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Perfluorinated Carboxylic Acids. Synthesis and Application.

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Dedicated to Professor Hermann-Josef Frohn on the Occasion of his 60th Birthday

In this article you will find data regarding perfluorinated carboxylic acids obtaining methods, in particular electrochemical fluorination of hydrocarbon derivatives in anhydrous hydrogen fluoride, perfluoroolefines and telomeric alcohols oxidizing, perfluoralkyliodides and carbon dioxide interaction in the presence of initiators. Some characteristics of perfluorinated carboxylic acids are discussed in this article. Using of these characteristics for creating of new semi-products, used for fluororganic synthesis is discussed here. Practical application examples of both perfluorinated carboxylic acids and semi-products based on them for creating of new generation fluorine materials are given in this article.

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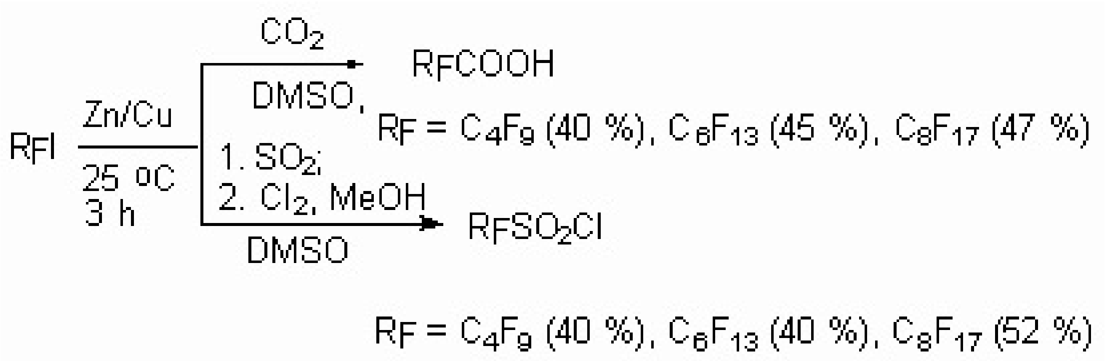
References

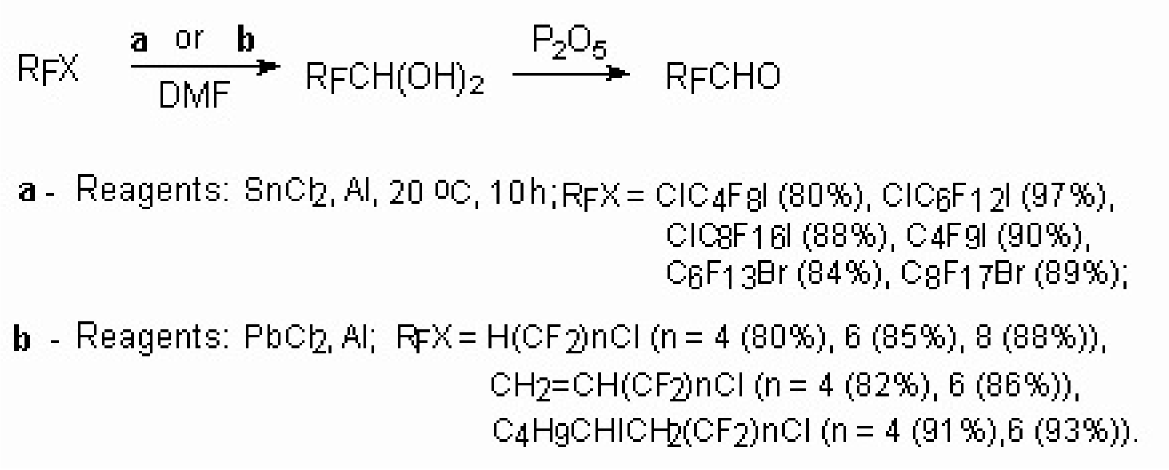
2.2.4. The transformations of perfluoroalkylhalogenides into perfluorocarboxylic acids under the initiators action.

Taking into account the availability of perfluoroalkylhalogenides, obtained in industry by telomerization of tetrafluoroethylene in the presence of galogenides sources, the great attention was paid to processes of their transformations to perfluorocarboxylic acids.

An interesting reaction was found at perfluoroalkyliodides, perfluoroalkylbromides and perfluoroalkylchlorides heating in DMF in the presence of bivalent tin ($SnCl_2$/Al) [85] or lead ($PbBr_2$/Al) compounds [87,88], promoted by aluminium: the terminal fragment of CF_2X was oxidized and perfluoroalkylaldehydes monohydrates were formed at that [85-88].



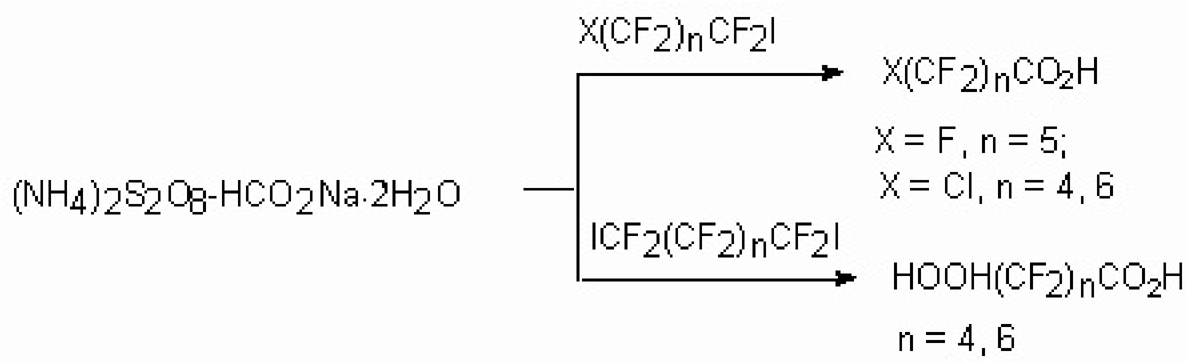
The reaction of perfluoroalkyliodides with CO_2 in the presence of Zn in DMSO is of interest, as a result of which perfluorinated carboxylic acid is obtained. Thus the interaction of $CF_3(CF_2)_7I$ with CO_2 in DMSO in the presence of zinc at 15 ^{o}C during 3 hours and after hydrolysis using aqueous NH_3 results in formation of $CF_3(CF_2)_7CO_2NH_4$ salt with the yield of 92 % [85-87]. The corresponding perfluoroalkylsulphochlorides are obtained in the analogous reaction with SO_2 with further oxidization of primary product using chlorine [87].

