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PRORRAMME

Sunday, June 26, 2016

16.00 - 20.00  Registration
18.00 - 21.00  Welcome Party

Monday, June 27, 2016

9.30 - 10.30  Opening Ceremony
              Chairman - A. M. Muzafarov

Memorial Session marking the 110th anniversary of Prof. I. L. Knunyants

10.30 - 13.30 SESSION 1
           Chairman - N. D. Chkanikov

10.30  O-01  S. M. Igumnov (Russia)
           CURRENT SITUATION AND DEVELOPMENT PROSPECTS IN FLUORINE
           CHEMISTRY

10.50  PL-01  V. G. Barabanov (Russia)
           STUDIES IN THE FIELD OF INDUSTRIAL FLUOROCHEMICALS CONDUCTED
           AT RSC “APPLIED CHEMISTRY”

11.20  O-02  B. Koksch (Germany)
           FLUORINE IN PePTIDE AND PROTEIN ENGINEERING

11.40 - 12.00 Coffee-break

12.00  PL-02  S. Fustero (Spain)
           NEW STRATEGIES FOR THE SYNTHESIS OF MONOFLUORINATED
           COMPOUNDS

12.30  PL-03  G. Sandford (United Kindom)
           SELECTIVE DIRECT FLUORINATION STRATEGIES

13.00  PL-04  V. I. Saloutin (Russia)
           THE NEW APPROACHES TO POLYFLUOROCONTAINING
           HETEROANNELED AZINES

13.30 - 14.30 Lunch

14.30 – 17.40 SESSION 2
             Chairman - N. Yu. Adonin

14.30  PL-05  N. Shibata (Japan)
           DEVELOPMENT OF SHELF-STABLE IODONIUM REAGENTS FOR FLUORO-
           FUNCTIONALIZATION REACTIONS

15.00  PL-06  T. Billard (France)
           FLUOROALKYLTHIOLATION REACTIONS: TOWARDS THE DEVELOPMENT
           OF A FAMILY OF MULTIPOTENT AND VERSATILE REAGENTS

15.30  O-03  V. E. Platonov (Russia)
           FORMATION OF POLYFLUOROARENES WITH BENZOTHIOPHENE AND
           THIENOPYRIDINE SKELETONS IN THERMAL REACTIONS OF
           POLYFLUORO-ortho-CHLOROARENETHIOLS WITH
           TETRAFLUOROETHYLENE
15.50  O-04  A. I. Rakhimov (Russia)
POLYFLUORINATION OF FUNCTIONALIC COMPOUNDS AND POLYMERS

16.10 - 16.30  Coffee-break

16.30  PL-07  A. D. Dil’man (Russia)
DIFLUOROCARBENE AS A BUILDING BLOCK

17.00  O-05  N. V. Vasilev (Russia)
PERSPECTIVE FLUORINE-CONTAINING REAGENTS FOR IMMUNOFLUORESCENCE ANALYSIS

17.20  O-06  V. G. Nazarov (Russia)
POLYMER SURFACE FLUORINATION – NEW DIRECTION OF RESEARCH AND APPLICATION

17.40 – 19.00  1th POSTER SESSION  P-01 – P-44

Tuesday, June 28, 2016

9.30  - 11.30  СЕССИЯ 3
Chairman - J. Kvičala

9.30  PL-08  J. Rábai (Hungary)
PRACTICE OF FLUOROUS BIPHASIC CHEMISTRY

10.00  PL-09  D. O’Hagan (United Kindom)
FLUORINE AS A STEREOELECTRONIC TOOL IN THE DESIGN OF PERFORMANCE ORGANIC MOLECULES

10.30  PL-10  Ya. V. Burgart (Russia)
POLYFLUOROCONTAINING 2-(HET)ARYLHYDRAZONO-1,3-DICARBONYL COMPOUNDS IN ORGANIC SYNTHESIS

11.00  PL-11  N. Yu. Adonin (Russia)
FLUORINATED ORGANOBOORON DERIVATIVES: NEW APPROACHES TO SYNTHESIS

11.30  – 12.00  Coffee-break

11th REGULAR GERMAN-RUSSIAN-Ukrainian symposium on Fluorine Chemistry

12.00 - 12.10  Opening Ceremony  Chairman – S. N. Osipov
M. Krispin, Coordinator of German House of Research and Innovation (DWIH)
Presentation of DWIH activities

12.10  – 13.30  SESSION 4  Chairman – S. N. Osipov

12.00  O-07  S. Riedel (Germany)
FLUORINE-RICH FLUORIDES: NEW INSIGHTS INTO THE CHEMISTRY OF POLYFLUORIDE ANIONS

12.25  O-08  A. S. Golubev (Russia)
4-FLUOROALKYL-9H-PYRIMIDO[4,5-b]INDOLES: SYNTHESIS AND CYTOTOXICITY

12.45  O-09  D. Lentz (Germany)
BUCKYBOWLS MEET FLUORINE
13.10  O-10  M. Finze (Germany)
FLUORO AND HYDRIDO CYANOBORATES

13.30 - 14.30  Lunch

14.30 - 16.00  SESSION 5
Chairman – S. Riedel

14.30  PL-12  V. G. Nenaidenko (Russia)
FLUORINATED ALKENES AND ACETYLENES IN THE SYNTHESIS OF
PRACTICALLY USEFUL COMPOUNDS

14.50  O-11  U. Radius (Germany)
NICKEL-CATALYZED DERIVATIZATION OF POLYFLUOROARENES
VIA C-F BOND CLEAVAGE

15.10  O-12  B. Hoge (Germany)
PERFLUOROALKYL SILOXAN DERIVATIVES

15.30  PL-13  B. A. Shainyan (Russia)
HIGHLY UNSATURATED AND HETEROCYCLIC COMPOUNDS ON THE
BASIS OF TRIFLUOROMETHANESULFONAMIDE

16.00 – 16.20  Coffee-break

14.30 - 18.20  SESSION 6
Chairman – A.S. Golubev

16.20  O-13  S. V. Kuznetsov (Russia)
POLYCRYSTALLINE MATERIALS FOR PHOTONICS ON THE BASIS
OF GROUP II AND GROUP III METAL FLUORIDES

16.40  O-14  M. Hopkinson (Germany)
VISIBLE LIGHT PHOTOREDOX ACTIVATION FOR THE PREPARATION OF
FLUORINATED COMPOUNDS

17.00  O-15  E. B. Shchegol’kov (Russia)
SYNTHESIS OF POLYFLUOROSALICYLIC ACID DERIVATIVES AND
THEIR BIOLOGICAL ACTIVITY

17.20  O-16  N. Ignat’ev (Germany)
CATALYSIS WITH TRIS(PENTAFLUOROETHYL)-
DIFLUOROPHOSPHORANE, (C2F5)2PF

17.40  O-17  V. E. Boyko (Russia)
SYNTHESIS AND STUDIES OF REACTIVITY OF SILICON-CONTAINING
ORGANOFLUORINE COMPOUNDS

18.00  O-18  Yu. G. Shermolovich (Ukraine)
SYNTHESIS OF FLUORINE-CONTAINING 1,4-TRIAZINE-1,1-DIOXIDES
FROM 1,1-DIHYDROPOLYFLUOROALKYL SULFONES
Wednesday, June 29, 2016

9.30 – 11.30 СЕССИЯ 7
Chairman - N. Shibata

9.30 PL-14 J. Květala (Czech Republic)
SYNTHESIS, APPLICATION AND RECYCLE OF TRANSITION METAL COMPLEXES BEARING HEAVY AND MEDIUM FLUOROUS NHC LIGANDS

10.00 PL-15 T. Yamazaki (Japan)
SYNHETIC APPLICATION OF 1-CHLORO-1,2,2,2-TETRAFLUOROETHANE

10.30 O-19 T. V. Mezhenkova (Russia)
GENERATION OF STABLE PERFLUOROBENZOCYCLOALKENYL CATIONS CONTAINING AN ELECTRON-WITHDRAWING PERFLUOROISOPROPYL GROUP IN THE CATIONIC CENTRE

10.50 O-20 V. I. Filyakova (Russia)
LITHIUM ENOLATES OF FLUOROALKYL-CONTAINING 1,3-DICARBONYL, 1,3,5- AND 1,2,4-TRICARBONYL COMPOUNDS IN ORGANIC SYNTHESIS

11.10 O-21 D. S. Pashkevich (Russia)
THE METHOD OF HYDROGEN FLUORIDE OBTAINING FROM AN AQUEOUS SOLUTION OF HEXAFLUOROSILICIC ACID

11.30 – 11.50 Coffee-break

11.50 – 13.30 СЕССИЯ 8
Chairman - V.M. Buznik

11.50 PL-16 S. A. Khatipov (Russia)
OUTLOOK FOR RADIATION TECHNOLOGY IN DEVELOPMENT OF NOVEL PTFE BASED MATERIALS

12.20 O-22 N. N. Loginova (Russia)
KEY ASPECTS OF CHEMISTRY AND TECHNOLOGY OF FLUORINATED OLEFINS POLYMERIZATION PROCESSES

12.40 O-23 V. V. Semenov (Russia)
PRODUCTION OF COMPOSITE MICRONEEDLES AND SUPERHYDROPHOBIC COatings FROM SUSPENSION OF CARBONYL IRON MICROPARTICLES IN FLUoroORGANIC BINDING

13.00 O-24 S. P. Krukovsky (Russia)
POLYPERFLUOROALKYLENOXIDES. SYNTHESIS, PROPERTIES, APPLICATIONS

13.20 – 13.30 Conference Sponsor Presentations

13.30 – 14.30 Lunch

14.30 – 17.10 SESSION 9
Chairman - S. A. Khatipov

14.30 O-25 A. P. Kharitonov (Russia)
DIRECT FLUORINATION – EFFECTIVE TOOL TO ENHANCE COMMERCIAL PROPERTIES OF POLYMER ARTICLES AND CARBON NANOMATERIALS

14.50 O-26 N. P. Prorokova (Russia)
PREPARATION AND PROPERTIES OF A NEW BICOMPONENT FLUORINE-CONTAINING FILAMENT
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<td>Ya. V. Zonov (Russia) CARBONYLATION OF PERFLUORINATED BENZOCYCLOALKENES AND ITS ALKYL AND PHENYL DERIVATIVES IN THE CO-SbF&lt;sub&gt;5&lt;/sub&gt; SYSTEM</td>
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12.40 O-40 G. F. Makhaeva (Russia)
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13.20 – 13.30 Conference Sponsor Presentations

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14.30 O-42 V. V. Chapurkin (Russia)
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14.50 O-43 A. A. Tyutyunov (Russia)
SYNTHESIS AND PROPERTIES OF PERFLUOROALKYL SULFONYL BROMIDES

15.10 O-44 M. N. Khrizanforov (Russia)
ELECTROCATALYTIC FLUORALKYLATION OF VARIOUS CLASS SUBSTRATES ES. FROM CROSS-COUPING TO C-H FUNCTIONALIZATION

15.30 O-45 S. A. Nalet’ko (Russia)
IONIC REACTIONS OF FLUORINE-CONTAINING 1,2-OXI- AND THIIRANES

15.50 O-46 V. P. Zelenov (Russia)
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16.10 O-47 L. N. Malyutin (Russia)
THE RESEARCH OF BERYLLIUM CONCENTRATE HYDROFLUARINATION PROCESS

16.30 – 17.30 DISCUSSION

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V. G. Barabanov, B. N. Maximov, V. A. Matalin (St.-Petersburg, Russia) |
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V. I. Saloutin, M. V. Goryaeva, O. G. Khudina, A. E. Ivanova,  
Ya. V. Burgart, O. N. Chupakhin (Ekaterinburg, Russia) |
| PL-05 | DEVELOPMENT OF SHELF-STABLE IODONIUM REAGENTS FOR FLUOROFUNCTIONALIZATION REACTIONS  
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Dieter Lentz (Berlin, Germany) |
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Udo Radius (Würzburg, Germany) |
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Berthold Hoge (Bielefeld, Germany) |
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(Darmstadt, Germany) |
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ABSTRACTS
The abstracts are published in an author’s version
STUDIES IN THE FIELD OF INDUSTRIAL FLUOROCHEMICALS CONDUCTED AT RSC “APPLIED CHEMISTRY”

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- The Parties of the Montreal Protocol on ozone-depleting substances (MP) many times brought a point about inclusion of the Kyoto protocol in the MP to start the regulation of hydrofluorocarbon (HFC) production/consumption. Some of the Parties, EU first of all, have already started phaseout of HFC (and some other greenhouse gases) production/consumption within their territories. The new challenges and perspectives concerning HFCs (HFC 134A, HFC 125, HFC 227ea, etc.) regulation stimulated our research on the novel HFC and PFC substituents such as fluorinated ethers, esters, ketones, and olefins having zero ODS and very low GWP values.

