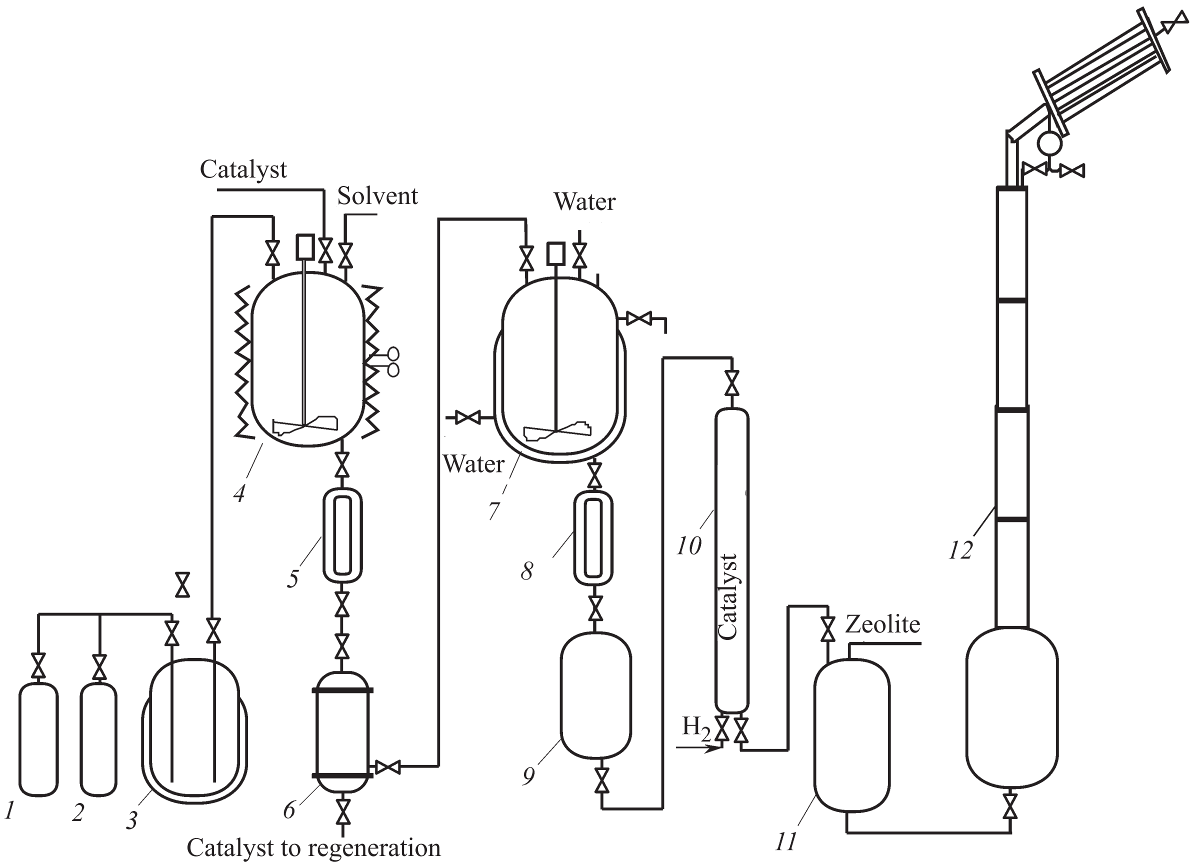
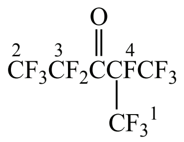


Fig. 3. The laboratory setup for perfluoroethyl isopropyl ketone in aprotic polar solvents. (*1*) Cylinder HFP; (*2*) cylinder HFPO; (*3*) mixer, (*4*) reactor, (*5, 8*) separators, (*6*) filter, (*7*) hydrolysis unit, (*9*) collection, (*10*) hydrogenation reactor, (*11*) drier, (*12*) fractionation unit.

ketone 68.2%, HFP dimer not present, $C_6F_{13}Cl$ 19.2%, high-boiling impurities 12.6%. The isolated product of chloro-fluoridation ($C_6F_{13}Cl$) was of boiling point 83°C, which corresponded to the data in [18].