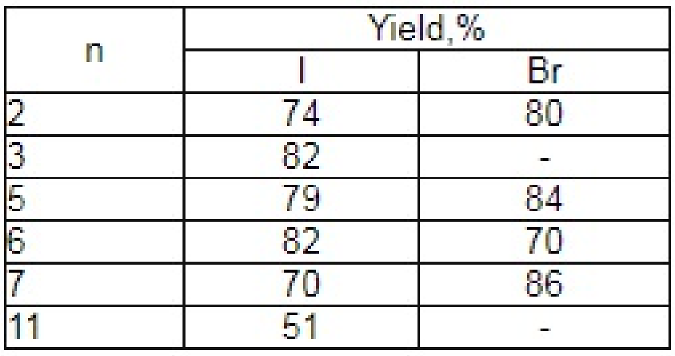


At oxidization of perfluoroalkyliodides R'I [R' = linear or branched cyclic perfluoroalkyl] using air oxygen in the organic dissolvent (alcohol) in the presence of catalyst (metallic cuprum) the corresponding perfluorocarboxylic acids RCOOH are formed [88]. For example, ethyl perfluorooctanoate is obtained out of perfluorooctyliodide and copper powder in ethanol at heating conditions at 50 ^{o}C during 12 hours (yield is equal to 87%).

Fluorine containing aliphatic mono- and dicarboxylic acids were obtained by interaction of perfluoroalkyliodides or bromides and CO_2 in the presence of complexes of VIII group transition metals with further hydrolysis of reaction products [89,90]. Thus, $CF_3(CF_2)_7CO_2H$ is isolated with the yield equal to 40 % in reaction of $CF_3(CF_2)_7I$ with CO_2 in DMF in the presence of $Pd(PPh_3)_4$ at 60 ^{o}C in autoclave with further hydrolysis. This points out the intermediate formation of perfluoroalkyl radical, which reacts with carbon dioxide.

It turned out, that using of rongalite- $NaHCO_3$ system in bipolar aprotic dissolvents (MeCN, DMF) in reaction with perfluoroalkyliodides and perfluoroalkylbromides, containing 3-12 carbon atoms ($Cl(CF_2)_nI$,where n = 4, 6, 8; $CF_3(CF_2)_nI$, where n = 5-7; $Cl(CF_2)_n$ NBr, where n = 4, 6) allows to obtain perfluorocarboxylic acid sodium salts with high yields (Table 3) [91-97]. This synthesis method of perfluorocarboxylic acids is much convenient compare to the known method of their obtaining, based on electrochemical fluorination and their derivatives.



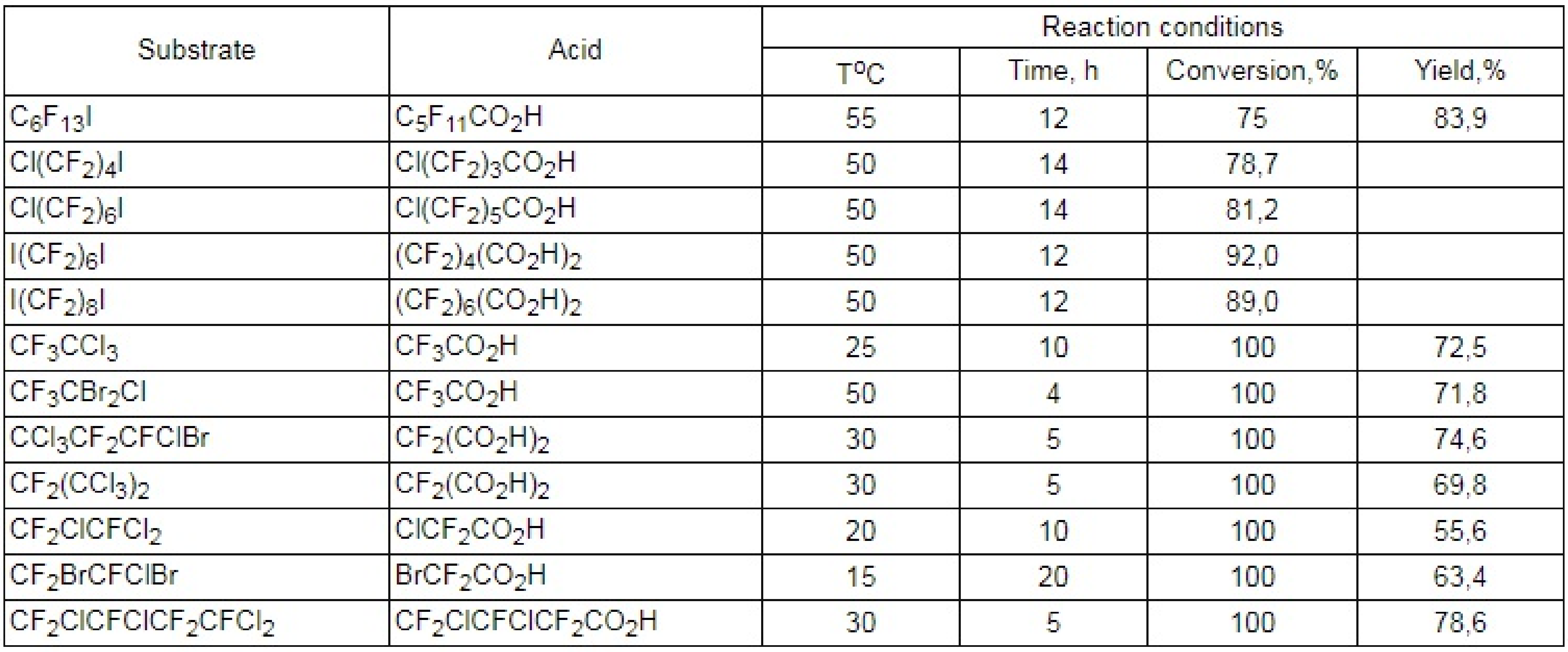


n	Yield,%	
	I	Br
2	74	80
3	82	-
5	79	84
6	82	70
7	70	86
11	51	-

If the process is carried out in the presence of alkenes and source of CO_2 then forming due to perfluoroalkyl radical addition according to multiply bond intermediate radical will react with CO_2 with forming of carboxylic acid. When using alcohol as dissolvent the product is corresponding ester of acid. Thus, $C_8F_{17}CH_2CH(Bu)CO_2Et$ was obtained with the yield equal to 67% by interaction of hex-1-ne and $C_8F_{17}I$. in the presence of K_2CO_3 and dichloro-*bis*-(triphenylphosphine)palladium in ethyl alcohol at 80 ^{o}C during 12 hours [98,99].

