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Synthesis and application of ω-bromoperfluoroalkylvinyl ethers

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Report 1. New method to synthesize ω-bromo-perfluoroalkylvinyl ethers.

Introduction.

In recent decades fluorine containing plastics and rubbers have found wide application in different fields of technique requiring high performance of composite materials(thermal and chemical stability, resistance to acids, industrial liquids, solvents, alkalis). The necessary physicochemical, physicomechanical and other characteristics are provided by creation of copolymers of various types.

Conventional homo- and copolymers on base of fluorine-containing olefins such as tetrafluoroethylene (TFE), vinylidene fluoride (VDF), perfluoroalkyl ethers have a number of known disadvantages. That is why fluoromonomers on the same basis containing different functional groups have recently attracted an increased interest. They possess positive properties of fluoroplasts excelling them in a number of such characteristics as hydrophily, electroconductivity, solubility, processibility, anti-adhesion and others.

The analysis of data from scientific -technical and patent literature has shown that a great part of modifiers consists of fluorinated vinyl ethers of the following general formula :

$CF_2 = CFOR_fX$ where R_f is fluoroalkyl fragment, X is different functional substituents(Cl , Br , CN , Y , C(O)OR, OC_6H_5, $C(O)CF_3$, SO_2F , $OCF=CF_2$, $CF-CF_2$ and others). The content of perfluoroalkylvinyl ethers in such polymers is relatively small but it makes the properties of copolymers significantly vary.

Sometimes to solve specific problems, a third monomer with similar properties is introduced to make individual types of polymer materials varying such additives as cross-link agents, fillers, plasticizers etc.

ω - bromo-perfluoroalkylvinyl ethers (BrAVE) are convenient base reagents to create new classes of fluoropolymers with different functional groups, as well as modifiers for fluoropolymers.

It has been determined experimentally that BrAVE are easy to copolymerize with TFE, VDF and other fluoroolefins by conventional methods. In this case the content of bromo-monomer in the copolymer amounts to 26%.

Modification of fluoroplasts may be accomplished by introducing BrAVE into reaction of copolymerization with TFE and other fluoroolefins followed by its cross-linking to make cross-linked fluoropolymers. Another modification method is using perfluorodivinyl ethers with different chain length in copolymerization. These ethers are easy to synthesize from appropriate BrAVEs.

To create special fluoropolymers with active centers, for example for ion-exchange membranes (IEM), it is difficult to attain desired results by copolymerization of fluoroolefins with fluorinated vinyl ethers containing the appropriate functional groups because of low reactivity of the latter. Therefore the copolymerization of fluoroolefins with BrAVE followed by bromine replacement with specific functional groups by means of polymer-analogous conversions seems perspective. Effectiveness of this method has been confirmed experimentally during processing granules and films for IEM synthesis with anion-active (alkyl-amine) and cation-active (carboxyl) groups.

In the report we briefly describe an original method developed by the authors to make BrAVE with different chain length.

In further reports we are going to give main routes for application of BrAVE monomers and some properties of fluoropolymers modified by them and possible fields of their application.

Principal stages of the process.

BrAVEs have been described in patent literature (Japan) as crosslinking monomers as a compound of the general formula of Br(CF2)nOCF=CF2 , while synthesis methods and properties of every specific compound have not been given.

We have selected BrAVEs with n=2 and n=4 as the most perspective and developed a fundamentally new synthesis method according to the following scheme:

$$Br(CF_2)nBr \xrightarrow[-Br_2]{SO_3F'} \underset{I}{Br(CF_2)nOSO_2F} \xrightarrow[-SO_2F_2]{F^-} \underset{II}{Br(CF_2)_{n-1}C(O)F} \xrightarrow{C_3F_6O} \underset{III}{Br(CF_2)nOCF(CF_3)C(O)F} \longrightarrow$$

$$\xrightarrow[O_3;\,-MF]{M_2CO_3} \underset{IV}{Br(CF_2)nOCF(CF_3)C(O)OM} \xrightarrow[-CO_2;-MF]{} \underset{V}{Br(CF_2)nOCF=CF_2}$$

Main raw material in the synthesis of BrAVE areα,ω- dibromoalkyles with different chain length (a method of their production is going to be described in further reports), covalent fluorosulfonates and hexafluoropropylene oxide.