Hydrogenation. In a reactor (a vertical column of a 0.8 m length and 0.25 m diameter equipped with a cooling jacket, measuring tank-metering, and filled with a catalyst (Pd 0.2%/BAU-2), raw ketone containing 19.2% of HPF dimer was dosed at the rate of 350–600 g h^{-1}. Simultaneously to the bottom of the column hydrogen was fed at a rate of 4.2–6.5 l h^{-1} at a temperature in the jacket –5…–10°C. The raw ketone effluent from the column was collected in the receiver. The reaction was monitored by chromatography. The composition of the

Table 4. ^{19}F NMR spectrum

Structure of compound	Carbon atom no.	$-\delta_{CCl_3F}$, ppm	Number of nuclei F	Multiplet	$J_{F^*-F^{**}}$, Hz
 $\overset{2}{C}F_3\overset{3}{C}F_2\overset{\overset{O}{\|}}{C}\underset{\underset{CF_3^{1}}{\mid}}{\overset{4}{C}F}CF_3$	1	72.5	6	d.t	$F^1–F^4$ 6.8; $F^1–F^3$ 2.9
	2	80.8	3	d	$F^2–F^4$ 6.4
	3	119.1	1	d.q	$F^3–F^4$ 28.7; $F^3–F^1$ 2.8
	4	189.2	1	t.sx	$F^4–F^3$ 28.8; $F^4–F^1$ 6.8

reaction mixture after hydrogenation was: ketone 71.3%, HFP dimer not present, $C_6F_{12}H_2$ 19.2, high-boiling impurities 9.5. The isolated product of hydrogenation ($C_6F_{12}H_2$) was of boiling point 71°C, which corresponded to the data of [18]. After completion of the hydrogenation the raw ketone (5.5 kg) was dried over calcined zeolite of CaA grade, then it was distilled. The experimental setup is shown in Fig. 3. Ketone yield of purity 99.9 wt% was 4.9 kg.

Identification of obtained perfluoroethyl isopropyl ketone [$CF_3CF_2C(O)CF(CF_3)_2$]. There is a characteristic absorption band for ketones in the IR spectrum (1780 cm^{-1}). Mass spectrum, *m/z*: 69 (CF_3 +), 100 (C_2F_4 +), 119 (CF_3CF_2 +), 147 [$CF_3CF_2C(O)$ +], 169 [$(CF_3)_2CF+$], 197 [$(CF_3)_2CFC(O)+$]. ^{19}F NMR spectrum of the obtained compound is shown in Table 4.

Production of perfluoroethyl isopropyl ketone by the direct catalytic interaction. Before starting of the operation in the mixer mixture of HFP and HFPO in a molar ratio of 1.03 : 1 was prepared. An amount of loaded components was controlled by weighing the cylinders.

Liquid mixture of HFP and HFPO was fed at a constant rate to an evaporation feeder, a pipe of a 450 mm length and 36 mm diameter, which was heated to 40°C, afterwards the mixture entered the isomerization unit (Fig. 4). The isomerization unit was a heated cylindrical container with a two-piece heating of a 600 mm length and 76 mm diameter with a supply of the reaction mixture, withdrawal of the reaction products, and water supply to the heat exchanger built into the center of the isomerization unit to remove heat from the reaction zone. In the isomerization unit isomerization of PFAF into HFPO and partial interaction of PFAF with HFP with the formation of the ketone occur. The reaction mixture from the isomerization unit was directed to a main synthesis reactor, which was a cylindrical container with the two-piece heating of a 1500 mm length and 70 mm diameter.

In the reactor and isomerization unit the prepared catalyst was preloaded (cesium fluoride supported on activated carbon BAU-2). HFPO was fed up to 0.3 MPa