- We develop technologies for the manufacture of functional fluorinated monomers and co-polymers and create ion-exchange membranes for contemporary fuel cells based on them. Such membranes, containing SO$_3$H or COOH groups, possess excellent chemical and thermal resistance, high selectivity in cation transfer, low electric resistance, and high mechanical strength.

- We carry out research and development of thermoplastic fluoropolymers (F-40, -2M, -MB, -4SF, etc.) and pilot production of films made of them by extrusion. Those films are widely applied in modern equipment intended for various industrial sectors. The methods are developed for the manufacture of new piezoelectric materials from fluoropolymers (F-2, etc.)

- We improve the technologies for the production of materials with high thermal and chemical stability, including liquids, oils, and greases with wide operating temperature range:
  - perfluoropolyethers based on hexafluoropropylene, and tetrafluoropropylene, having boiling points from 80 to 320°C/mm Hg and solidifying point -80°C or lower;
  - perfluorinated tertiary amines (RF)$_3$N, RF = C$_2$F$_5$, C$_3$F$_7$, -C$_4$F$_9$ with boiling points from 65 to 185°C, solidifying points from -50 to -145°C, having excellent dielectric properties, viscosity indices, etc.;

- We develop technologies for the manufacture of efficient surfactants (fluorosurfactants) from perfluorinated polyoxacarbonic and sulfonic acids for applications as foaming agents in fire-fighting compositions, oil improvers, etc.

- We develop technologies for the manufacture of fluorochemicals for medical applications and produce the test batches of:
  - inhalation anesthetic sevoflurane,
  - inert fluorocarbons with high solving capacity of oxygen and other gases for applications as gas-transportation media, conservation materials, etc.
NEW STRATEGIES FOR THE SYNTHESIS OF MONOFLUORINATED COMPOUNDS

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Monofluoroalkenes have recently attracted synthetic interest mainly due to their effect on the pharmacological properties of bioactive molecules as well as in other fields such as material sciences and organic chemistry\textsuperscript{1}. First, we describe an efficient synthesis of cyclic monofluorinated homoallylic amines consisting of an initial diastereoselective nucleophilic addition of non-fluorinated nucleophiles to (\textit{R})-(\textit{tert}-butanesulfinyl)imines, followed by a ring-closing metathesis reaction as one of the key steps\textsuperscript{2}.

On the other hand, the asymmetric allylboration of carbonyl compounds has played a pivotal role in synthetic organic chemistry for more than 30 years. However, only since the advent of the new century have catalytic enantioselective methods been developed. The second part of the present lecture will explain the novel application of functionalized allylboronates such as γ-silylallyl pinacolate derivatives in a catalytic enantioselective allylboration process. Furthermore, the synthetic usefulness of the hereby–obtained α-silylhomoallylic alcohols has been showcased by their transformation into enantioenriched fluorinated allylic alcohols, which are difficult to obtain by other means\textsuperscript{3}.

Finally, we have developed a palladium-catalyzed 1,1-fluoroarylation of deactivated terminal olefins by a three-component coupling of alkenes, arylboronic acids and N-fluorobenzenesulfonimide. The reaction was extended to an asymmetric transformation that generated chiral benzyl fluorides in good to excellent enantioselectivities. This method emerges as a powerful strategy for the β-fluorination of carbonyl derivatives. Despite tremendous efforts in the development of new strategies to introduce the C-F bond next to an electron-withdrawing group to form α-fluorinated carbonyl compounds, only a few examples of incorporating fluorine at the b-position of carbonyl compounds have been reported\textsuperscript{4}.

\textit{The research was supported financially by the Spanish MINECO (Project No. CTQ2013-43310) and the Generalitat Valenciana (Project No PROMETEOII/2014/073).}

\textsuperscript{4} Unpublished results.
In an on-going research programme at Durham aimed at developing widely applicable effective selective direct fluorination methodology, we have been exploring the use of elemental fluorine, a previously under-utilised reagent in organic chemistry, for the synthesis of fluoro-organic systems. Methodology for the preparation of, for example, a range of fluorinated aliphatic, carbonyl, aromatic and heterocyclic systems have been established and scaled-up by our industrial collaborators for use in the synthesis of commercially important pharmaceutical intermediates. Recent advances in the development of selective direct fluorination methodology for pharmaceutically important targets will be discussed\(^1\).

THE NEW APPROACHES TO POLYFLUOROCONTAINING HETEROANNELED AZINES

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The new ways to the synthesis of pharmacologically promising heterocondensed azines from polyfluoroalkyl-3-oxo ester derivatives are discussed in this report. These derivatives are known as the basic block-synthons in organic chemistry.

Heteroannelated pyrimidines formation based on the cyclization of 2-methylidene-3-polyfluoroalkyl-3-oxo esters with hetarylamines is considered. It is shown that the heterocycles functionalization is determined by the nature of substituent in the methylidene moiety. The specific features of azolo- and azinopyrimidines formation from 2-aryl- and 2-ethoxymethylene-3-polyfluoroalkyl-3-oxo esters are analyzed.

The methods of polyfluoroalkylated pyrimidines heteroannelation in the reactions of bis-alkylation and bis-methylation are discussed in the second part of the report. The multicomponent cyclization of 6-polyfluorouracyles with formaldehyde and primary amines leading to pyrimido[2,1-b]thiadiazines via the double aminomethylation is described.

In addition, the aspects of the new three-component cyclization of polyfluoroalkyl-3-oxo esters with methylcarbonyl compounds and diamines to synthesize hexa(tetra)hydroimidazo[1,2-a]pyridinones and octahydro[1,2-a]pyrimidinone are given in the final part.

The work was financially supported by the Program UB RAS N 15-21-3-5

DEVELOPMENT OF SHELF-STABLE IODONIUM REAGENTS FOR FLUORO-FUNCTIONALIZATION REACTIONS

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Organofluorine compounds now constitute a major family of pharmaceuticals and agrochemicals that have attracted considerable interest over several years in these markets. Notable success witnessed in recent synthetic fluorine chemistry is obviously related to the development of new fluoro-functionalization reagents, such as fluorination and trifluoromethylation reagents, and their usage under new catalytic systems supported by the meticulous work of organic chemists involved in fluorine chemistry and organometallics. Many shelf-stable reagents have been developed for this purpose, and it is not surprising that researchers are continuously eager for new fluoro-functionalization reagents, since new reagents often encourage an encounter with efficient synthetic methodology useful for the synthesis of sought-after organofluorine compounds on the drug market. In this context, our group has been publishing original reagents for fluorination, trifluoromethylation and trifluoromethylthiolation reactions. In the lecture, I introduce novel fluoro-functionalization reagents developed in my group.

Fluorine (F) and sulfur (S) atoms have been individually recognized over the past couple of decades to be important structural elements with biological activities in drugs. These facts, together with the recent successful observation on the market that the trifluoromethyl (CF$_3$) group is frequently found in pharmaceuticals and agrochemicals, has led medicinal chemists to explore the use of the trifluoromethylthio (SCF$_3$) group as a strategic functional component to assist in drug discovery. In recent years, more than a dozen attractive synthetic methods for introduction of the SCF$_3$ group into target compounds have been successively reported. In this context, the difluoromethylthio group (SCF$_2$H) has emerged as a next potential subject in this field. While SCF$_3$ is entirely lipophilic, the SCF$_2$H group has the potential to be a weak hydrogen-bonding donor, which results in a suitable hydrophilic/hydrophobic balance of SCF$_2$H-substituted molecules. Thus, incorporation of SCF$_2$H into biologically active molecules should permit the efficient design of novel, viable drug candidates. We disclose herein an investigation of novel shelf-stable electrophilic difluoromethylthiolation reagents 2 and their reactivity towards a variety of nucleophiles (Figure 1).

![Figure 1. Novel Difluoromethylthiolation Reagents 1](image_url)

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PL-06

**FLUOROALKYLTHIOLATION REACTIONS: TOWARDS THE DEVELOPMENT OF A FAMILY OF MULTIPOTENT AND VERSATILE REAGENTS**

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Due to their specific properties, fluorinated compounds find use in a large panel of applications, from life science to materials. These last years, the association of fluorinated groups with sulfur atom has emerged to propose innovative substituents with original and unprecedented properties. The trifluoromethylthio group (SCF$_3$), with its high lipophilicity (Hansch parameter $\pi_R = 1.44$)$^1$, has been the most studied, but some other moieties, such as SCF$_2$H, began to emerge.

However, despite this high interest for these emerging fluorinated substituents, methods to easily introduce them onto organic compounds were still limited until recently.$^2$

In this context, we have developed a new family of versatile reagents, namely the fluoroalkanesulfenamides, which are easy to synthesize and shelf-stables.$^3$ Depending on the conditions, these reagents can behave as electrophilic or nucleophilic species.$^4$ They can be also implied in cross-coupling reactions.$^5$ Therefore, a large panel of various trifluoromethylthiolated molecules can be easily synthesized. Furthermore, because of the modularity of the fluorinated part, other fluoroalkylthio substituents can be also obtained, from higher fluorinated homologs to functionalized fluorinated moiety. For instance, molecules bearing the unknown DCF$_2$S group could be readily obtained.$^6$

![Fig. 1. Versatility of fluoroalkanesulfenamides](image)

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DIFLUOROCARBENE AS A BUILDING BLOCK

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Difluorocarbene can be used as a building block for the synthesis of compounds containing difluoromethylenene fragment.

Interaction of difluorocarbene with organozinc reagents followed by the reaction with electrophiles leads to products of three component coupling.\(^1\)

\[
\begin{align*}
\text{RZnBr} & \quad \text{E} \\
\quad \quad \rightarrow \\
\text{Nu} = \text{RZnBr} & \quad \text{Nu} = \text{Hal}^+, \text{H}^+, \text{NO}^+ \\
\text{E} = \text{allylBr, 1-bromoalkyne} & \quad \text{E} = \text{allylBr, 1-bromoalkyne}
\end{align*}
\]

We showed that CF\(_2\)-fragment can be inserted into C-C bond of ketones. The method involves three consecutive steps, namely silylaltion, difluorocyclopropanation, and ring opening. However all these steps can be performed in one pot\(^2\).

\[
\begin{align*}
\text{OSiMe}_3 & \quad \text{R}^1 \quad \text{R}^2 \\
\quad \downarrow & \quad \quad \rightarrow \\
\text{OSiMe}_3 & \quad \text{Me}_3\text{SiO} \\
\text{R}^1 \quad \text{R}^2 & \quad \text{R}^1 \quad \text{R}^2
\end{align*}
\]

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The evolution of fluororous chemistry started with the isolation of a few drops of fluorocarbons and the recognition of their unique physical-chemical properties, such as inertness, high oxygen solubility, non-toxicity, and easy separation.\(^1\) The fluorous phase (catalyst or reagent phase) is the lower layer of a liquid-liquid two phase system and it is rich in perfluoroalkane type solvents, while the presence of the fluorous components in the upper layer (product phase: mostly organic phase) could be negligible in case of phase equilibrium at lower temperatures (Fig 1). Such fluororous biphasic systems (FBS) could become one-(liquid) phase systems by the increase of temperature thus allowing the execution of chemical reactions under homogeneous conditions coupled with easy product isolations via liquid-liquid separations at lower temperatures.\(^2\) Some years later the FBS concept was expanded with the technologies of fluorous synthesis and fluorous mixture synthesis.\(^3\)

**Fig. 1.** The original drawing of a fluorous liquid-liquid biphasic system.\(^2\) The lower phase consists of a fluorocarbon type solvent and a fluorous catalyst or fluorous reagent which is designed to be preferentially soluble there; while the upper phase could be any immiscible liquid including hydrocarbons as well.

Last two decades we studied the underlying principles of FBS by synthetic and analytical methods coupled with QSAR analyses. We showed that specific fluorophilicity discloses linear correlation with the calculated Hildebrand parameter of the F-compounds. Most of the target fluorophilic compounds were prepared from commercial F-building blocks such as perfluoroalkyl iodides, perfluoroalkane carboxylates, F-alcohols and derivatives. Effective separation of fluorous compounds was based on their inherent physical properties.