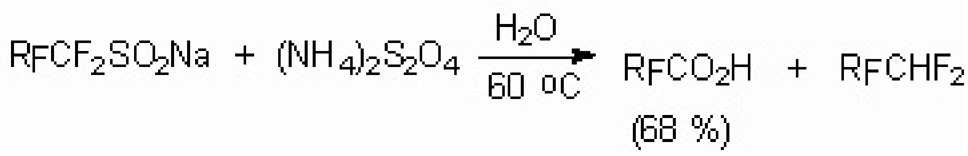
Such reductive-oxidative systems as $(NH_4)_2S_2O_8$-HCOOH-H_2O allow to transform selectively perfluoroalkyliodidesα,ω-diiodoperfluoroalkanes compounds like R_FCCl_3, $R_FCFBrCl$, R_FCBr_2Cl, R_FCFCl_2 and others into corresponding polyfluorocarboxylic acids and diacids (table 3) [101-103].

Table 3. *The transformation of polyfluoroalkylhalogenides into corresponding acids under the influence of $(NH_4)_2S_2O_8$-HCOONa*$2H_2O$ system in DMF [95].*

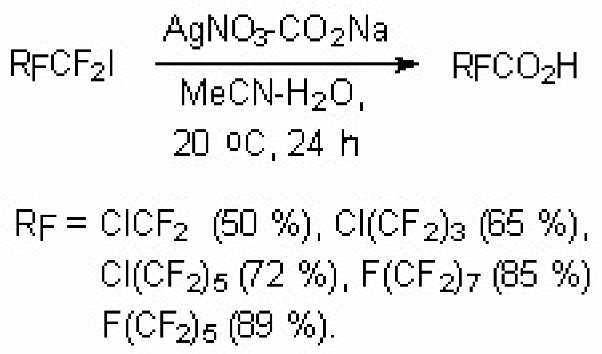


Substrate	Acid	Reaction conditions			
		T°C	Time, h	Conversion,%	Yield,%
$C_6F_{13}I$	$C_5F_{11}CO_2H$	55	12	75	83,9
$Cl(CF_2)_4I$	$Cl(CF_2)_3CO_2H$	50	14	78,7	
$Cl(CF_2)_6I$	$Cl(CF_2)_5CO_2H$	50	14	81,2	
$I(CF_2)_6I$	$(CF_2)_4(CO_2H)_2$	50	12	92,0	
$I(CF_2)_8I$	$(CF_2)_6(CO_2H)_2$	50	12	89,0	
CF_3CCl_3	CF_3CO_2H	25	10	100	72,5
CF_3CBr_2Cl	CF_3CO_2H	50	4	100	71,8
$CCl_3CF_2CFClBr$	$CF_2(CO_2H)_2$	30	5	100	74,6
$CF_2(CCl_3)_2$	$CF_2(CO_2H)_2$	30	5	100	69,8
$CF_2ClCFCl_2$	$ClCF_2CO_2H$	20	10	100	55,6
$CF_2BrCFClBr$	$BrCF_2CO_2H$	15	20	100	63,4
$CF_2ClCFClCF_2CFCl_2$	$CF_2ClCFClCF_2CO_2H$	30	5	100	78,6

Sodium salts of perfluoroalkansulphinic acid together with oxidation-reduction reagent $(CH_4)_2S_2O_4$ were used to obtain corresponding carboxylic acids [104-106].



Analoqously $AgNO_3$-HCO_2Na system catalyzes reaction in aqueous acetonitril [107].



1,1,1-trifluorotrichloroethan (CCl_3CF_3) can produce trifluoroacetic acid in the presence of different oxidizing agents (table 4) [102]. The reaction must go according to the following scheme [102].

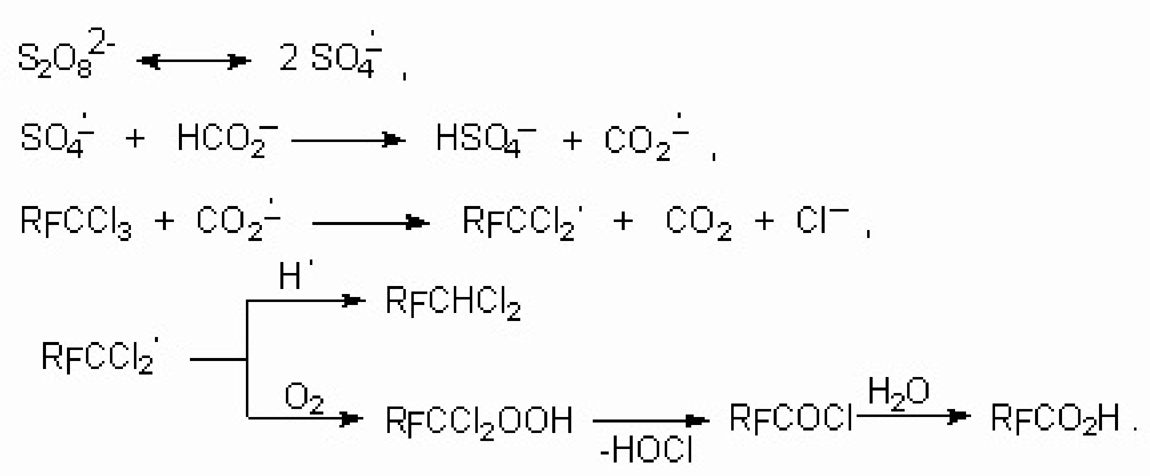


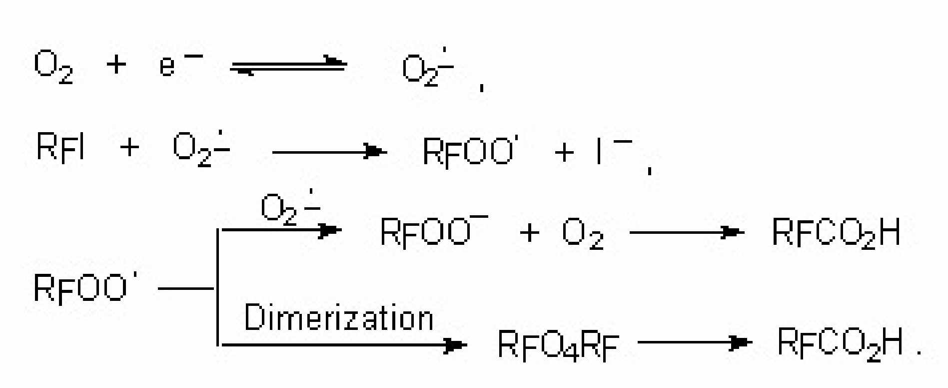
Table 4. *Conversion of CF_3CCl_3 into trifluoroacetic acid in the presence of different oxidation-reduction systems [102].*