The synthesis of BrAVE monomers in this report is described taking as example R-114b2 (1,2-dibromtetrafluoroethane), the most available refrigerant in Russia, and R-318b2 (dibromodecafluorobutane).

Synthesis ω -bromo-perfluoroalkylfluorosulfates.

To produce monofluorosulfonates (1), covalent fluorosulfonate (peroxydisulfuryldifluoride, $S_2O_6F_2$; chlorine fluorosulfonate, $ClOSO_2F$; bromine fluorosulfonate, $BrOSO_2F$ or their mixtures) is added slowly to the starting dibromoalkane (R-114B2 or R-318B2 respectively) at vigorous stirring at a temperature of 40-50 ^{o} C at a mole ratio of 1:1-3:1.

To initiate the process, a catalytic amount of bromine is added for more active formation of bromine fluorosulfonate:

$$Br_2 + XOSO_2F \longrightarrow BrOSO_2F$$

, X= Cl^- , $^-OSO_2F$. To optimize the process, the order of mixing and ratio of reagents have been investigated.
According to our data, an addition of dibromoalkane to the fluorosulfatating mixture is inexpedient because of great exothermicity of the reaction and difficulties in heat removal.

The optimal mole ratio of FSC-PSF/dibromoalkane is 1.3:1. Further increase in amount of fluorosulfatating agent leads to an increase in the content of di-substitution product (bis(fluorosulfonyloxy)perfluoroalkane)-BIFS in the reaction products:

$$Br(CF_2)nBr + 2ClOSO_2F \longrightarrow FO_2SO(CF_2)nOSO_2F + Cl_2\uparrow$$

A prolonged boiling of the reaction mixture gives a similar result.

The content of the reaction products versus the ratio of the reagents is plotted in Fig.1

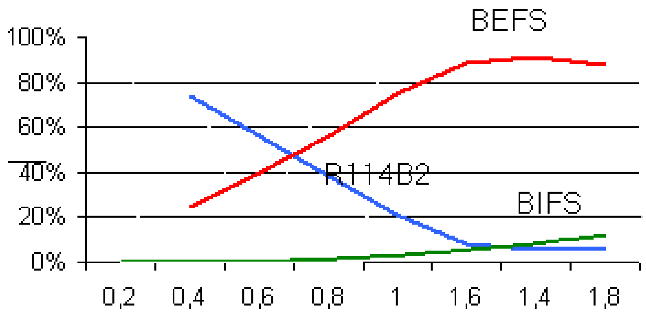


Fig.1 Yield of mono-and di-substituted products of fluorosulfatation of R-114B2 versus the ratio of the reagents.

The content of the goal product in the reaction mixture under optimal conditions was 92-95%.

Elemental bromine and chlorine are formed together with the goal product as a result of the reaction. Chlorine is blown away during the synthesis to an absorbing column, bromine and unreacted fluorosulfonate can be removed from the reaction mass by means of a solution of soda or alkali, but it is more reasonable to treat the reaction mass with tetrafluoroethylene at stirring and cooling. At that in case of bromoperfluoroethylfluorosulfate, the starting R-114B2 is recovered and additionally the goal product is formed:

$Br_2 + CF_2 =CF_2$ -> $BrCF_2 CF_2 Br$

BrOSO

$_2$ F + $CF_2 =CF_2$ -> $BrCF_2 CF_2 OSO_2 F$

The reaction products were separated on a packing rectification column, the yield of the goal products was up to 90%, and the purity was up to 99-99,5%.

Synthesis of fluoroanhydrides ω-bromoperfluorocarbonic acids.