Since the CF\(_3\)-group was predicted and observed as the most effective fluorophilic substituent,\(^4\) introduction of nonafluoro-tert-butylalcohol – first synthesized and reported by Knunyants and Dyatkin\(^5\) – its use as a fluorous building block became evident. In addition, the (CF\(_3\))\(_3\)C-group as opposed to the classical longer perfluoroalkyl-groups (C\(_n\)F\(_{2n+1}\), n > 6) does not have negative environmental concerns.\(^6\)

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FLUORINE AS A STEREOELECTRONIC TOOL IN THE DESIGN OF PERFORMANCE ORGANIC MOLECULES

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The lecture will then illustrate some of examples of incorporating fluorine into organic molecules. For example the CF$_2$ group can be used to influence alicyclic ring conformation. The CF$_2$ likes to adopt corner locations in such rings and this can influence the fragrance potency of analogues of musk lactones and ketones.\textsuperscript{2,3}

![Figure 1](image1.png)

\textbf{Figure 1.} The location of CF$_2$ groups alters the macrocyclic ring conformation of musk ketones

This discussion will extend to cyclohexanes containing four and six fluorine atoms around the ring.

Different diastereoisomers lead to very different physical properties.

![Figure 2](image2.png)

\textbf{Figure 2.} Cyclohexanes with 1,3 diaxial C-F bonds are polar with a +ve and a –ve face.

\textbf{References:}

POLYFLUOROCONTAINING 2-(HET)ARYLHYDRAZONO-1,3-DICARBONYL COMPOUNDS IN ORGANIC SYNTHESIS

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The synthetic potential and peculiarities of polyfluorocontaining 2-(het)arylhydrazono-1,3-dicarbonyl compounds are considered. Due to the structural features they can react at 1,3-dicarbonyl fragment and/or with the participation of the hydrazone NH group to give a variety of open-chain or heterocyclic systems. So these compounds are promising reagents for coordination, heterocyclic and medicinal chemistry. The use of fluorinated derivatives has significant differences from the chemistry of non-fluorinated analogues. The most interesting reactions are the cyclizations of 2-(het)arylhydrazones-1,3-dicarbonyl compounds with binucleophiles, which proceed regioselectively in the case of fluorinated derivatives. This approach can be applied in targeted synthesis of heterocycles. Special attention is paid to aspects of a possible practical application of the synthesized derivatives.

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FLUORINATED ORGANOBORON DERIVATIVES: NEW APPROACHES TO SYNTHESIS

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Fluorinated organoboron derivatives are representatives of a specific class of organoelement compounds. This arises from the significant effect of several fluorine atoms on the reactivity of organic moiety itself as well on reactions at boron atom. Peculiarities of poly- and perfluorinated organoboron compounds with respect to the well studied non-fluorinated analogues require the elaboration of new synthetic pathways to them and very often, these routes are sufficiently differ from ones that used traditionally. In general, they are based on the transformation of polyfluoroorganogroups bonded to boron atom (without C-B cleavage) and methods of carbon—boron bond formation\textsuperscript{1}.

This report is focused on the preparation of polyfluoroorganyltrifluoroborates, M[R\textsubscript{F}BF\textsubscript{3}]. These salts are important key reagents in syntheses of polyfluorinated derivatives of polyvalent iodine(III, V), bromine(III, V), and xenon(II, IV). In addition M[R\textsubscript{F}BF\textsubscript{3}] are synthons for introduction of polyfluorinated moieties into organic molecules by Suzuki-Miyaura cross-coupling reaction.

Traditional route to borates M[R\textsubscript{F}BF\textsubscript{3}] consists in reaction polyfluorinated organomagnesium and organolithium compounds with boron-containing electrophiles and subsequent replacement of ligands at boron by fluorine atoms. Despite common character, this route is very limited in series fluoroorganoborates because of instability of polyfluoroorganylmagnesium or –lithium nucleophiles or intermediate products.

Here we present new alternative approaches to the synthesis of M[R\textsubscript{F}BF\textsubscript{3}] based on modification of polyfluorinated aryl, alkenyl, and alkynyl groups R\textsubscript{F} = C\textsubscript{6}F\textsubscript{5}, R\textsuperscript{1}CF=CF (R\textsuperscript{1} = F, Cl, C\textsubscript{4}H\textsubscript{9}, C\textsubscript{n}F\textsubscript{2n+1}), R\textsuperscript{2}C≡C (R\textsuperscript{2} = CF\textsubscript{3}, C\textsubscript{6}F\textsubscript{13}) by the action of nucleophilic, electrophilic and radical reagents whereas BF\textsubscript{3} group remains intact. Photoinduced isomerization of polyfluoroalkenyltrifluoroborates allows us to obtain salts which are not easily available in different ways. The peculiar reactivity of perfluoroorganyltrifluoroborates is illustrated by comparison with reactions of corresponding hydrocarbon analogues.

\textsuperscript{1} Adonin, N.Y. and Bardin, V.V. Russ. Chem. Rev. 2010, 79(9), 757-785
Organofluorine chemistry is one of the fastest growing area of modern organic chemistry, because many fluorine-containing compounds have a high biological activity. To date, approximately 25-30% all pharmaceuticals contain fluorine. The great role of fluorinated compounds in agrochemistry and the material science cannot be also overestimated. At the same time the known methods of direct introduction of fluorine or fluorinated moieties do not always possess appropriate selectivity and effectiveness. Hence, there is a great demand for the elaboration of new synthetic methods in this field.

Fluorinated functionally substituted olefins and acetylenes have a great potential for the construction of molecules having fluorine or perfluoroalkyl groups attached to desired position. Several years ago a novel catalytic olefination reaction was discovered by our group. Unsubstituted hydrazones of aldehydes and ketones can be transformed into alkenes R_1R_2C=CXY under treatment with CHal.xy in the presence of catalytic amount of copper salts. This reaction allows us to synthesize a variety of fluorinated alkenes and acetylenes using cheap and affordable freons. These fluorinated building blocks were successfully used in the synthesis of fluorinated heterocyclic compounds, which are perspective for medicinal chemistry.
UNSATURATED AND HETEROCYCLIC COMPOUNDS ON THE BASIS OF TRIFLUOROMETHANESULFONAMIDE

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Trifluoromethanesulfonamide (triflamide) and its derivatives are drastically distinct in their chemical and physico-chemical properties from the non-fluorinated analogues because of the presence of a strong electron-acceptor triflyl group CF$_3$SO$_2$. We present the results of the latest research in the field of the chemistry of unsaturated and heterocyclic derivatives of trifluoromethanesulfonamide (Fig. 1): the methods of synthesis, chemical properties, tautomerism, peculiarities of molecular and electronic structure, mechanisms of the reactions. Introduction of unsaturated substituents expands the synthetic potential of triflamide derivatives. In addition in the cases when the molecule contains a free NH group, the compounds are strong NH-acids capable of self-association.

The methods of synthesis, structural features and chemical behavior of unsaturated derivatives of triflamide containing the C=N bond – alkylidene- and alkenylidenetriflamides TfN=CHR (R = alkyl, alkenyl), N-triflylamidines TfN=CH–NR$_2$ and N-triflylguanidines TfN=C(NR$_2$)$_2$ are also considered.
SYNTHESIS, APPLICATIONS AND RECYCLE OF TRANSITION METALS BEARING HEAVY AND MEDIUM FLUOROUS LIGANDS

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With the aim to exploit the potential of fluorous separation methods in homogeneous catalysis, we synthesized during the last several years a series of palladium and ruthenium precatalysts for coupling reactions and various variants of metathesis reactions.

In addition to the possibility of the precatalyst/catalyst recycle, we were also aimed in adding further desirable properties to our precatalysts. Thus, several precomplexes bear stereogenic centers and works attempting their separation into pure enantiomeric forms capable of enantioselective processes are in progress. Furthermore, we were interested in selectivity or activity of the complexes synthesized. Hence, all our complexes contain polyfluoroalkylated NHC ligands improving the stability of the precatalysts. Modification of the imidazolium ring with racemic secondary polyfluoroalkylated ponytails resulted in formation of diastereomeric mixture of imidazolium salts, which were employed in the synthesis of PEPPSI catalyst analogue 1 (Fig. 1) bearing unsaturated NHC ligand. Its catalytic activity in model Suzuki coupling was only moderate, however, analogous complex 2 bearing more stable NHC ligand and polyfluoropolyoxaalkanoate ligands displayed excellent activity in this model reaction.

Stable ruthenium second generation metathesis precatalysts of alkene metathesis bear saturated NHC ligands. Using diimines and polyfluororganometallic compounds, we hence synthesized stereoselectively threo-bis(polyfluoroalkylated) diamines and from them the corresponding saturated NHC ligands containing complexes 3-5. While we were able to obtain complexes 3 with enantiomerically enriched polyfluoroalkanoate ligands displaying improved selectivity but significantly decreased stability, complex 4 bearing polyfluoroalkylated tertiary groups in the NHC ligands was more robust than commercial precatalyst and highly active at high temperature formation of the tetrasubstituted double bond by metathesis. Finally, precatalyst 5 is the first Hoveyda-Grubbs precatalyst analogue with extremely rapid initiation phase enabling to perform alkene metathesis at low temperatures.

Fig. 1. Examples of fluorous transition metal precatalysts synthesized in our laboratory
SYNTHETIC APPLICATION OF 1-CHLORO-1,2,2,2-
TETRAFLUOROETHANE

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Versatility of fluorine-containing small molecules are well recognized especially as industrial raw materials and a variety of fluorinated ethanes have been employed for such a purpose$^1$. In this talk, we would like to disclose the utility of 1-chloro-1,2,2,2-tetrafluoro-ethane 1 for the construction of 2-chloro-2,3,3,3-tetrafluoropropanols 3$^2$ and the corresponding propylamines 4$^3$, and their conversion to $\alpha$-fluoro-$\alpha,\beta$-unsaturated carboxylic acid derivatives 5 and $\alpha$-amino acids 6, respectively (Scheme 1). During this investigation, we became interested in the stability of the anionic species 2 because the similar anions like CF$\text{3}$CHXLi$^4$ were known to furnish the products like CF$\text{2}=\text{CXCH(OH)R}^1$ by the reaction with R$^1$CHO after elimination of LiF, followed by further deprotonation of the vinylic proton. Moreover, no generation of CF$\text{3}$CH$\text{2}$Li has been reported thus far$^5$, but the corresponding copper$^6$ and palladium$^7$ species were nicely employed for the coupling with aryl iodides as well as vinyl bromides, and aryl boronic acids, respectively. Our computation for a variety of CF$\text{3}$CX$\text{XY}$Li successfully demonstrated that, when at least one hydrogen is included as X or Y, ready LiF elimination should be occurred with the energy barriers in a range of 2.6 kcal/mol (X=Y=H) to 8.0 kcal/mol (X=H, Y=F), while up to 20.2 kcal/mol of activation energy (X=Y=F) was required when X and Y are halogen atoms. These results nicely explain the nature of CF$\text{3}$CX$\text{XY}$Li for reactions with electrophiles.

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PL-16

OUTLOOK FOR RADIATION TECHNOLOGY IN DEVELOPMENT OF NOVEL PTFE BASED MATERIALS

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PTFE possesses a unique set of physical and chemical properties providing flexibility and wide range of its applications. Until present, global trends in the improvement of PTFE properties were its chemical modification by addition of small amounts (below 1 mol %) of a comonomer to tetrafluoroethylene at the polymerization and filling with organic and inorganic fillers. Drawbacks of these methods are: (1) low level of improving properties by chemical modification (2) very weak interfacial interaction between filler particles and polymer matrix what leads to interfacial cleavage, porosity, and inhomogeneous structure of composites. In addition, the developed methods do not eliminate the main disadvantage of PTFE, its superplasticity due to the features of supramolecular structure.

In recent years, a radiation technology of PTFE modification has been developed, solving the problems of superplasticity, high creep, and low wear resistance of PTFE and retaining all its advantages.

In this work we review scientific basis and prospect for further development of radiation technology of PTFE modification. This technology provides materials with various properties, including filled PTFEs of various functionality whose performance outranks worldwide alternatives. The technology is based on the initiation of supramolecular reorganization at the level of crystalline domains, fibrils, lamellae, and spherulites, a process proceeding in PTFE under irradiation above the melting point.

We review the data on the structure and properties of PTFE that obtained by $^1$F NMR, IR spectroscopy, DSC, WAXS, SAXS, high-resolution electron microscopy and state main concepts and mechanisms of radiation modification of PTFE.

Examples are given for practical applications of novel materials in mechanical engineering, valve production, aerospace and nuclear industry.

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CURRENT SITUATION AND DEVELOPMENT PROSPECTS IN FLUORINE CHEMISTRY

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Rapid development of organofluorine chemistry started in the course of producing the atom bomb, it was discovered that fluorinated materials are good in keeping of UF₆, which is required for separation of uranium isotops. This was both a blessing and a curse for organofluorine chemistry: on one hand, there were financing and rapid development, on the other hand – secrecy. Even now, when there is no funding anymore, by inertia, since it was established before, there is no special course of organofluorine chemistry in any academic institutions and universities, though organofluorine chemistry gave a large amount of useful products. Here are only products, which are produced in > 100 T/year.