System	Reaction conditions				
	Solvent	T°C	Time, hours	Conversion,%	Yield,%
$(NH_4)_2S_2O_8$ - HCO_2Na	DMF	25	10	100	95
H_2O_2 - $FeSO_4$	DMF-H_2O	40	0,5	100	100
$NH_4)_2S_2O_8$ - $Na_2S_2O_4$	DMF-H_2O	35	5	100	100
H_2O_2 - $Na_2S_2O_4$	DMF-H_2O	40	1	100	100
$KBrO_3$ - $Na_2S_2O_4$	DMF-H_2O	45	3	85	100
$(PhCO_2)_2$ - $PhNMe_2$	DMF	30	16	25	100

In this case the generation of polyfluoroalkyl radical under the influence of $CO_2^{\cdot -}$ anion-radical the key stage. It is known, that other anion-radicals can carry out such transformations. Thus it is stated [108,109], that corresponding acids (yields up to 50%) are formed out of perfluorobutyliodide, perfluorooctyliodide and α,φ-diiodoperfluorobutane under the influence of electrochemically generated molecular oxygen $O_2^{-\cdot}$ anion-radical.

$$CF_3(CF_2)_2CF_2I + 4e^- + O_2 \xrightarrow{DMF} CF_3(CF_2)_2COO^- + I^- + 2F^-$$

The reaction goes according to the following scheme:



In the presence of $(NH_4)_2S_2O_8$ the corresponding perfluoroalkancarboxylic acids are the products of reaction of perfluoroalkansulphinic acid sodium salt with alkenes along with compounds, possessing multiply bonds, that can be explained by hydrogenolysis C-Hal [104-106,108-110].

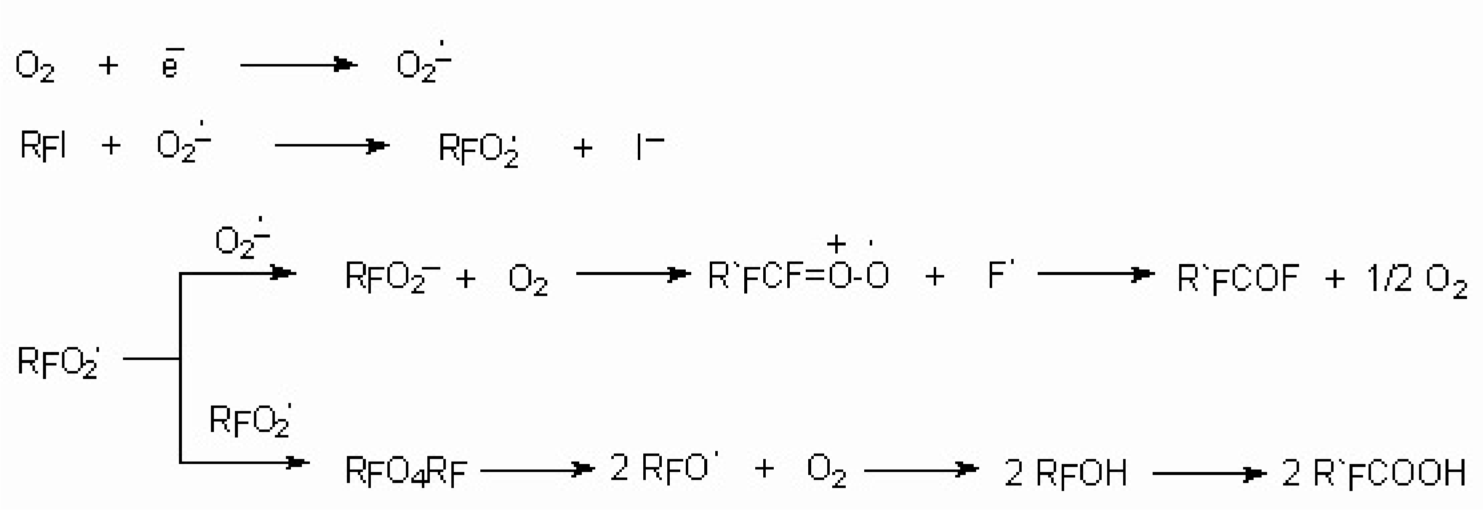
It should be noted, that for the first time this approach was realized for reactions of some aromatic compounds with perfluoroalkyliodides and equimole amount of peroxide. We can suppose, that optimal conditions for carring out of such reactions will be found and they will take their place in the processes of perfluoroalkylation using perfluoroalkyliodides.

The interaction of (*E*)- and (*Z*)-1,2-difluoro-1-iodalkens and (*E*) and (*Z*) β-difluoro-β-iodstiroles with carbon oxide in the presence of catalyst $Pd(PPh_3)_2Cl_2$ at 70-105 °C and in the presence of alcohol and trialkylamine form esters of carboxylic acids. (table. 5). It should be noted, that in these reactions the complete changing of configuration takes place.

Table 5. *The interaction of perfluoroalkenyliodides and carbone oxide in the presence of catalyst.*

Configuration	R	Product	T°C	Yield,%
Z	Bu^t	(*E*)-$Bu^tCF=CFCO_2Bu$	105	85
Z	Bu^{sec}	(*E*)-$Bu^{sec}CF=CFCO_2Bu$	105	92
Z	Ph	(*E*)-$PhCF=CFCO_2Bu$	105	89
E	Bu^n	(*Z*)-$Bu^nCF=CFCO_2Et$	85	33
E	Bu^n	(*Z*)-$Bu^nCF=CFCO_2Et$	95	82
Z	4-$MeOC_6H_4$	(*E*)-$MeOC_6H_4CF=CFCO_2Bu$	80	86
Z	4-CNC_6H_4	(*E*)-4-$CNC_6H_4CF=CFCO_2Bu$	80	96
Z	4-$CF_3C_6H_4$	(*E*)-4-$CF_3C_6H_4CF=CFCO_2Bu$	80	89
E	4-$MeOC_6H_4$	(*E*)-4-$MeOC_6H_4CF=CFCO_2Bu$	70	86