Fluoroanhydrides ω - bromoperfluorocarbonic acids(2) were prepared by decomposition of alkylfluorosufates in a medium of a polar aprotic solvent (diglyme, adipodinitrile) in the presence of anhydrous fluoride of alkali metal (K,Na,Cs).

Decomposition ω - bromoperfluoroethylfluorosulfate (BEFS) was carried out at room temperature at a mole ratio of KF:BEFS=0.15-0.5:1 in a flask equipped with a stirrer and a cooler cooled to minus 50 ^{O} C. At that the forming fluoroanhydride ω - bromoperfluoroacetic acid (b.p.=0- -1 ^{O} C) was recycled to the reactor and sulfuryldifluoride (by-product) was condensed in a trap (-78 ^{O} C).

After the completion of decomposition, the reaction mass was heated to 50 ^{O} C without cooling the cooler and the producing fluoroanhydride ω - bromoperfluoroacetic acid was condensed in a trap (-78 ^{O} C) and then transferred into a cylinder.

The investigations made have shown that such a procedure to eliminate fluoroanhydride ω - bromoperfluoroacetic acid makes possible to attain the maximum yield of the product (90%). Another method, producing and storage of producing fluoroanhydride of w - bromoperfluoroacetic acid as potassium alkoxide in a solution of diglyme or ADN, leads to significant losses due to alkoxide dissociation and low boiling point of the fluoroanhydride.

$BrCF_2CF_2O^-K^+ \rightleftharpoons BrCF_2COF + KF$

Synthesis of fluoroanhydride cω -bromoperfluorobutyric acid was carried out similarly at a temperature of decomposition of 50-60°C. The goal fluoroanhydride was distilled from the reaction mass (b.p.=57-58°C), purified by rectification. The yield was 85-90%.

Synthesis of fluoroanhydrides ω-bromo-2-trifluoromethyl-3-oxaperfluorocarbonic acids.

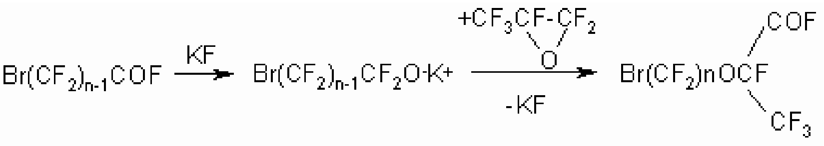
The synthesis of compounds (3) was carried out according to a classical scheme widely used in laboratory practice by means of hexafluoropropylene addition to fluoroanhydrides of appropriate perfluorocarbonic acids(2). The reaction is carried out in the presence of anhydrous fluorides of alkali metals in a medium of different polar aprotic solvents: glymes, nitriles, tetrahydrofurane, dimethylsulfoxide etc.. Diglyme and tetraglyme possessing higher solvating ability are used most often.

However the conducted experiments have shown that the use of diglyme leads to a partial substitution of the bromine atom in the molecule of addition product (3) and to the formation of fluoroanhydrides of perfluoropolyoxa-carbonic acids in the reaction products. Analysis of the solid residue of the reaction mass has shown the presence of bromine-anion.

Therefore as a solvent in the stage of HFPO addition we used adiponitrile dried by distillation under vacuum over P_2O_5.

The reaction was carried out in two ways:

1.Alkoxide was produced at atmospheric pressure, stirring, room temperature then HFPO was bubbled into the reaction mixture at 0-5°C:



This method is laborious, requires a long time and is distinguished by low productivity and not high enough yield, especially in case of low-boiling products (n=2).

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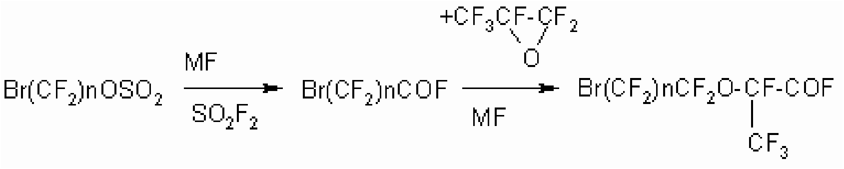
.A method of HFPO addition under pressure is more effective. KF and ADN were charged into a reactor, evacuated, the starting fluoroanhydride was added, the reaction mixture was stirred for 2-3 hours to produce alkoxide, cooled with liquid nitrogen and HFPO was added. The reactor was gradually heated to room temperature at stirring to the pressure drop stopping.