I. Inert gases – halons and freons.
II. Fluorine monomers and polymers on their basis;
III. Fluoroolefin oxides and products on their basis;

1) All these products are turned into fluoroelastomers and fluoroplastics (Teflon is one of them).
   It is planned to increase the capacity in production of polymers to 500 thousand tons to 2025.
2) Surfacants.
3) A range of fluorine acetic acids – basic products for pharma and agro-industry.
4) Long-chain perfluoroacids and sulfoacids mainly for surfactants and coatings.
5) Adducts of perfluoroalkyl iodides to ethylene form the basis for production of large amounts of substances and materials.
6) Fluoroaromatics – agrochemicals and pharmaceuticals.
7) Perfluoroarometics – agrochemicals, pharmaceuticals, and special materials.

Organofluorine chemistry gradually increases its presence in our life and it has serious basis: the content of fluorine in Earth crust is more then that of iodine, bromine, and even chlorine.

Only explored reserves of fluorine in form of fluorites come up to 2.4 × 10⁸ T.
The market price is significantly lower than the iodine or bromine price.

This makes fluorine chemistry one of promising directions for the development of science and industry.
FLUORINE IN PEPTIDE AND PROTEIN ENGINEERING

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Fluorine has emerged as a “magic element” in medicinal chemistry, crop, and materials science. The introduction of fluorine into small molecules and biopolymers has a wide range of effects on their physicochemical properties, often desirable, but in most cases unpredictable. The fluorine atom imparts the C-F bond with low polarizability, high polarity, and the ability to significantly affect the behavior of neighboring functional groups. The ways in which fluorine influences protein stability and function, as well as peptide-protein interactions, are not easily generalized and, thus, a rational design applying fluorinated amino acids in peptide and protein engineering is currently not possible.

Our group has established a research program that aims at understanding the impact of fluorination in the context of peptide and protein environments and this talk will cover several aspects of our current efforts.
FORMATION OF POLYFLUOROARENES WITH BENZOTHIOPHENE AND THIENOPYRIDINE SKELETONS IN THERMAL REACTIONS OF POLYFLUORO-ORTHO-CHLOROARENETHIOLS WITH TETRAFLUROETHYLENE.

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It has previously been shown that the co-pyrolysis of pentafluorobenzenethiol, heptafluoropara-thiocresol with tetrafluoroethylene (TFE) in a flow system gave mainly perfluoroindan. In order to develop a more general method for preparation of polyfluoroindananes we considered it reasonable to study thermal reactions of polyfluoro-ortho-chloroarenethiols with TFE. Polyfluoro-ortho-chloroarene thiols were obtained from polychlorofluoroarenes and KSH.

We showed that co-pyrolysis 2,5-dichloro-3,4,6-trifluorobenzenethiol, 2-chloro-4-trifluoromethyl-3,5,6-trifluorobenzenethiol with TFE at ~600ºC in a flow system gave mainly compounds with benzothiophene skeleton (Scheme 1).

![Scheme 1](image1)

In the reactions of 2,4,5-trichloro-3,6-difluorobenzenethiol and 6-chloroctafluoroindan-5-thiol with TFE, the compounds with benzothiophene skeleton were also formed.

Compounds with thienopyridine skeleton were formed in the reaction of 3-chloro-2,5,6-trifluoropyridine-4-thiol with TFE at 510-530 ºC in a flow system. The major product of this reaction was heptafluoro-2,3-dihydrothieno[2,3-c]pyridine (1c) (Scheme 2).

![Scheme 2](image2)

Formation of compounds 1a-c with participation of the intermediate polyfluorinated spiro radical σ-complexes is proposed.

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Polyfluorination of HO-, HOOC- groups in producible alkanes and polymers is becoming more effective polyfluorinated agents as α-chloroalkyl polyfluoroalkylethers. For example, ethanolysis of α-chloroalkyl polyfluoroalkylethers, \( RCH_2OCH(CH_3)Cl \), \( R=HCF_2CF_2, HCF_2(CF)_2, HCF_2(CF)_3 \), are shown that ethanolysis is going with energy of activation (in \( \text{kDg/mol} \)): \( HCF_2CF_2 - 187.2 \), \( HCF_2(CF)_2 - 193 \), \( HCF_2(CF)_3 - 209.8 \), \( CH_3CH_2 - 184.6 \). Energy of activation for ethanolysis is maximal for alcohols with the most long polyfluorinated chain: \( HCF_2(CF)_3CH_2 > HCF_2(CF)_2CH_2 > HCF_2CF_2CH_2 \).

\[
\text{ROCH(CH}_3\text{)Cl} + \text{C}_2\text{H}_5\text{O} \cdots \text{HOCl}_2\text{H}_5 \rightarrow \text{HCl} + \text{C}_2\text{H}_5\text{OH} + \text{ROCH(CH}_3\text{)OCl}_2\text{H}_5
\]

It is shown the influence length of polyfluorinated chain: in line: tetrafluoropropyl-, octafluoropentyl-, dodecafluoro-heptyl chlorosulphites on reaction with alcohols. Cyclohexane reacts similarly (catalysis \( \text{N,N-dimethylformamide} \)):

\[
\text{H(CF}_2\text{CF}_2\text{)nCH}_2\text{OS(O)Cl} + \text{ROH} \rightarrow \text{H(CF}_2\text{CF}_2\text{)nCH}_2\text{OR} + \text{SO}_2 + \text{HCl},
\]

где \( n = 1, 2, 3 \), \( R - \text{cycle- C}_6\text{H}_{11} \)

Polyfluoroalkylethers were obtained from cyclohexane was obtained in yield 82% (tetrafluoropropyl ether), 75% (octafluoropentylether), 65% (dodecafluoroheptyl ether). Polyfluoroalkyl chlorosulphites used for introduction of polyfluoroalkyl groups in HOOC-groups of carboxymethyl cellulose. The effect of vibration about 100 Hertz for 0,5-2% solutions was discovered. Polyfluorinated groups are introduced in polymers by radical polymerization using polyfluoroperoxide initiators.

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1 Rakhimov A.I. et.al. Fluorine Notes. 2015, №4(98).
Fluorinated 1,3-dicarbonyl compounds have been used in immunofluorescence analysis (IFA) of diseases and pathologies for more than 30 years. Achievements in the field of the development of new fluorination benzo- and dibenzoheterocycle reagents as well as their complexation with europium ion and luminescence-spectral properties are discussed in the report. Application potential of the developed reagents as markers in biomedical analysis and fluorinated substitutions effect on the luminescence stability have been estimated.

The methods of nanodispersion development containing the fluorinated 1,3-dicarbonyl compounds complexed with europium ion are considered. Direct doping of the polysterine and silicate types of nanodispersions causes formation of intensely luminescent nanoparticles, which are examined as a basis for biochip development.
POLYMER SURFACE FLUORINATION – NEW DIRECTION OF RESEARCH AND APPLICATION

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In this review, the recent studies in the field of surface modification of polymers and some new results are discussed. In previous research, it was experimentally shown with some examples that the currently well understood method of surface fluorination of polymer films is very effective for the formation of surface heterogeneous (mosaic) chemically (and sometimes morphologically) nonuniform structures differing in the degree and scale of localization. As a result of the exchange of hydrogen atoms for fluorine atoms, a surface modified layer with a chemical structure analogous to that of a polyfluorinated polymer is formed. With variation in the modification conditions, the degree of polymer fluorination and the degree of substitution of hydrogen atoms for fluorine atoms in a polymer chain can be controlled. The fluorinated layer has a higher chemical stability along with improved tribological, biocompatibility, and barrier properties and, in the case of oxyfluorination, adhesion characteristics.

The mentioned combination of the modification methods makes it possible to obtain surface layers that are relatively stable against environmental effects and that are characterized by the maximum hydrophobicity (for fluorination, close to that of PTFE) or the maximum hydrophilicity (for sulfonation, exceeding those of well-known polar polymers). The modification through preliminary fluorination allows the formation of universal inert surface layers and the following controlled manipulations that result in the formation of the desired chemical design and pattern.

The methods of heterogeneous macro, micro and nanostructure formation on the surfaces of polymer films via their modification with gaseous fluorine have been considered. The successive fluorination and sulfonation of polyolefin films allows the synthesis of heterounit bi and polyfunctional molecular fragments, thereby providing controlled chemical structuring at the nanolevel within a macromolecular segment. The combined use of the above methods of polymer surface modification and intermediate film deformation under uniaxial tension results in the formation of surface microzones with fluorinated and sulfonated structures. Fluorinated and sulfonated macro and microzones are formed via mechanical fracture of the fluorinated layer before sulfonation or via shielding of the polymer surface before sulfonation according to a given pattern through photolithographic methods. The practical applications of polymer films with heterogeneous surface structures are discussed. Approaches to the development of systems for the directed microfluidic transfer of target compounds on film surfaces by “molecular rail channels,” which is based on significant differences in the physicochemical properties of modified regions, were discussed.

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FLUORINE-RICH FLUORIDES: NEW INSIGHTS INTO THE CHEMISTRY OF POLYFLUORIDE ANIONS

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In the recent years several high oxidized metal based compounds have been investigated under cryogenic conditions using matrix-isolation spectroscopy. Quantum-chemical calculations confirm these experimental assignments and provide fruitful information’s about the stability and properties of such cryogenic compounds.

In this context the formation of free polyfluorides under cryogenic conditions have been discovered. Polyfluoride anions have been investigated by matrix-isolation spectroscopy and quantum-chemical methods. For the first time the higher polyfluoride anion $[F_5]^{-}$ has been observed under cryogenic conditions in neon matrices. Beyond this, new techniques have been developed to prepare ion-pair complexes such as $M^+[F_3]^{-}$ in the gas-phase.

Here we present our latest research results of such aforementioned compounds.

Figure. Polyfluoride Anions

References

4-FLUOROALKYL-9H-PYRIMIDO[4,5-b]INDOLES: SYNTHESIS AND CYTOTOXICITY


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9H-Pyrimido[4,5-b]indoles are an important class of heterocyclic compounds. Substances bearing a 9H-pyrimido[4,5-b]indole ring system are used in the design of new antitumor agents\(^1\). We developed a synthetic approach to new 4-fluoroalkyl-9H-pyrimido[4,5-b]indoles by an intramolecular Heck cyclisation of 4-anilino-6-fluoroalkyl-5-iodopyrimidines in the presence of Pd(OAc)_2 or CuI as catalysts.

We found that CuI is the most effective catalyst for the synthesis of 4-trifluoromethyl-containing 9H-pyrimido[4,5-b]indoles. However, the synthesis of 4-difluoromethyl-containing 9H-pyrimido[4,5-b]indoles proceeded more effectively in the presence of a palladium catalyst.

Individual 4-fluoroalkyl-9H-pyrimido[4,5-b]indole derivatives showed preferential cytotoxicity toward the human myeloid leukemia K562 and colon carcinoma HCT116 cell lines at low submicromolar concentrations whereas non-malignant counterparts were less sensitive. Mechanisms of cytotoxicity and a detailed synthesis of 4-fluoroalkyl-9H-pyrimido[4,5-b]indoles are discussed.

BUCKYBOWLS MEET FLUORINE

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Geodesic polyarenes became the focus of attention not only because they can be considered as substructures of fullerenes with three-dimensional bowl-shape or the polar end-caps of carbon nanotubes, but also because of their own chemical and physical properties. Corannulene (C\textsubscript{20}H\textsubscript{10})\textsuperscript{1} and sumanene (C\textsubscript{21}H\textsubscript{12})\textsuperscript{2} are the best-studied buckybowl compounds and various synthetic routes have been published. As demonstrated by us\textsuperscript{3} and others\textsuperscript{4} introduction of electron withdrawing substituents like fluorine or perfluoroalkyl alters the properties of these compounds drastically.

Herein we report various routes which allow a systematic introduction of perfluoroalkyl groups in specific positions of corannulene. Using appropriate substituted alkynes offers the introduction of specific substitutents in 1,2-position of the corannulene. Carbon-carbon cross-coupling reactions using perfluoroalkyl copper reagents or palladium catalyzed reactions permit the selective synthesis of specific regio isomers.

The electronic and structural properties of new compounds were investigated by UV-vis spectroscopy and cyclic voltammetry. Evaluation of non-covalent interactions in the solid state which generate each structural motif, are supported by single-crystal X-ray diffraction data.