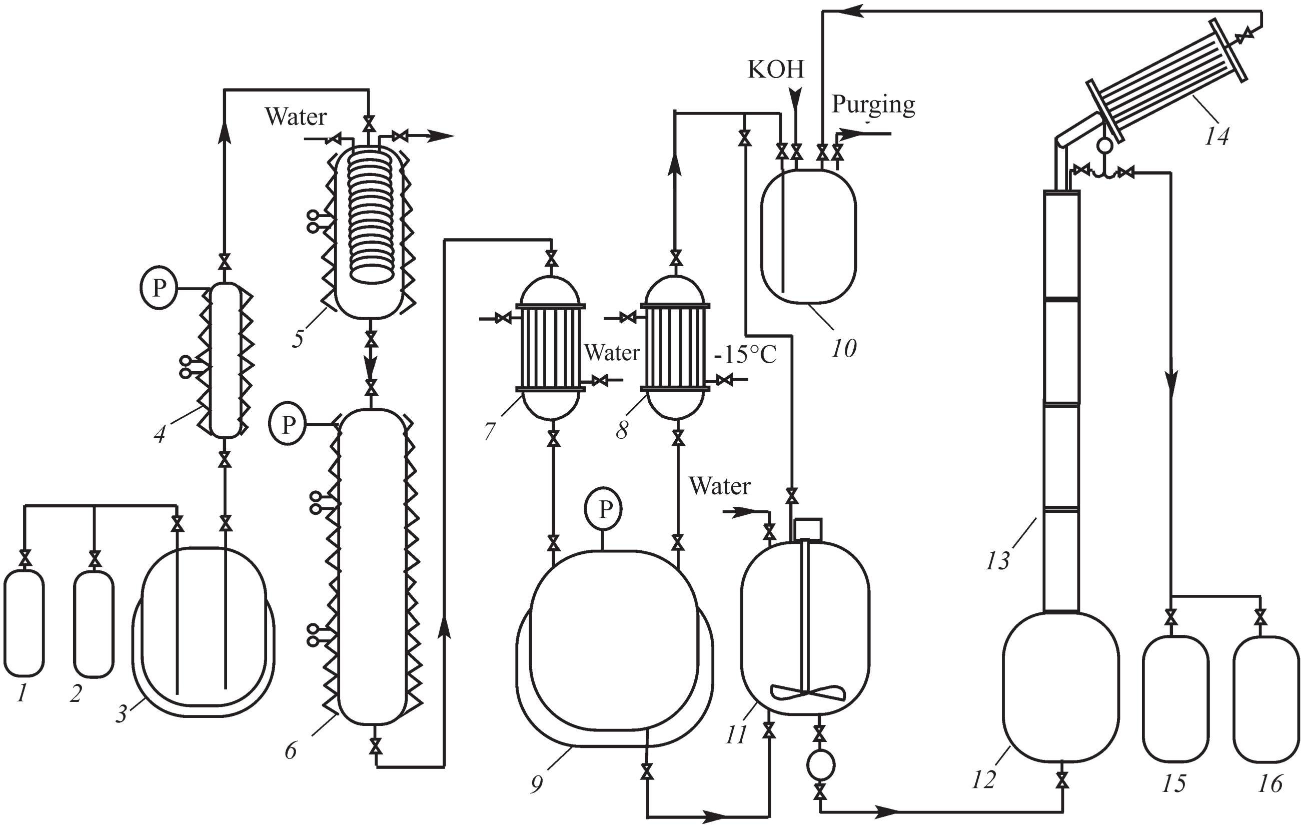


Fig. 4. The laboratory setup for perfluoroethyl isopropyl ketone in a flow mode. (*1*) Cylinder HFPO; (*2*) cylinder HFP; (3) Mixer, (*4*) evaporator dosing, (*5*) isomerization unit, (*6*) reactor with two sectional heating, (*7, 8*) heat exchange devices, (*9*) receiver of raw, (*10*) absorber, (*11*) apparatus for cleaning from acid impurities, (*12*) cube of column, (*13*) distillation column, (*14*) reflux, (*15*) a receiver of intermediate fraction, (*16*) a receiver of the finished product.

and kept for 2 hours for activation the catalyst.

The resulting mixture was fed at a rate of 1.2 kg h^{-1} at a temperature of 80–95°C and a pressure of 0.25–0.3 MPa for 7 h. The reaction product was collected in a receiver cooled to –10°C. The reaction products were weighed (8.05 kg), analyzed by chromatography, and directed to the washing step from acid impurities in the device with a stirrer. Washing was performed for 2 h at a ratio of crude PFEIK : water = 1 : 4. After washing the raw ketone (7.8 kg) was directed to the distillation.

For distillation a steel distillation column was applied filled with nichrome helices. A column height was 2 m; outer diameter, 0.052 m; a volume of a cube, 18 dm^3. A column reflux was cooled to –15…–20°C. Pressure on the column was maintained from 0 to 0.05 MPa. The temperature in the cube must be controlled so as to ensure an optimal mode of the column.

In the laboratory pilot plant 60 kg of PFEIK samples were obtained with basic substance content 99.99%.