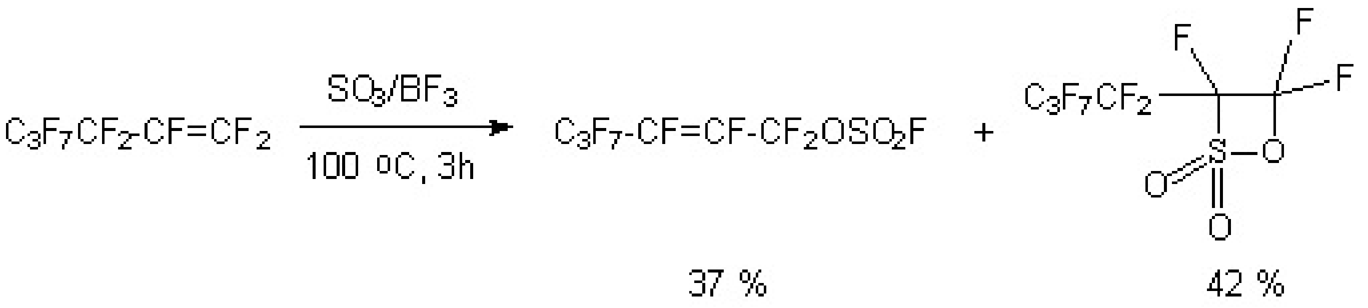
It is shown [107], that electrolysis of perfluorobutyliodide at carbon cathode in the presence of oxygen in dimethylformamide results in formation of perfluorobutanoic acid. In this process the key part plays forming at current action oxygen anion-radical, which influencing on perfluorobutyliodide produces $C_4F_9O_2$ radical.

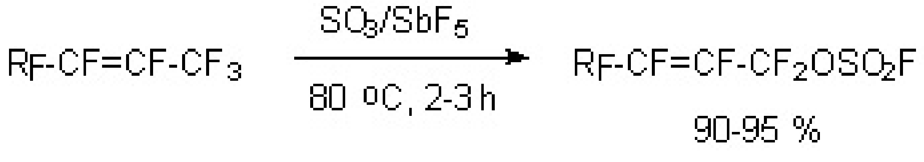


Perfluoroalkyliodides are oxidized by oxygen in the presence of catalysts (copper) in the medium of organic solvent up to perfluorocarboxylic acids [110]. For example, perfluorooctyliodide in ethyl alcohol in the presence of metal copper at 50 ^{0}C in 12 hours results in formation of ethyl perfluorooctanoate with the yield of 87%. [110].

2.2.5. Perfluorocarboxylic acids synthesis out of other compounds classes.

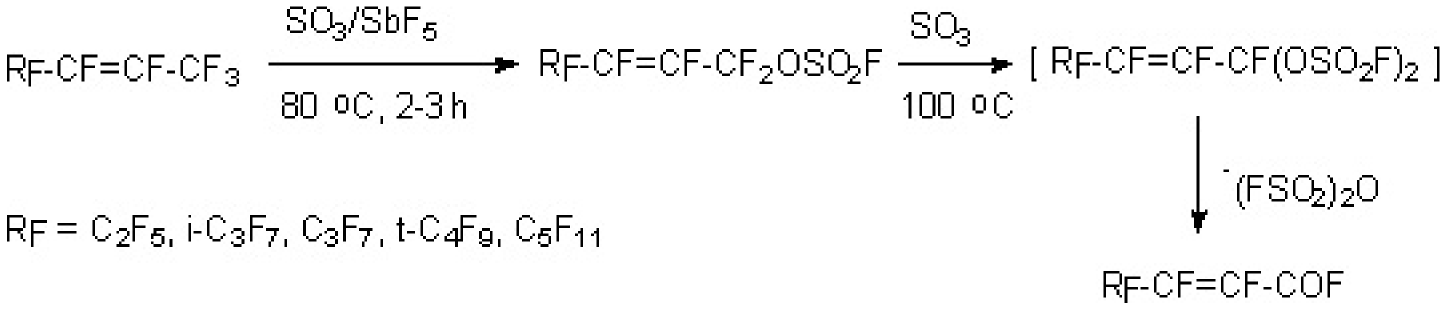
Terminal fluoroolefines of aliphatic series in non-catalytic reaction with SO_3 form on β-sultones, while at catalysis using boron compounds (BF_3) the formation of unsaturated fluorosulphate in big amounts is observed [112]. At the same time the catalysis of SbF_5 reactions of internal perfluoroolefines with SO_3 produces exclusively unsaturated fluorosulphates [113,114].





$R_F = C_2F_5, i\text{-}C_3F_7, C_3F_7, t\text{-}C_4F_9, C_5F_{11}$

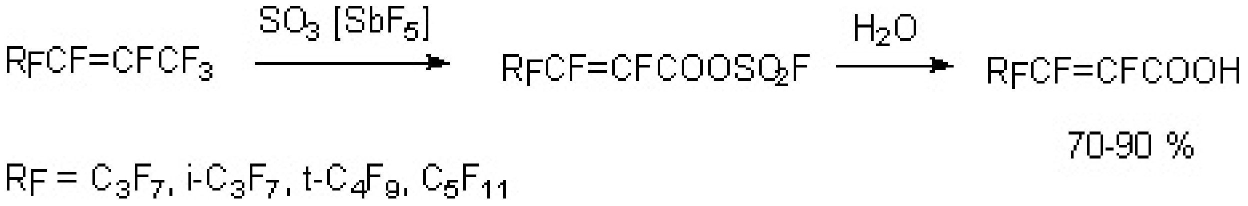
The reaction is not accompanied by migration of double bond; the stereoisomeric composition corresponds exactly to the stereoisomeric composition of reacting olefine, at trans- isomers react faster, than cis-isomers.



Polyfluoroalkylfluorosulphates are colorless, mobile, resistant to hydrolysis liquids (n<8) or solid compounds (n>8), stable at long-term storage. Their most important property is their changing fcω-hydroperfluorocarboxylic acids fluoroanhydrides at processing using metal fluorides. This is used as polyfluorinated carboxylic acids obtaining method [52].

$$H(CF_2)_nOSO_2F \xrightarrow[-SO_2F_2]{MF} H(CF_2)_{n-1}COF \xrightarrow[-HSO_3F]{(FSO_2O)_2} FSO_2O(CF_2)_{n-1}COF$$

The further replacement of hydrogen for FSO_2O group results in formation ω-fluorosulphonyl-oxy-perfluoroacylfluorides, *which there are the initial products for ion-exchange membranes*. In case of SO_3 [SbF_5] excess the saponification of CF_3 groups and formation of corresponding carboxylic acids take place [114].