References

FLUORO AND HYDRIDO CYANOBORATES

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Cyanoborate anions, e.g. \([\text{B(CN)}_4]^–\), \([\text{BF}_x(\text{CN})_{4-x}]^–\), and \([\text{BH}_x(\text{CN})_{4-x}]^– (x = 1–3)\), exhibit high chemical and electrochemical stabilities. Ionic liquids (ILs) based on these borate anions are low-viscous, low-melting and thermally very robust salts. Because of the combination of these properties salts containing these borate anions in general and ionic liquids in special are valuable materials for electrochemical applications, e.g. as components of electrolytes for dye-sensitized solar cells (DSSCs).

In recent years, we have developed new and efficient syntheses for many of these borates. These syntheses include Lewis-acid catalyzed reactions as well as electrochemical fluorinations (ECF, Simons process). Furthermore, the properties of the borates have been studied in detail. \(\text{K}[\text{BF(CN)}_3]\) is a valuable starting material for the preparation of salts of the homoleptic cyanoborate anion \(\text{B(CN)}_3^{2–}\) that reacts as a boron-centered nucleophile and that provides an elegant access to a broad variety of different tricyanoborates (e.g. \(\text{K}[\text{CH}_2=\text{CHCH}_2\text{B(CN)}_3]\) and \(\text{K}[\text{C}_6\text{F}_5\text{B(CN)}_3]\)). In addition, salts of the \(\text{B(CN)}_3^{2–}\) anion are starting materials for salts of the homoleptic hexacyanoborate dianion \([\text{B}_2(\text{CN})_6]^{2–}\). This diborane (6) derivative exhibits unprecedented chemical and electrochemical stabilities, as evident for example by the successful preparation of the oxonium salt (H\(_3\)O\(_2\))[B\(_2\)(CN)\(_6\)]. Furthermore, a first selective synthesis for a salt of the \([\text{BHF}_3]\) anion, which represents the first well-defined mixed fluorohydridoborate anion, was developed.

The research was supported by Merck KGaA (Germany).

1 N.V. Ignat’ev et al. J. Fluorine Chem. 2015, 177, 46-54.
NICKEL-CATALYZED DERIVATIZATION OF POLYFLUOROARENES VIA C-F BOND CLEAVAGE

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The selective synthesis of fluoroarene compounds has become a subject of growing interest due to the prominent role such species play in many modern pharmaceuticals, agrochemicals and other industrially important products.\(^1\) An attractive route for the selective substitution of fluoroarenes is based on the functionalization of activated aromatic C–F bonds derived from readily available perfluoroarenes. The presentation covers the synthesis and reactivity of NHC-stabilized nickel complexes, which transfer the complex fragments $[\text{Ni}(\text{R}_2\text{Im})_2]$ ($\text{R}_2\text{Im} = 1,3$-Di(organyl)imidazole-2-ylidene) in stoichiometric and catalytic reactions under mild conditions, and their use in the functionalization to polyfluorinated arenes.\(^2\) We are currently developing convenient methodologies to generate and use suitable, partially fluorinated organic precursors. These strategies employ, for example, (i) C-F functionalization of polyfluoroaromatics or (ii) use of the polyfluoroaromatics or fluoroaryl boronic ester in subsequent Suzuki-Miyaura coupling reactions. A smart way to achieve this goal would employ fluoroaromatic boronic acids or boronate esters. Arylboronic acid esters are versatile reagents in organic synthesis, especially in substituent conversions or in the widely employed Suzuki-Miyaura cross-coupling reaction. Transition-metal-catalyzed direct C-H borylation of arenes\(^3\) and borylation of aryl halides\(^4\) has emerged as one of the most important mild and attractive routes for the synthesis of aryl boronates in recent years. The conversion of fluoroaromatics into arylboronic esters via C-F bond activation, however, is relatively unexplored and was restricted to noble metal catalysts until recently. A focus of the contribution will be thus on the use of NHC nickel complexes in carbon-fluorine activation and the use of these processes in catalytic borylation.\(^5\)

The research was supported by the Deutsche Forschungsgemeinschaft (DFG).


PERFLUOROALKYL SILOXAN DERIVATIVES

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Recently we reported on the successful synthesis of thermally stable tris- and tetrakis(pentafluoroethyl)silanes and -silicates. The corresponding trifluoromethyl silicon derivatives are barely known, due to the high fluorophilicity of the silicon centre as well as the high stability of difluorocarbene.

Although tris- and tetrakis(pentafluoroethyl)silanes exhibit a remarkably thermal stability, they tend to hydrolyze to Si-OH moieties, which is accompanied by the liberation of pentafluoroethane. Therefore, all attempts to synthesize polymeric bis(pentafluoroethyl)silicone, \([S(C_2F_5)_2O]_n\), via the treatment of \((C_2F_5)_2SiCl_2\) with water lead to a complex reaction mixture due to hydrolysis. Just as well, reaction of \((C_2F_5)_3SiCl\) with water yields not the desired disiloxane \((C_2F_5)_3SiOSi(C_2F_5)_3\).

Finally, oxidation of \((C_2F_5)_3SiH\) with \(NO_2\) at low temperatures allow the characterization of \((C_2F_5)_3SiOH\). Due to its high condensation tendency, increased temperatures lead to decomposition via hydrolysis, caused by the generated \(H_2O\). However, oxidation of \((C_2F_5)_3SiH\) and \((C_2F_5)_2SiH_2\) in the presence of molecular sieves allows the isolation of \((C_2F_5)_3SiOSi(C_2F_5)_3\) and generation of polymeric bis(pentafluoroethyl)silicone resins, \([S(C_2F_5)_2O]_n\).

![Diagram of chemical reactions](image)

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POLYCRYSTALLINE MATERIALS FOR PHOTONICS ON THE BASIS OF GROUP II AND GROUP III METAL FLUORIDES

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Polycrystalline materials, based on alkaline earth fluorides doped rare earth elements, have been of significant interest for photonics scientists for decades. Use of the single crystals of similar composition is quite complicated, for they are prone to cleavage that leads to mechanical failure of optical materials in the course of their usage. Also, preparation of high quality and large aperture single crystals is quite complicated. One can improve mechanical properties and corresponding laser endurance of said fluoride optical materials by shifting to polycrystalline specimens, but the latter requires a development of their synthetic technology.

Our report covers results of the preparation of fluoride ceramics materials by deep plastic deformation of their single crystals as well as by hot-pressing their powders, namely:
- we have developed a novel synthetic technique for preparing fluoride precursor powders by obtaining an intermediate compound capable to release a fluorinating agent under thermolysis conditions;
- we have determined the requirements for precursor powders that can be used in compacting technology processes;
- we have determined the requirements for the single crystals that can be used in deep plastic deforming processes;
- we have prepared fluoride ceramic specimens with the same thermal conductivity and similar spectrum generation properties as their single crystal analogs (Fig. 1);
- we have determined the ways and means for the improvement of mechanical properties of fluoride ceramics materials (micro-hardness and fracture toughness) in comparison with their single crystal analogs;
- we have developed a novel scientific area of study, physics, chemistry and technology of nanofluorides.

Fig. 1. CaF\textsubscript{2}:Yb (3 mol.% Y) ceramics prepared by deep plastic deformation of its single crystal.
VISIBLE LIGHT PHOTOREDOX ACTIVATION FOR THE PREPARATION OF FLUORINATED COMPOUNDS

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The incorporation of fluorine or fluorine-containing groups into organic molecules can have a dramatic impact on their chemical and biological properties. In particular, fluorinated pharmaceuticals often exhibit improved potency compared to their non-fluorinated analogues and are more metabolically stable\textsuperscript{1}. The comparative lack of fluorine-containing natural products means that access to these compounds relies heavily on synthetic organic chemistry and many options are now available involving either nucleophilic or electrophilic sources of fluorine.

We became interested in the development of new radical methodologies for the installation of fluorinated groups onto organic molecules using visible light photoredox catalysis. This emerging field serves as a remarkably mild and environmentally-attractive approach to generate reactive radical or radical ionic intermediates in a controlled fashion, and allows for the harnessing of energy from abundant visible light in organic chemistry\textsuperscript{2}.

Focusing initially on the trifluoromethyl group, we developed a radical-polar crossover ring expansion process that exploits single electron transfer steps inherent to photoredox catalysis\textsuperscript{3}. In further studies, we turned our attention to the highly lipophilic and electron-withdrawing trifluoromethylthio (SCF$_3$) group, which has been identified as a promising group for incorporation into pharmaceuticals. Using simple halide salts to activate bench-stable electrophilic trifluoromethylthiolating reagents towards photoredox catalysis, we developed a dual catalytic system that gives access to SCF$_3$ radicals under mild conditions. This strategy allowed for the synthesis of diverse SCF$_3$-containing styrene derivatives and could also be applied in radical-polar crossover processes involving ring expansion or cyclisation\textsuperscript{4}.

Fig. 1. Visible light-promoted dual catalyzed trifluoromethylthiolation of alkenes.

This research was supported financially by the DFG (Leibniz Prize) and the Alexander von Humboldt Foundation.

SYNHTESIS OF POLYFLUOROSALICYLIC ACID DERIVATIVES AND THEIR BIOIGOCAL ACTIVITY

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We have developed a practical method for polyfluorosalicylic acids\textsuperscript{2} synthesis via nucleophilic \textit{ortho}-mono-substitution of fluorine atom in the commercially available polyfluorobenzoic acids\textsuperscript{1} with magnesium methoxide followed by hydrolysis. Polyfluorosalicylic acids\textsuperscript{2} are the convenient synthons for creation of fluorinated analogs of the known salicylic derivatives drugs. We have obtained the fluorinated analogs of methyl salicylate\textsuperscript{3}, aspirin\textsuperscript{4}, and sodium salicylate\textsuperscript{5} as a result of polyfluorosalicylic acids\textsuperscript{2} modification at carbonyl and hydroxyl groups. Esters\textsuperscript{3} are the suitable reagents for fluorinated analogs of salicylamides\textsuperscript{6}. We have provided the synthetic methods for fluorinated analogs of \textit{para}-aminosalicylic acid\textsuperscript{7} and the various N-substituted derivatives\textsuperscript{8} via nucleophilic substitution of fluorine atom in \textit{para}-position of esters\textsuperscript{3}.

The experiments \textit{in vitro} have been carried out for synthesized compounds in order to evaluate the ability of cyclooxygenase-1 inhibition and diffusion via cell membranes. An anti-inflammatory and analgesic action has been studied in experiments \textit{in vivo}. A toxicity and tuberculostatic activity has been evaluated. It has been found that an efficiency of fluorinated derivatives is comparable to that of non-fluorinated analogs or higher. In addition, the structural optimization of fluorinated products is required owing to their toxic properties.

This work was financially supported by RSF (№ 16-13-10255) and the Program «The PNRPU - EPFL collaboration on Metabolism and Diabetes». 
CATALYSIS WITH TRIS(PENTAFLUOROETHYL)-DIFLUOROPHOSPHORANE, (C₂F₅)₃PF₂

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Difluorotris(pentafluoroethyl)phosphorane, (C₂F₅)₃PF₂, (liquid, b.p. 92°C) is a novel highly active Lewis acid catalyst for organic syntheses¹. Only a small quantity of this catalyst is required to complete the Diels-Alder reaction of α,β-unsaturated ketones or aldehydes with conjugated dienes or cyclodienes. The developed protocol is more convenient than the procedures reported in the literature. Several cyclohexene, naphthalene and norbornene derivatives were obtained in moderate to good yields².

The Michael addition reaction of 1,3-β-diketones or β-ketoesters (Michael donors) and linear or cyclic unsaturated ketones (Michael acceptors) proceeds under mild conditions with low catalyst, (C₂F₅)₃PF₂, loading and results in the formation of the addition products in moderate to high yields (Scheme 1)³.

![Scheme 1](image_url)

Scheme 1. Michael addition catalyzed by difluorotris(pentafluoroethyl)phosphorane, (C₂F₅)₃PF₂.

Only 0.1 to 1 mol% loading of phosphorane (C₂F₅)₃PF₂ is required to complete the Strecker reaction within some minutes at room temperature (Scheme 2)¹.

![Scheme 2](image_url)

Scheme 2. Strecker reaction catalyzed by difluorotris(pentafluoroethyl)phosphorane, (C₂F₅)₃PF₂.

SYNTHESYS AND STUDY OF THE REACTION ABILITY SILICONCONTAINING FLUOROORGANIC DERIVATIVES.

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Fluorine-containing alkyl and arylsilanes are universal reagents for introduction fluoroaliphatic and fluoroaromatic group in different classes organic and elementoorganic compounds.