The optimal mole ratios were: KF:FA=0.5-0.8:1; HFPO:FA=1.2:1

After the synthesis completion the contents of the reactor was poured out to a separating funnel, the lower fluoroanhydride layer was separated and distilled to fractions. The content of the goal addition product in the mixture was 60-70 vol.%. The admixtures were HFPO dimer and a product of addition of two molecules of HFPO. After rectification the goal product was separated with 98-99% purity.

Production of fluoroanhydrides ω -bromoperfluorocarbonic acids (2) and products of HFPO addition to them (3) is carried out under similar conditions in a medium of dehydrated aprotic solvent in the presence of fluoride of alkali metal. Therefore there was investigated a possibility (and expediency) to carry out both stages in the same reactor unit in different variants described by the general scheme:



There are two ways to realize the scheme:

The first one: to separate intermediate fluoroanhydride of w-bromoperfluoro-carbonis acid with following addition of HFPO to it.

The second way is HFPO feeding into the reaction mass produced in the previous stage without fluoroanhydride (3) separation with further separation of the goal product.

Experiments have shown that the scheme of consecutive synthesis is quite acceptable to produce small laboratory samples, but in this case a decrease in the yield of the goal product is inevitable because one of the reactions is carried out under nonoptimal conditions. However here equipment get-up is easier and the use of low-temperature reagents to separate the intermediate anhydride is excluded.

To produce a very pure product of HFPO addition in big quantities, it is reasonable to use the first scheme with intermediate separation and using optimal reaction media. But here a special equipment is necessary to provide low-temperature collection ω -anhydride(3) and then HFPO addition at an elevated pressure.

Production and purification of salts of ω-bromo-2-trifluoromethyl-3-oxaperfluorocarbonic acids. The goal ω -bromoperfluoroalkylvinyl ethers were produced by pyrolysis of addition products (4) in different ways: pyrolysis of a dry salt produced preliminarily or liquid pyrolysis of a salt produced directly in a solvent.

Dry salts (4) were produced by hydrolysis and neutralization of addition products (3) with aqueous solution of KOH,NaOH,Na_2CO_3. The solution was evaporated to dryness, the residue was pounded with pestle, water traces were removed by azeotrope distillation with benzene, the dry salt after repeated pounding with pestle was dried under vacuum (5-10mm mercury column) at a temperature of 110-120^{o}C for 5-10 hours.

The absence of moisture is the necessary condition of the pyrolysis. Otherwise the formation of side hydrogen-containing products, hydrides, occurs.

Method to produce and purify salts ω-bromo-perfluoro-alkyloxaalkylen carbonic acids on a laboratory scale.

Sodium salt ω -bromo-perfluoro-2-methyl-3-oxavaleric acid was taken as an example. It was synthesized from the appropriate fluoroanhydride by its treatment with soda in the presence of catalytic amounts of water.

It is easy to produce the mentioned salts in principle by consecutive hydrolysis of the appropriate fluoroanhydrides and treatment of the acid produced with soda. But it is rather difficult to purify the salt produced from hydrogen fluoride and residue moisture. Hydrides retard the copolymerization process of fluorovinyl ethers with fluoroolefins, therefore the content of hydrides in the goal product is strictly limited: 0.1%. Moreover, hydrides form azeotropes with vinyl ethers that makes difficulties for their purification and reduces the yield.

Some ways of technological routes have been studied:

a). Interaction of the fluoroanhydride with crystal hydrates of the following composition: $Na_2CO_3*5H_2O$. The salt formation runs very smoothly; to remove moisture, salt was first dried by common methods and the crushed salt was then evaporated at heating to 100-120^{o}C.

b). Mixing fluoroanhydride, soda and catalytic amounts of water in different combinations with use of benzene. Here moisture is easy to remove as azeotrope with benzene.