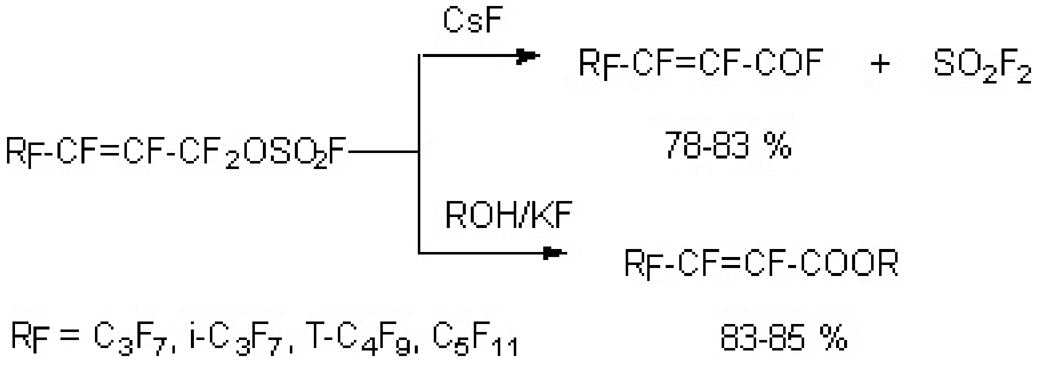


$$R_FCF{=}CFCF_3 \xrightarrow{SO_3\,[SbF_5]} R_FCF{=}CFCOOSO_2F \xrightarrow{H_2O} R_FCF{=}CFCOOH$$

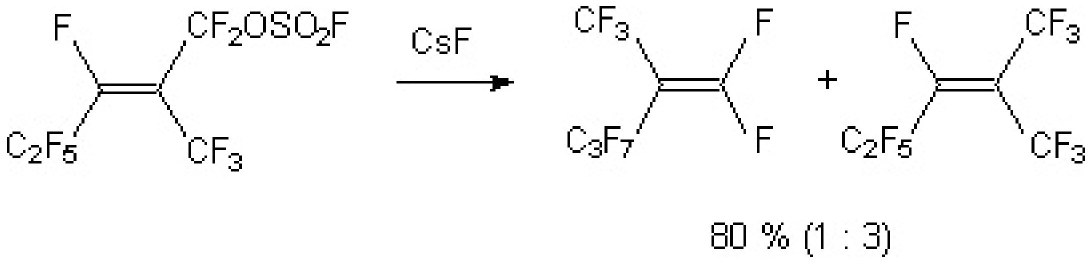
70-90 %

R_F = C_3F_7, i-C_3F_7, t-C_4F_9, C_5F_{11}

It turned out, that perfluoroalkenoyl fluorides are also formed at interaction of perfluoroalken-2-ylfluorosulphates with CsF according to sulfur atoms, anβ-unsaturated perfluorocarboxylic acids esters are formed at alcohol influence in the presence of KF [111,116].



It should be kept in mind, that the reaction like this with linear alkenylfluorosulphates, containing iα-position voluminous perfluoroalkyl groups, results not in formation of corresponding acids, but in formation of two perfluoroolefines mixture [117,118].



At alkali metals halogenides action on perfluoroalken-2-ylfluorosulphates the products of direct FSO_2O-group replacement for halogenide ions [118,119].

$$R_F\text{-}CF{=}CF\text{-}CF_2OSO_2F \xrightarrow[\text{sulpholane}]{KI} R_F\text{-}CF{=}CF\text{-}CF_2I$$

70-80 %

R_F = i-C_3F_7, t-C_4F_9

$$i\text{-}C_3F_7\text{-}CF{=}CF\text{-}CF_2OSO_2F \xrightarrow{LiCl} i\text{-}C_3F_7\text{-}CF{=}CF\text{-}CF_2Cl$$

85 %

For example, trifluoroacrylic acid haloidanhydride is obtained out of perfluoroallylfluorosulphate ($CF_2{=}CFCF_2OSO_2F$) by action of KBr or NaBr in ether (diglyme, sulpholane) [120].

The important moment of carboxylic acid fluoroanhydride reactivity is their changing into salts under the action alkali metals fluorides, such salts contain perfluoroalkoxi group, able to substitute easily moving groups in organic molecules. For example, perfluoroalkylallyl ethers became available after working out of chemistry and technology of perfluoroallylfluorosulphates due to condensation of the last mentioned with perfluoroalkoxy-anion according to the scheme [111] :

$$R_FCOF \xrightarrow{MF} R_FCF_2O^-M^+ \xrightarrow{FSO_3CF_2CF=CF_2} R_FCF_2OCF_2CF{=}CF_2 + MSO_3F$$

Perfluoroallyl cations, generated by action of SbF_5 on internal perfluorolefines transform into corresponding perfluorinated acids fluoroanhydrides. Thus, 1-trifluoromethoxyperfluoroallyl cation turns transform into trifluoroacryloate fluoride, an important semi-product of fluororganic synthesis [121].

3. Characteristics of perfluorocarboxylic acids and practical application of fluoromaterials obtained on their base.

3.1. Decarboxylation and decarbonylation of perfluorocarboxylic acids.

Among characteristics of perfluorocarboxylic acids we should first of all mention the transformation of carboxylic group. Depending on conditions during these processes different products are obtained. At that perfluoroalkyl fragment can also participate in these processes. Thus, polyfluorinated carboxylic acids $H(CF_2CF_2)_n$ COOH (n = 1-5) at alkali action transform into terminal perfluoroolefines with different length of perfluoroalkyl substituent. The obtaining method of terminal perfluoroolefines is based on this.