We described a method of synthesis perfluoroorganosilanes C\textsubscript{1} – C\textsubscript{8}.

\[ \text{R}_1\text{Hal} + \text{RSiMe}_3 \xrightarrow{\text{Zn/Cu, Solv., } T^\circ\text{C}} \text{R}_1\text{SiMe}_3 \]

Difluoromethyl(trimethyl)silane was produced from Ruppert–Prakash reagent.

\[ \text{CF}_3\text{SiMe}_3 + \text{NaBH}_4 \xrightarrow{\text{Solv.}} \text{HCF}_2\text{SiMe}_3 \]

were synthesized Bromdifluoromethyl(trimethyl)silane was synthesized by the brominating reaction of the difluoromethyl(trimethyl)silane.

\[ \text{HCF}_2\text{SiMe}_3 + \text{Br}_2 \xrightarrow{} \text{BrCF}_2\text{SiMe}_3 \]

Trimethyl (trifluoromethyl)silane was produced by the Swarts fluorination of the trichlormethylsilane

\[ \text{CCl}_3\text{SiMe}_3 \xrightarrow{\text{SbF}_5} \text{CF}_3\text{SiMe}_3 \]

We prepared polyfluoroaromatic silicon derivatives and studied their oxydadion.

![Diagram of reaction products]
SYNTHESIS OF FLUORINE-CONTAINING 1,4-THIAZINE-1,1-DIOXIDES FROM 1,1-DIHYDROPOLYFLUOROALKYL SULFONES

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Alkyl-1,1-dihydopolyfluoroalkyl sulfones are promising reagents for organic synthesis, in particular, dehydrofluorination of these compounds with amines allows to obtain reactive fluorine-containing enamines\(^1\). Starting from 2,2,3,3-tetrafluoropropyl tosylate we obtained functionally substituted sulfone 1 and bis-(2,2,3,3-tetrafluoropropyl)sulfone 2 and found that their dehydrofluorination in the presence of primary amines and ammonia results in the formation of 1,4-thiazine derivatives. Sulfone 1 forms ethyl-4-aryl-5-(difluoromethyl)-3,4-dihydro-2H-1,4-thiazine-3-carboxylate 3 under triethylamine and aromatic amines action, and sulfone 2 in analogous conditions forms 3,5-bis-(difluoromethyl)-1,4-thiazine 4.

The obtained products 3 and 4 are the first representatives of polyfluoroalkyl substituted derivatives of 1,4-thiazine. New fluorine-containing heterocycles may be interesting as potentially biologically active compounds and as reagents for the further chemical transformations due to the presence of reactive centers in their molecules.

GENERATION OF STABLE PERFLUOROBENZOCYCLOALKENYL CATIONS CONTAINING AN ELECTRON-WITHDRAWING PERFLUOROISOPROPYL GROUP IN THE CATIONIC CENTRE

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When perfluoro-1-alkylbenzocyclobutenes were dissolved in an excess of SbF\textsubscript{5} with addition of SO\textsubscript{2}ClF, perfluorinated 2-alkylbenzocyclobuten-1-yl and 1-alkylbenzocyclobuten-1-yl cations were generated. Thus, perfluoro-1-methylbenzocyclobutene (1) gave perfluoro-2-methylbenzocyclobuten-1-yl cation (1a) with the equilibrium being shifted towards the precursor. Similarly, perfluorinated 2-ethylbenzocyclobuten-1-yl (2a) and 1-ethylbenzocyclobuten-1-yl (2b) cations were generated from perfluoro-1-ethylbenzocyclobutene (2), but in this case cation 2b was detected in small amounts whereas cation 2a and precursor 2 were in the solution in equal amounts. In contrast, perfluoro-1-isopropylbenzocyclobutene (3) gave mainly perfluoro-1-isopropylbenzocyclobuten-1-yl cation (3b) and small amounts of perfluoro-2-isopropylbenzocyclobuten-1-yl cation (3a).

When perfluoro-1-methylindane (4) and perfluoro-1-ethylindane (5) were dissolved in SbF\textsubscript{5}-SO\textsubscript{2}ClF, perfluorinated 3-methylindan-1-yl cation (4a), 3-ethylindan-1-yl (5a) and 1-ethylindan-1-yl (5b) were formed in small amounts. In these cases equilibrium was shifted towards the precursor. In contrast, dissolution of perfluoro-1-isopropylindane (6) in SbF\textsubscript{5}-SO\textsubscript{2}ClF led to perfluoro-1-isopropylindan-1-yl cation (6b) without cation 6a and the precursor.

\begin{center}
\begin{tabular}{c c c c c c}
\hline
\textbf{R} & \textbf{SbF\textsubscript{5} - SO\textsubscript{2}ClF} & \textbf{1a} & \textbf{2a} & \textbf{3a} & \textbf{1b} & \textbf{2b} & \textbf{3b} \\
\hline
CF\textsubscript{3} & 1a, 80% & 2a, 48% & 3a, 9% & 1b & 2b, 4% & 3b, 91% \\

C\textsubscript{2}F\textsubscript{5} & 4a, >95% & 5a, 5% & 6a & 4b & 5b, 8% \\

CF(CF\textsubscript{3})\textsubscript{2} & 5, 87% & 6b, 100% & & & & \\
\hline
\end{tabular}
\end{center}

The DFT (B3LYP/6-31G\textsuperscript{*}) calculations of total energies of the compounds and cations in the gas phase have been performed. Calculated relative stabilities of cations were in agreement with the experimental data.

We gratefully acknowledge the Russian Foundation for Basic Researches (project No. 16-03-00348) for financial support.
LITHIUM ENOLATES OF FLUOROALKYL-CONTAINING 1,3-DICARBONYL, 1,3,5- AND 1,2,4-TRICARBONYL COMPOUNDS IN ORGANIC SYNTHESIS

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The results of our own research, as well as published data on the preparation and use in organic synthesis of lithium enolates of 1,3-dicarbonyl compounds (1,2), 1,3,5-triketones (3), and 1,2,4-tricarbonyl derivatives (4,5), are summarized. The simple synthetic methods and available reagents (such as polyfluorocarboxylic esters, methyl ketones, ethyl acetate and derivatives of 1,2-diketones) are used to synthesize these lithium enolates.

These compounds are considered to be valuable polyfunctional building-blocks due to the presence of conjugated bonds system in their structure and several electrophilic and nucleophilic centres.

Lithium enolates 1-5 proved to be versatile reagents for the synthesis of wide range of substances: homo- and heterometallic complexes, fluoroalkyl compounds (β-diketones per se and their oximes, β-hydroxy ketones, β-aminovinyl ketones), fluoroalkyl containing heterocycles (isoxazoles, pyrazoles, pyrimidines, pyridazines etc.), heterocyclic ensembles (dipyrzaoles, pyrazolopyrimidines, indazolopyridazines, pyrazolylquinazolines, pyrazolylbenzothiazoles) and fused heterocyclic systems (quinolines, coumarins, 1,8-naphthyridines, furopyrazines, benzo-andnaphthodiazipines, triazolopyridazines, triazolopyrimidines, pyrazolopyrimidines, benzimidazolopyrimidines, benzimidazoquinazolines, benzoquinolines, benzophenanthridines etc.).

The diversity represented by above mentioned fluoroalkyl multifunctional compounds can be synthesized in 2-3 steps through developed methods, based on esters of polyfluorocarboxylic acids.

This study was performed in the framework of the Federal Program for Support of Leading Scientific Schools (project no. NSh-8922.2016.3.).
THE METHOD OF HYDROGEN FLUORIDE OBTAINING FROM AN AQUEOUS SOLUTION OF HEXAFLUOROSILICIC ACID

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Almost all industrial fluorine compounds are produced using anhydrous hydrogen fluoride (AHF) or fluorine, produced from AHF.

An industrial production of AHF is based on the sulfuric acid decomposition of high-quality natural calcium difluoride CaF$_2$ (fluorspar). Required grade fluorspar reserves are exhausted in Russia, so fluorspar have to be imported. Therefore, the development of methods for AHF obtaining from other fluorine-containing materials, including man-made, is an urgent task.

Considerable amount of aqueous solution of hexafluorosilicic acid (HFSA) is formed at production of phosphate fertilizers using fluoroapatite containing silicon dioxide. Currently, the HFSA is neutralized and solid fluorides are placed on sludge fields.

The amount of fluorine circulating in the fluoroapatite processing is about several million tons per year. Therefore, aqueous solutions of HFSA are useful to consider as a fluorine-containing raw material in the development of new technologies for production of AHF.

The authors of this report have developed a scientific basis of a two-stage method of AHF obtaining with aqueous solutions of HFSA using as a raw material. In the first stage, the interaction of aqueous solution of HFSA with ammonia or ammonia water gives ammonium polyfluoride (APF) NH$_4$F·nHF. In the second stage, PFA is gasified with the formation of gas-phase ammonia and hydrogen fluoride. This mixture is fed for the catalytic decomposition of ammonia on the elements.

The catalyst should not change its properties in the presence of hydrogen fluoride in the second stage of the process. The GIPH-55$^1$ catalyst consisting generally of fluorides of chrome and magnesium conforms to this requirement. Experimental research shows that the measured rate of dissociation of ammonia is about 0.1 mole$_{NH_3}$·c$^{-1}$·m$^{-3}$ in temperature range of 450–550°C with a pressure of 0.1 MPa.

Thus, the proposed method can be considered as a basis for the development of industrial technology of AHF obtaining with HFSA using as a raw material.

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KEY ASPECTS OF CHEMISTRY AND TECHNOLOGY OF FLUORINATED OLEFINS POLYMERIZATION PROCESSES

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Ways of fluoropolymer (FP) synthesis were developed in a 40-50a years of the 20th century with use of the general theoretical ideas of polymerization processes and experiments on production of polymers other classes known by then. For polymerization of fluoroolefines (FO) the most available and easy way in the water environment with persulfate initiation has been chosen, the limitations of which were soon shown, especially at synthesis of melt-processible FP. Ideas of FO polymerization features were formed in process of information accumulation, in essence in parallel with development of FP production.

By consideration of scientific and technological data on FP production it is possible to formulate two basic principles of achievement of the maximum FP potential realization grounded on their chemical nature: preparing of damage-free polymer on synthesis stage or elimination of the at polymerization formed defective fragments by means of additional treatments on processing stages.

In world practice of FP production the combination of easy, available synthesis methods to receive "semi-product" with its additional processing which is generally directed to stabilization of end groups is widely used. For preparing especially pure FP types hard processing by gaseous fluorine at high temperatures, applicable only for the perfluorinated FP is applied.

In Russia the option of preparing damage-free polymer on synthesis stage as the strategic production development direction has been chosen. For realization of this task regularities of polymerization in complex hetero-phase systems with participation of gaseous FO and produced insoluble FP are studied and colligated. The basic organization principle of effective FP production processes – creation the systems of damage-free synthesis which most significant elements are choice of the initiator, assessment of reactionary ability in actual FP synthesis processes conditions; definition of the formation mechanism and ways of elimination of defective fragments is formulated and confirmed.

It is shown that for fluorine- and hydrogen-containing FP preferable initiators are the organic peroxides forming unpolar stable end groups and for perfluorinated have to be near to macromolecule composition.

The observation is made about the building mechanism of unstable oligomeric fractions at FO precipitation polymerization and the solutions to reduce their negative influence on quality of FP are found.

The presented colligation can be considered as a short result to the coming 70 anniversary (2017) since the beginning of researches and developments executed by big group of representatives of the Russian fluoropolymer school – founders of FP production in Russia.
PRODUCTION OF COMPOSITE MICRONEEDLES AND SUPERHYDROPHOBIC COATINGS FROM SUSPENSION OF CARBONYL IRON MICROPARTICLES IN FLUOROOrganic BINDING

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The way of obtaining composite iron - fluoropolymeric magnetic needles in length to 20 mm by self-assembly of carbonyl iron microparticles in a solution fluoroorganic varnish LF-32L in a vertical magnetic field is offered. Resistance of the generated structures in relation to water solutions of acids increases as HCl - HNO₃ - H₂SO₄. They withstand heating to 200°C. Iron dissolution result in to formation of porous fluoropolymeric covers curling or conserving the linear form after loss of filler. Properties of needles and covers are investigated by FTIR spectroscopy, scanning electronic, atomic-powered and optical microscopy.

Fig. 1. A bundle of iron-fluoroplastic magnetic needles (a), a surface of needle to (b) and after removal of iron microparticles (c) by water solution HCl.

Curing process of a thin layer of suspension of carbonyl iron microparticles in a fluoroorganic varnish on a permanent magnet surface is investigated. It is shown, that microparticles are exposed to self-organisation and form vertical structures which give a covering superhydrophobic properties.

Fig. 2. Fragments of a superhydrophobic covering (a, b), a water drop on a surface (c).
POLYPERFLUOROALKYLENOXIDES: SYNTHESIS, PROPERTIES, APPLICATIONS

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Polymers that contain polyperfluoroalkylene oxide units in the chain outstand with the high thermal stability ($T_{\text{decomp}} \approx 300 - 400^\circ C$) and low temperature resistance ($T_g$ as low as $-140^\circ C$). They have a low surface energy and therefore are hardly wettable with organic solvents and water. This makes them useful in designing of materials with a set of valuable properties.