Determination of heat of isomerization. Insulated dewar with evacuated walls was filled with 25% solution of sodium chloride (bp 107°C). Liquid mixing was carried out with a magnetic stirrer. Inner temperature measurement was performed by a mercury thermometer with an accuracy of ±0.05°.

The calorimeter was previously calibrated in the operating temperature range (T = 60–80°C) with the help of a spiral heater of variable power, which is fixed. (Evaluation of heat loss to the environment was made relative to the rate of temperature falling in a saline solution pre-heated to 80°C after disconnecting the heat source. Cooling rate did not exceed 0.5° h^{-1} that corresponded to a power loss $Q_{av} = 0.01(T - T_{av})$, W, and did not exceed 10% of the power dissipation).

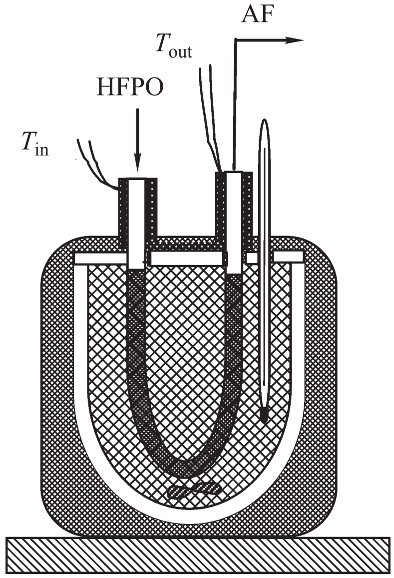


Fig. 5. Determination of heat effect of the isomerization of HFPO to acid fluorides.

Then, the starting product, HFPO, was passed through the reactor also placed in a liquid medium. The reactor was a U-shaped pipe filled with the catalyst CsF deposited on activated carbon (pre-dried at T = 250° C and activated by passing the initial product at T = 80–90°C).

HFPO was passed through the reactor for 4.75 h at a constant flow g = 39.58 g h^{-1}, and every 15 minutes a temperature increase of liquid due to heat release was recorded.

In the course of the isomerization of HFPO the temperature of aqueous solution increased from initial T_0 = 60°C to 71.7°C.

In the process the composition of products at the reactor outlet was analyzed several times. Chromatographic analysis showed that the isomerization during product residence in the reactor proceeded with a conversion of above 99% and with a fairly good selectivity (> 90%). The main part of the laboratory plant is shown schematically in Fig. 5.

The determined heat of reaction of HFPO into acid fluoride in view of an error was $Q_r = 65.78 \pm 3.35$ kJ mol^{-1}.

CONCLUSIONS

Synthesis of perfluoroethyl isopropyl ketone by the interaction of perfluoropropionic acid fluoride with hexafluoropropene and of hexafluoropropene oxide with hexafluoropropene was investigated. The interchangeability of hexafluoropropene oxide and perfluoropropionic acid fluoride was demonstrated.

It was shown that the yield of the product using the aprotic polar solvents depends on the preparation of the catalyst and solvents and does not exceed 63.5%. The methods of isolation of perfluoroethyl isopropyl ketone from the reaction mixture by hydrolysis of the reaction mixture and subsequent hydrogenation on the catalyst (palladium) supported on activated carbon, were developed, which allowed obtaining the target product with a purity of 99.95 wt% and content of 2-perfluoromethyl pentene no more than 20 ppm.

An efficient method of the direct catalytic production of perfluoroethyl isopropyl ketone by interaction of hexafluoropropene with perfluoropropionic acid fluoride or hexafluoropropene oxide.

An efficient highly selective catalyst cesium fluoride deposited on activated carbon BAU-2, AG-3 or SKT-6 was developed in an amount of 5–20 wt% of carbon. The catalyst enables production of perfluoroethyl isopropyl ketone at 65–95°C and provides operation time up to 800 hours.

The macrokinetics of the interaction of hexafluoropropene with both perfluoropropionic acid fluoride and hexafluoropropene oxide was examined, the optimal conditions of perfluoroethyl isopropyl ketone synthesis were established, the mechanism of interaction proceeding via alkali metal perfluoropropionate formation was suggested, the reactor for the pilot plant of production of perfluoroethyl isopropyl ketone was calculated.

The pilot setup for production of perfluoroethyl isopropyl ketone in the pilot plant of FSUE RSC "Applied chemistry" was designed and created.

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