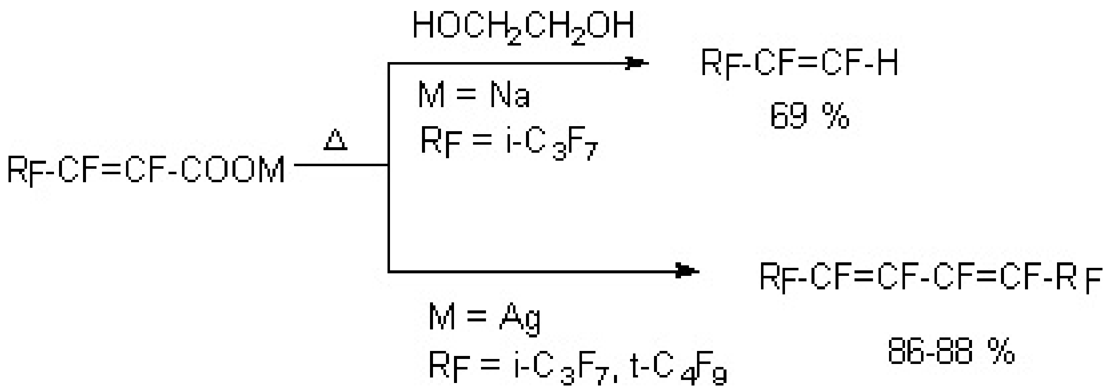
$$H(CF_2CF_2)_nCOOH \xrightarrow[270\ ^oC]{NaOH} H(CF_2CF_2)_{n-2}CF{=}CF_2$$

Perfluorocarboxylic acids natrium salts can be used, at that the yield is stable and almost quantitive [122].

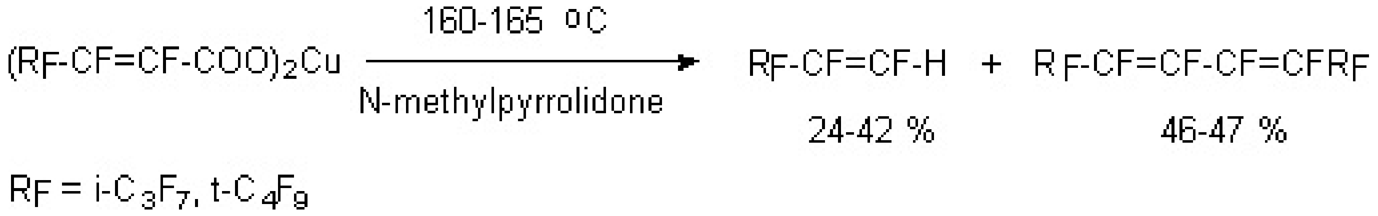
$$CF_3CF_2CF_2COONa \xrightarrow{245\text{-}253\ ^oC} CF_3CF{=}CF_2 + CO_2 + NaF$$

Best results are obtained at carrying out decarbonylation of perfluorocarboxylic acids halogenanhydrides and their alkyl ethers in the presence of catalysts (oxides of metals Mg, Cr, Ba, Zn, Al, Ni, Si), promoted by using of 20-50 % alkali metals halogenides at 100-300 ^oC. The yield of terminal perfluoroolefines reaches 95 % [108].

The reactions α,β-unsaturated perfluorocarboxylic acids, going with their decarboxylation, open the way to synthesis of different compounds of ethylene and acetylene series [123]. For example, thermal decomposition of Na perfluorβ,γ-unsaturated perfluorocarboxylic acids carboxylates in ethylene glycol results in formation of 1-hydroperfluoroalkenes-1, while the one (decompositon) of carboxylates Ag of these acids results in formation of perfluorinateα-diens [123,124].



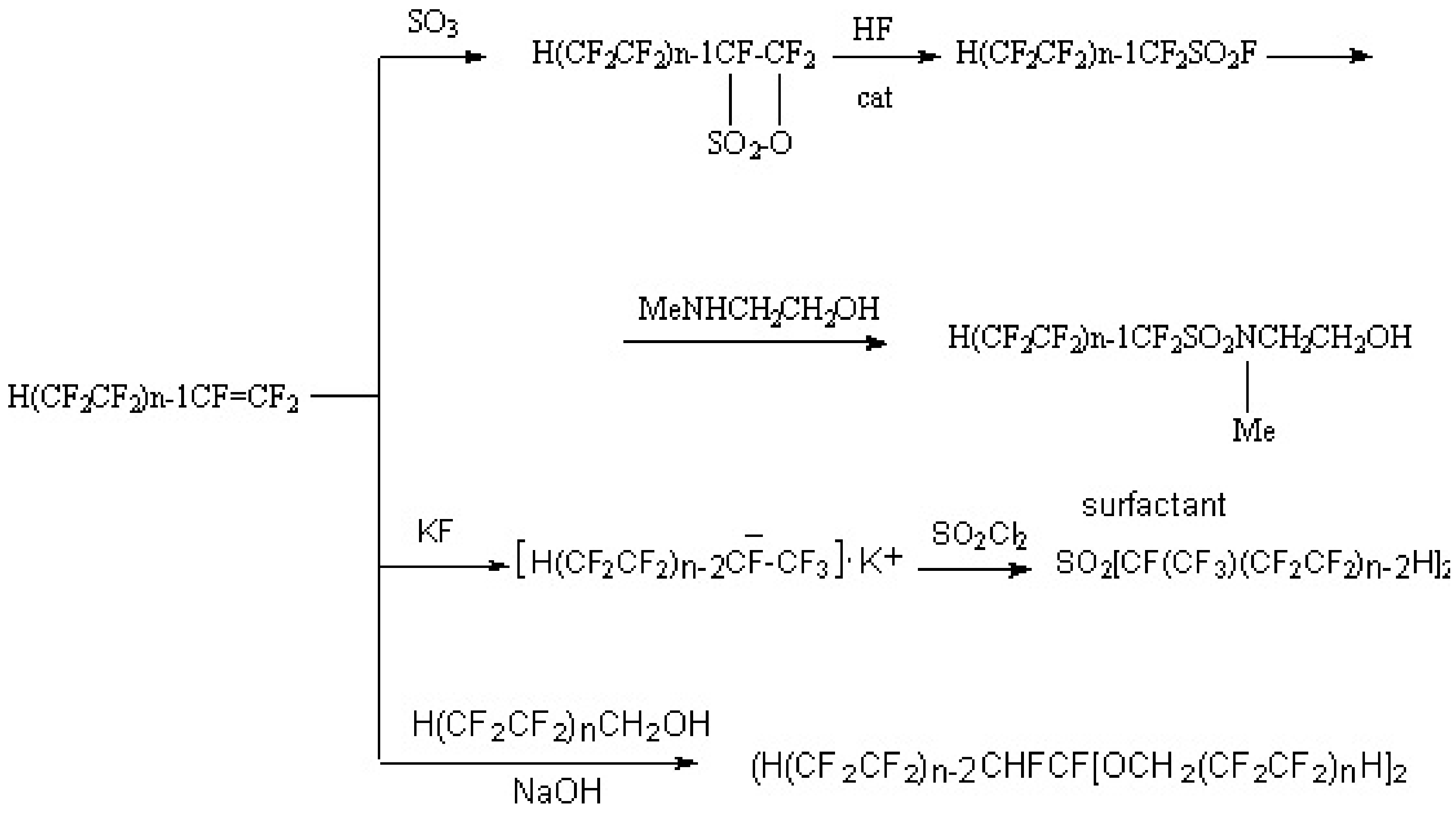
Thermal decomposition of copper perfluoroalkenylcarboxylates Cu^{2+} in high-boiling organic solvents, for example in N- methylpirrolidone or sulfolane, results in formation of mixture of 1,3-diens and 1-hydroperfluoroalkens-1 [124].