Methods for the synthesis of amides of oligomeric perfluoroalkylene carbonic acids with reactive trialkoxysilyl groups $R_F COH(N(CH_2)_3Si(OC_2H_5)_3$ where $R_F = CF_3CF_2OCF(CF_3)CF_2OCF(CF_3)$- (Ftorsam-39, a protective agent) have been developed. These compounds are readily soluble in organic and organofluorine solvents and impart high hydro- and oleophobicity to materials such as limestone, marble and others. Contact angles were 130-140° with water, 90-95° with decaline, and 110-120° with engine oil M6-12G. The Ftorsam-39 concentration normally was 2-5%. It was also applied as an additive to oils, varnishes and enamels. Water emulsions of Ftorsam-39 have been recently developed with perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoic acid utilized as an emulsifier.

A hydrolysis of Ftorsam-39 in air followed by polycondensation of the hydrolysis products (20-100°C) gives a solid polymer whose macromolecule incorporates mainly two structural fragments.

$$\begin{align*}
\text{Si} & \quad \text{O} \\
\text{(CH}_2)_3\text{NHC(O)}R_F & \quad \text{H} \\
\end{align*}$$

An onset of the polymer mass loss was observed at 300°C, $T_g = 230^\circ C$ and $T_f = 270^\circ C$. By mass spectrometric data, volatile products of the polymer pyrolysis in vacuo at 340°C were represented for more than 90% by a monohydro derivative of 2H-heptadecafluoro-5-methyl-3,6-dioxanonane. To improve the cold resistance of rubbers on the basis of SKF-32 (a copolymer of vinylidenefluoride and trifluorochloroethylene), a few modifiers, i.e. oligomeric perfluoroalkylene oxides with reactive allylamide groups, were synthesized. E.g. rubber with the brittleness temperature ($T_{\text{br.}}$) $-48^\circ C$ and elasticity coefficient ($K_{\text{el.}}$) 0.45 at 20°C was prepared as a result of the modifier addition to SKF-32, whereas without the modifier $T_{\text{br.}} = -36^\circ C$ and $K_{\text{el.}} = 0$.

Branched oligomers and cross-linked polymers were prepared from perfluoroalkylene oxides with peroxide groups in the chain and perfluoro-1,3-butadiene. The copolymerization was performed at 150-220°C. $T_g$ of the copolymers was $-145^\circ C$.

Oligomeric perfluoroalkylene triazines were recommended as efficient inhibitors of the thermal destruction of perfluorinated polyethers in the presence of metals and their oxides.

A solvent-free method for the synthesis of perfluoroalkyleneimidoxylamidines from dinitrils and ammonia was elaborated.
DIRECT FLUORINATION – EFFECTIVE TOOL TO ENHANCE COMMERCIAL PROPERTIES OF POLYMER ARTICLES AND CARBON NANOATERIALS

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The direct fluorination is an effective method of the polymer and carbon nanomaterials surface modification. For majority of glassy polymers only upper surface layer several nm to several μm in thickness is modified, but the bulk properties remain unchanged. Direct fluorination of polymers proceeds at room temperature spontaneously with sufficient for industrial applications rate. Polymer articles of any shape can be treated. Results of the fundamental study of several research groups over the world will be reviewed. The main attention will be paid to description of commercial properties improvement of polymer articles and materials by direct fluorination. Barrier properties of polymer vessels and bottles can be enhanced by a factor of 10 to 500 depending on the nature of penetrating liquid and up to 50 times for oxygen. Gas separation selectivity of polymer membranes and hollow fiber membrane modules can be highly improved: for the case of He/CH$_4$ and H$_2$/CH$_4$ mixture by a factor of 10-50, depending on the polymer membrane nature. Adhesion properties and printability of polymer films and articles are markedly improved under fluorination. Direct fluorination of single-used hospital cloth and linen may result in a total suppression of gram-positive and gram-negative bacteria reproduction. Sorption ability of polymer sorbents can be improved by a factor of 2-2.5. Antibacterial resistance of surgery clothes and hospital lining can be highly improved. Direct fluorination followed by a grafting of monomers can make the polymer surface hydrophobic or hydrophilic depending on the grafted monomer nature. Direct fluorination highly decreases the polymer friction coefficient. Direct fluorination of carbon nanofibers and nanotubes accompanied with a gaseous monomers graft polymerization highly improves their solubility in polar and nonpolar solvent and facilitates further modification by ordinary “wet” chemistry methods. Tensile strength and modulus of polymer composites filled with fluorinated highmodulus polymer fibers or fluorinated carbon nanomaterials can be highly increased (by several tens % for thermosetting and by a factor of several times for thermoplastic composites). Fluorinated carbon nanomaterials can be used as solid lubricants.

The research has been supported by the grant of the Russian Science Foundation 15-13-10038 (concerning reinforcement of polymer composites) and by State Contract 16.711.2014/K from the Ministry of Education and Science of the Russian Federation (modification of CNT).
PREPARATION AND PROPERTIES OF A NEW BICOMPONENT FLUORINE-CONTAINING FILAMENT

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Filaments produced from polytetrafluoroethylene (PTFE) have an almost absolute chemical resistance. Such filaments are required for materials and devices that operate in aggressive environments. However, processing of PTFE in fibrous products is difficult because the polymer can’t be transferred to the melt without decomposition and is not soluble in known solvents. Therefore, filaments on the base of fluoropolymers are manufactured according to special and complicated, costly and environmentally dangerous technologies and have a very high cost.

A perspective way to reduce cost of fluoropolymer filament is to replace PTFE filament to bicomponent filament, the core of which consists of low-cost filament forming thermoplastic polymer such as polypropylene, and the surface consists of a layer of PTFE. However, because of the high chemical inertness PTFE has a very small adhesion to nearly all surfaces, that’s why its durable fixing on a surface of a filament is very difficult.

In this paper we consider a simple and an effective method of modifying polypropylene filaments in the process of their producing from melt to impart them properties similar to fluoropolymer filaments: an extremely high chemical resistance, a low friction coefficient¹². The method is based on the formation of ultrathin, continuous, uniform coating of PTFE on the surface of each filament which forming the yarn. Adhesion of PTFE coating to polypropylene is provided by applying a dilute suspension of finely divided PTFE on the surface of the semi-cured polypropylene filament on an oiling step. In future, the filaments are subjected to orientational drawing. In the process of orientational drawing the coating, due to the ability of PTFE to a pseudo fluidity and a high thermal expansion coefficient, becomes uniform and oriented. The modified polypropylene filament get an extremely high resistance to nitric acid and sodium hydroxide. Its coefficient of friction is close to the coefficient of friction of PTFE, and the strength is significantly higher than the strength of a conventional polypropylene filament. The coating of PTFE is highly resistant to operational stress.
VULCANIZING AGENTS FOR PERFLUORINATED RUBBERS
WITH NITRILE GROUPS. CROSS-LINKING MECHANISM.
PROPERTIES OF COMPOSITES

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Vulcanization topology is accomplished through the formation of a 3D network between polymer chains and thus, the rise of composite material reversible strain.

On 19 July 2016 the synthesis of bis(p-oxiphenyl)-hexafluoropropane marks its 58-year long history. On the day I.L.Knuniants, N.P.Gambarian, et al. [1] synthesized the first representative of new class compounds for dipole curing of fluorine-containing rubbers (trade mark Bisphenol AF). Structure modification of the product with amine groups, the substitution of perfluoroalkyl groups (R_F) for one of tri-fluoromethyls.[2] allows the line of vulcanizing agents for perfluorinated rubbers:

\[
\text{X} \quad \text{where X=\text{-OH, -SH}} \\
\text{R = CF}_3, \text{-CF}_2\text{OCF}_2\text{OCF}_3, \text{-CF}_2-\text{(CF}_2\text{O})_n\text{OCF}_3
\]

At present, if X = OH, R_F=CF_3, the above compound is the only commercial agent curing the nitrile group of perfluororubbers: 2,2-bis(3-amine-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (BOAF), that ensures a high level of composite physical and mechanical properties. Spectroscopy evidences for a complex process of vulcanization and the formation of oxazole and triazine cycles, as well as end groups of different nature.

In 2008 new vulcanizing agents classed with imidoylamidines (DPIA-65) were synthesized by V.A.Gubanov, A.N.Kollar, M.A.Volkova and I.M.Tsypkina.

\[
\text{CF}_3, \text{CF}_2\text{OCF}_2\text{OCF}_2, \text{-CF}_2-\text{(CF}_2\text{O})_n\text{OCF}_3, \text{where n = 1-8; m=0 - 5}
\]

Peculiar features of the new agents behavior are melting low temperature (94,2 ÷ 95,2°C), high physical and mechanical characteristics of clear unfilled vulcanizates.

Two-step vulcanization process for fluorinated rubbers has been proved by spectroscopy. Composite materials resist super-corrosive media (F_2, O_2, etc.) at high temperatures. Perfluoro-bis-amidoximes and perfluoro-bis-hydrazidines were also offered as vulcanizing agents by L.S.German, S.P.Sterlin, Yu.V. Zeifman, A.H.Kollar, et al. However, composite materials with the use thereof show markedly lower physical and mechanical properties.
NOVEL FLUORORGANOSILICONE COATINGS: PREPARATION AND PROPERTIES.

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Novel fluororganosilicone compounds have been developed for the production of various coatings.

The hydrolysis of trifunctional alkoxysilanes $\text{R}_F\text{OCH}_2\text{Si(OR}_F\text{)}_3$, where $\text{R}_F = \text{CH}_2\text{CF}_3$ (1), $\text{CH}_2\text{CF}_2\text{CF}_3$ (2), $\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3$ (3), or $\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ (4), initiated by atmospheric moisture in the presence of 3-aminopropyltriethoxysilane yields ladderlike polysiloxanes under the mild conditions. The coatings are found to consist of the orderly arranged macromolecules and coating surfaces are smooth and hydrophobic. The coating hydrophobicity significantly increases, whilst the refractive indexes decrease with the increase of fluorine concentration in the films and with increase of silicon substituents length. Thin-films coatings based on the monomers 5 and 6 contain less fluorine concentration and so they are less hydrophobic. Their feature property is extraordinary low refractive indexes (1.31-1.32) over a wide range of the wavelengths and in combination with high hardness. In addition, these polysiloxane films are completely transparent in UV, visible, and near IR region.

![Compounds 1-5](image)

Compounds 1-5 were used for aerosil surface modification. The small quantity of fluorinated filler significantly influences on the properties of the hydrophilic polymers based coatings. The fluorinated substituents improve the surface morphology, hydrophobicity and property stability.

We successfully used fluororganodialkoxysilanes 7-9 as additives to sol based methyltriethoxysilane for superhydrophobic coating formation.

![Compounds 7-9](image)

The increase of the number of fluorocarbon groups in dialkoxysilane causes the improved hydrophobic coating properties. Their contact angles of a water droplet exceed 150° (up to 163°) and the roll-off angle <10° that proves these coatings demonstrate superhydrophobic properties. Thus, they can be explored as an efficient anti-icing and self-cleaning surfaces.
PHASE INTERFACE AND STRUCTURING IN FILLED PTFE IRRADIATED ABOVE MELTING POINT

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It has been shown that gamma-irradiation of unfilled PTFE slows down its wear rate by five orders of magnitude\(^1,2\).

Here we analyze effect of high-temperature gamma-irradiation on the mechanical and self-lubrication properties, nature of phase interface, morphology and structuring for PTFE filled with various fillers. Crystal lattice parameters, degree of crystallinity, crystalline domain size for \([100]\) direction are reported and discussed for filled PTFEs, both uniradiated and irradiated above the melting point. X-ray diffraction, high-resolution electron microscopy, DSC, densitometry, mechanical end tribological tests were used in this analysis.

In unirradiated PTFE composites the filler particles has no prominent effect on the structuring in the polymer matrix. The filled PTFE exhibit structures with fibrils packed in parallel across lamellas, similar to the structures observed in unfilled PTFE. Filled PTFE is featured with cleavage at the phase interface between filler and polymer matrix, high porosity, and inhomogeneity of structure.

Irradiation above the melting point of polymer matrix leads to formation of centrosymmetric structures (axiolites) with fibrils directed radially with respect to filler particles located in the centers of these structures. In addition, porosity decreases and phase cleavage between the phases disappears. Strengthening of interaction between phases is explained by radiation-induced grafting of macromolecules (and low-molecular-weight products of radiolysis) to the surface of filler particles. The observed changes in structure lead to significant improvement of mechanical and tribological properties: wear rate decreases by one-two orders of magnitude and elastic modulus, hardness and yield strength increase (up to two times). Relationships between supramolecular structure of filled PTFEs and their macroscopic properties are discussed.