Both methods can be used to make the salts of necessary quality. Using different methods of purification, samples of sodium, potassium, lithium salts of 5-bromo-perfluoro-2-methyl-3-oxavaleric acids were produced and tested during the pyrolysis process.

It has been found during the producing of aggregative samples, that hygroscopicity of K-salts does not allow to dry them by the mentioned methods to a sufficient degree.

Producing ω-bromo-perfluoroalkylvinyl ethers.

Influence of the composition and quality of the salts on the quality and yield of fluoroalkylvinyl ethers has been determined during this study.

Dry samples of sodium, potassium and lithium salts were subjected to pyrolysis at a temperature up to 300^{o}C. At a temperature up to 120-140^{o}C there was no evidence of decomposition of the salts. At 160^{o}C the pyrolysis degree does not exceed 5% that is due to some local overheating in our opinion. At a temperature above 300^{o}C sometimes uncontrolled reaction took place accompanied with self-heating the reaction mass (made red-hot) and complete destruction of the reagents. Therefore the yields of the goal monomer were determined at two temperatures: 180^{o}C and 250^{o}C.

The yield of the monomer was calculated according to its content in the pyrolyzate condensed in traps cooled to -78^{o}C.

The pyrolyzate was up to 96-97% of the goal product under the optimal conditions. Further purification was carried out by rectification on a "Perkin-Elmer" preparative column. The yield of vinyl ethers was 87-90% and the purity of 99.5-99.9%.

The yield of the pyrolyzate at a temperature of 180-250^{o}C differs by 0.8-1.8% that is within the experimental error, that means that the yield does not practically depend on the temperature.

In a row Li-Na-K the yield of the goal monomer is increasing from 66-68% to 85.0-85.5% that is in accordance with the size of the cation and the data on hygroscopicity of the salts.

The liquid pyrolysis makes it possible to reduce the reaction temperature to 140-180^{o}C. In this case requirements for drying the starting components remain the same. A solvent, diglyme or adiponitrile, was preliminarily kept over drying agent under vacuum. Soda or potash was calcined at 250-300^{o}C in vacuum with periodical pounding.

The method consists in a slow addition of fluoroanhydride to a suspension of carbonate in a solvent at vigorous stirring and cooling to 10-15^{o}C. The control over the salt formation is executed by intensity of carbon dioxide liberation. After the completion of salt formation the temperature is slowly raised to 120-140^{o}C and then to 180^{o}C condensing the pyrolysis products in traps (-78^{o}C). The content of the goal product in the pyrolyzate is 80-90% and the yield is 85-90%.

The individuality of the compounds produced has been determined by GLC method, the structure has been confirmed by 19FNMR, 1H proton NMR, IRS analyses.

A choice of the solvent (diglyme, acetonitrile,adiponitrile) in the pyrolysis process is of great importance.

Diglyme and adiponitrile have been found to be the most suitable and the process runs much actively in the first pyrolysis conditions.

The produced samples of ω-bromoperfluoroethyl- and ω-bromoperfluoro-butylvinyl ethers with a purity of 99.5-99.8% were used as co-monomers with tetrafluoroethylene and vinylidene fluoride to modify fluoroplasts and synthesize fluoropolymers with functional groups.

Conclusions.

The framework of the paper does not allow to describe in detail all features of all the stages of the process of BrAVE synthesis, but the authors believe that the above information is quite enough to evaluate effectiveness and perspective of the proposed synthesis method for monomers of new class which can solve the problems of fluoroplasts modification and creation of new perspective fluoropolymers with different functional groups.

Specific methods and ways to synthesize semi-products should be chosen, traditions and specific opportunities of research organizations in raw materials and equipment taken into account. Moreover, one should have in mind that both the goal ω-bromo-perfluoalkylvinyl ethers and bromine-containing intermediate compounds are high-toxic substances. They belong to the 2nd class of danger and require the appropriate safety and protective measures.