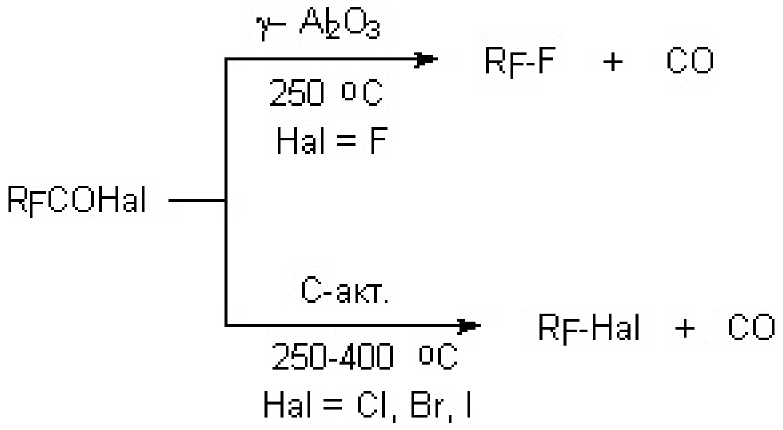
Halogenides and esters of perfluorocarboxylic acids are subject to decarboxylation at 100-300 °C in the presence of catalysts (oxides of magnesium, calcium, barium, zinc, nickel) resulting in formation of perfluoroolefines or perfluoroalkylvinyl ethers with the yield close to 95% [125].

Terminal perfluorolefines can be semi-products to obtain:

1. polyfluoroalkansulpho-acids and on their base the surface active materials and electrolytes for lithium batteries and rechargeable accumulators,
2. new chelation for salts of rare elements,
3. creation of high-temperature liquid dielectrics, heat-transfers and hydraulic liquids.



At the same time at perfluorocarboxylic acids fluoroanhydrides passage over Al_2O_3 decarbonylation with perfluoroalkanes formation is going. It should be noted, that at these conditions chloro- and bromoanhydrides of corresponding acids do not change using of activated carbon is required to carry out this process, at that chloro-and bromperfluoroparafines are formed [126].



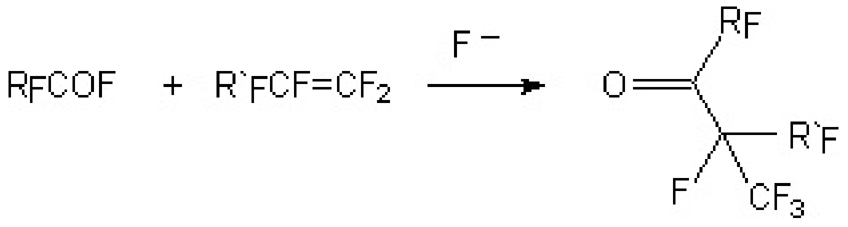
If in the system there are sources of halogenide-ions (for example, alkali metals halogenides, haloids etc.) then the thermolysis of perfluocarboxylic acids chloroanhydrides, conducted in flow reactor at atmospheric pressure and 250-350 0C in the presence of potassium iodide, will result in formation of iodoperfluoroalkanes with the yield of 80-85%, and heating of mixture of perfluorinated acids fluoroanhydrides and bromine at 300-450 ^{0}C at activated carbon will result in formation of bromoperfluoroalkanes [126].

Thermal reactions of sodium and potassium salts of mono- and di-perfluorocarboxylic acids (temperatures 150-250 0C) result in processes of decarboxylation and formation of hydrocarbons with end group CF_2H. By the example of thermal decarboxylation of perfluoropolyetherdicarboxylic acids with the structure $ROOCCF_2$-R_F- CF_2COO, which was produced at oxidizing polymerization tetrafluoroethylene with O_2 at UV-irradiation, were studied the kinetics and reaction products.

$$KOOCCF_2OCF_2COOK + H_2O \rightarrow HCF_2OCF_2COOK + KHCO_3$$

Temp. ^{0}C	140	160	180	200
k_s (s^{-1})	$1.1 \cdot 10^{-5}$	$7.2 \cdot 10^{-5}$	$5.1 \cdot 10^{-4}$	$2.2 \cdot 10^{-3}$

Perfluorinated carboxylic acids are presented as reagents for introduction of R_FCO or R_FCOO fragments and they are rather deeply and thoroughly studied [131]. We will point out, for example, acylation of compounds with active hydrogen atom, that are used for temporarily blocking of OH and NH_2 groups in carbohydrateū and peptides, acetylation of aromatic compounds according to Friedel-Crafts with formation of perfluoroalkylarylketones, reactions with metalo-organic compounds with formation of perfluoroalkyl-containing tertiary alcohols, addition to olefins and acetylene reactions, including different unsaturated fluorinated systems in the presence of fluoride- ions for synthesis of perfluorinated dialkylketones. This important synthetic achievement, using fluorine carb-anion intermediate products, for example:



In connection with high need of partly fluorinated alcohols their obtaining approach based on their esters of perfluorocarboxylic acids is developing. Thus, reduction of esters of carboxylic acids like R_FCOOR [$R_F = CF_3(CF_2)_m(CH_2)_n$ (m = 0-20, n = 0-5), $H(CF_2)_m(CH_2)_n$ (m = 1-20, n = 0-5), $(CF_3)_2CF$, $CF_2{=}CF$, $CF_2{=}CFCF_3$; R = Me, Et, n-Pr,
i-Pr] by $NaBF_4$ action in teterahydrofurane produce the corresponding alcohols [132].

For example, $CF_3(CF_2)_6CH_2OH$ alcohol is obtained out of methyl perfluorooctanoate with the yield equal to 98.3 % (100 % conversion). Like this the reduction of perfluoro(hexyldecylacetate) is carried out by action of $NaBF_4$ in the special solvent up to perfluoro-1H,1H-2-hexyldecanol [133].

Thereby, there are no special difficulties at target setting of carbonyl-containing compound synthesis based on perfluorocarboxylic acids. We consider discussion of these questions inexpedient, and we'll dwell on practical application of these fluorine materials.

To be continued