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CREATION NEW GLASS/POLYMER COMPOSITE MATERIALS WITH USE OF TELOMERE SOLUTIONS OF TETRAFLUOROETHYLENE.

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New approach to production of fluorinated glass polymer composites based on the use of impregnation glass fiber filler radiation-synthesized solutions of low molecular weight polymers (telomers) of tetrafluoroethylene. A new telomers of TFE with different terminal functional groups in a number of solvents of different chemical nature (pentafluorochlorobenzol (PFCB), trifluorotrichloroethane, butyl chloride (BC), ethyl acetate (EA), acetone) is synthesized for this purpose. The kinetics and the mechanism of a telomerization and the main properties of the received telomeres are investigated. As fiberglass filler used the standard industrial and caramelized aluminoborosilicate glass fabric with a plain fabric weaving (production of the NGO "Fiberglass" Polotsk). It is shown that when the content of the fluoropolymer introduced only a few percent, the composite acquires the properties of PTFE for water repellency, heat resistance, and resistance to aggressive media. Existing on the market, very limited in scale of production, glass/polymer composites with PTFE binder containing in its composition to 70-80% PTFE. The proposed technology is characterized by low production cost of the composite, and the simplicity of its production due to the exclusion from the traditional scheme of production of PTFE products expensive and energy-intensive operations of sintering PTFE powder weights. The totality of the experimental results suggests the feasibility of using different telomere to modify the glass. Telomeres are synthesized in acetone, PFCB, BC, EA technologically useful for modifying fiberglass filler providing product high degree of water repellency. A comprehensive approach to the choice of technology in relation to a particular practical problem. For example, telomeres in EA have no high thermal stability, but, on the other hand, they are more eco-friendly, than the telomeres synthesized in PFCB, BC and acetone. The experiments achieved increased resistance glass/polymer composite material in terms of long-term exposure to water, high temperatures and chemically aggressive environments while significantly lowering it contained quite expensive polytetrafluoroethylene. Features of the offered technology which doesn't have so far analogs in world practice, and area of possible practical application of the created technology are considered.

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PERFLUORINATED POLYMERS
FOR MEMBRANE SEPARATION OF GASES

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Since invention of polytetrafluoroethylene (PTFE) in 1938th perfluoropolymers occupy some niche due to a combination of various properties (low surface and cohesive energies, high chemical resistance, low electroconductivity and permittivity, low refractive index, etc). Most of the perfluorinated homo- and copolymers (for instance, PTFE, Teflon FEP) are semicrystalline and, therefore, have low gas permeability and could not find application in membrane gas separation. Nevertheless, since 1980th and 90th three types of amorphous glassy polymers have been applied in industry and have attracted an attention as prospective materials for membranes (Teflons AF, Hyflons AD and Cytop). First two groups are copolymers of TFE and perfluorodioxoles while Cytop is aliphatic perfluorinated ring polyether. At the same time, a perfluorinated polyether with SO3H-groups (Nafion 117), a well-known material for H-conductive membranes, was investigated. Recent study by Mukaddam et al showed that Nafion 117 has unexpected potential in separation of fuel gas. During last years novel perfluorinated homo- and copolymers (i) polyhexafluoropropylene and its copolymer with perfluoromethylvinyl ether, (ii) perfluoropropylvinyl ether, and (iii) perfluorinated dioxolane-dioxolane copolymers were investigated.

Hydrocarbon gases and vapors are known to have lower solubility coefficients in perfluorinated polymers in comparison with those in “hydrocarbon” polymers. Therefore, perfluorinated polymers occupy favorable positions on Robeson diagrams (logarithmic dependencies of separation factor vs. permeability coefficient of a gas) for gas pairs containing hydrocarbons (He/CH4, N2/CH4, CO2/CH4, CO2/C2H6, etc) forming own trend. In presentation, we plan to discuss a nature of such unusual behavior of perfluorinated polymers and some aspects of their application in membrane gas separation.
EFFECT OF IRRADIATION ON MOLECULAR AND SUPRAMOLECULAR STRUCTURE OF PTFE. DESTRUCTION OR CROSS-LINKING?

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Effect of ionizing radiation (IR) on polymers is conventionally regarded as a competition of chain scission and cross-linking. Scission of macromolecules decreases molecular mass of polymer and deteriorates its mechanical properties, while cross-linking acts in an opposite way.

PTFE exhibit unusual behavior: effects of radiation cannot be explained on the basis of simple destruction/crosslinking concept for various irradiation conditions: in vacuum and in air, below and above melting point, at low and high absorbed dose.

Here we review the state of the art for the studies of the irradiation effect on the properties and molecular and supramolecular structure of PTFE. Problems in determining crystallinity and crystal domain size, fine structure of lamellae, and hierarchy of supramolecular structures are discussed in connection with mechanical and self-lubricating properties of intacted and irradiated PTFE. Original results on the radiation effects in a wide ranges of temperature (25–380 °C) and absorbed dose (5–5000 kGy) were obtained using wide angle X-ray scattering, DSC, high-resolution scanning electron microscopy, DMA, and two-stage chemical etching of the surface\textsuperscript{1,2}. A special emphasis is made on the analysis of features in the changes of molecular and supramolecular structure by irradiation of PTFE above the melting point.

Regardless of the irradiation temperature, the main product of PTFE irradiation is the scission of C–C bonds in the macromolecular backbone. Radiation yield of scission is above 0.3 per 100 eV below the melting point and 1.5–2.0 per 100 eV above the melting point. An assumption about cross-linking (or long-chain branching) which made in some recent publications is not validated experimentally. A mechanism of anomalous (both for sign and magnitude) changes in the properties of PTFE and their relationship with reorganization of supramolecular structure is discussed.

This work was supported by the Russian Foundation for Basic Research (project No. 13-08-12049).

\textsuperscript{1} S.A. Khatipov et al. \textit{Poverkhnost’ Rentg., sinkhrotron. i neutron. issled.} 2014, (9), 39-46.
CARBONYLATION OF PERFLUORINATED BENZOCYCLOALKENES AND ITS ALKYL AND PHENYL DERIVATIVES IN THE CO-SbF₅ SYSTEM

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We have found that perfluorinated benzocycloalkenes and a number of its derivatives undergo carbonylation under the action of CO in the presence of SbF₅. These transformations are the first example of carbonylation of perfluorinated organic compounds. The reactions proceeds at room temperature and atmospheric pressure, addition of two and more CO molecules occurs in a number of cases. Thus, perfluoroindane (1) in the CO–SbF₅ system adds two CO molecules to form acyl fluoride (2). Perfluorinated 1-alkyl-indanes and -tetralins (3) undergo monocarbonylation at the substituted position of the aliphatic ring.

Perfluorinated benzocyclobutene derivatives in the analogous conditions undergo carbonylation/four-membered ring opening tandem reaction. Thus, perfluorobenzocyclobutene (4) adds two CO molecules to form isochromene (5). Perfluoro-1-alkylbenzocyclobutenes (6) undergo monocarbonylation at the substituted position of the four-membered ring to form acrylic acid derivatives (7). 1,2-Disubstituted perfluorobenzocyclobutenes (8) in the reaction with CO–SbF₅ at 20°C give indan-2-one derivatives (9). Perfluoro-1,2-diethylbenzocyclobutene adds three CO molecules, perfluoro-1,2-diisopropylbenzocyclobutene – two, and perfluoro-1-methyl-2-phenylbenzocyclobutene – only one. Increase in the reaction temperature up to 70°C leads to isochromenes (10) formations. Carbonylation of perfluoro-1-phenylbenzocyclobutene also gives perfluoro-4-phenylisochromene.

We gratefully acknowledge the Russian Foundation for Basic Research (project No. 16-33-00121, No. 16-03-00348) for financial support.
INTERNAL AND CYCLIC PERFLUORO-OXIRANES IN THE SYNTHESIS OF FLUORINE-CONTAINING HETEROCYCLES


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Fluorinated oxiranes are of great importance to fluoroorganic chemistry because of their high reactivity and numerous applications. They are a convenient building blocks to synthesize of various fluorine-containing heterocycles.

Some new fluorine-containing N,O,S-heterocycles were synthesized as a result of interaction of internal and cyclic perfluorooxiranes with series of bifunctional nucleophilic reagents. Continuing our study on reactivity of perfluoroepoxides, we have investigated the nucleophilic attack directivity in reactions of asymmetric internal perfluorooxiranes with binucleophiles and stereoisomeric compound composition by NMR $^1$H, $^{13}$C, $^{19}$F spectroscopy and X-ray crystallography.

This research was supported financially by the Ural Branch of Russian Academy of Sciences (projects no. 15-21-3-5, 15-21-3-6, 15-21-7).
Over the past four decades dozens of new perfluorocarbon emulsions (PFCEM) could not overcome the barrier of clinical trials, other than Russian medicament Perftoran, though it has some disadvantages. The leading cause was a biological activity of EMPF such as unpredictable immediate or delayed anaphylactoid reactions. Urgent reactions occur at the beginning of intravascular infusion of EMPF due to activation of the complement system (the innate immune defense mechanisms). They could be initiated by the contact of blood and the emulsion particles stabilized by nonionic surfactants especially if the particle size exceeds 100 ÷ 150 nm. Late reactions occur in a few hours. As a rule they are associated with activation of "arachidonic acid cascade", if EMPFC is stabilized by phospholipids and the emulsion particle size exceed 250-300 nm. Anaphylactoid reactions also depend on the characteristics of the immune status of the recipient. To mitigate the risk of anaphylactoid reactions transfusiologists use desensitizing agents and inhibitors of the immune response.

Unfortunately until now there were no the systematic studies needed to establish the dependence of the reactogenicity on the physical and chemical properties of perfluorocarbons and bromperfluorocarbons, type and quality of surfactants, changes of adsorption layer and size of particles after transportation and storage of EMPF, influence of a water-salt environment and status of immunity. Our experience showed that it is necessary to study each new EMPF separately. The lack of adequate biological criteria don't permit to reveal reactogenicity in vitro or in vivo on animals. At the present time anaphylactoid reactions are determined too late only at the stage of clinical trials.
THE FLUOROCARBON EMULSION FOR PHOTODYNAMIC THERAPY

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Porphyridinoids are widely used as photosensitizers for photodynamic therapy of cancer. These compounds generate reactive oxygen species (ROS) upon light irradiation (650-780 nm). A low oxygen content in tumors (hypoxia) is a major factor that limits the efficacy of photodynamic therapy.

We hypothesized that a fluorocarbon emulsion resembling the blood substitute "Perftoran" and modified by porphyrins soluble in the fluorocarbon phase would possess the following advantages:

\begin{itemize}
  \item a high oxygen capacity
  \item a physiologically acceptable size of emulsion particles
  \item a reasonable time to remain stable in the body
  \item a significantly longer lifetime of singlet oxygen in perfluorocarbons compared with aqueous media.
\end{itemize}

The solubility of the porphyrin in the fluorocarbon phase was achieved by introduction of perfluoroaliphatic fragments (at least four substituents with the length varying from C\textsubscript{4} to C\textsubscript{8}). Perfluoroalkoxy substituted porphyrins were synthesized using a nucleophilic substitution of the fluorine atom by polyfluoroalkohols.

The fluorocarbon emulsion with porphyrins was prepared by ultrasonic dispersion. The ratio of components (fluorocarbon-surfactant-water) was the same as in "Perftoran". The photosensitized ROS generation was shown by the example of the formation of singlet oxygen (\textsuperscript{1}O\textsubscript{2}). As criteria the value of the quantum efficiency of phosphorescence \textsuperscript{1}O\textsubscript{2} was chosen. It was higher for our samples compared with known tetraaryl-substituted analogs.

Phototoxicity of the emulsion with selected porphyrins was demonstrated on cultured human tumor cells.

\textsuperscript{2}Belyaeva E.V. at al. \textit{Fluorine Notes}, 2015, \textbf{5}(102).
PHOTODAMAGE OF TUMOR CELLS CAUSED BY NOVEL FLUORINATED PORPHYRINS DISSOLVED IN PERFLUOROCARBON

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Porphyrians and their analogues are known as agents for antitumor photodynamic therapy (PDT). Photosensitizers cause cell damage due to their ability to generate oxygen in an excited singlet state of the triplet, so the presence of a sufficient amount of molecular oxygen in the tumor is critical for phototoxicity. Saturation of the tumor with oxygen can increase the efficacy of PDT; in hypoxic tumors the oxygen depot formed by photosensitizers makes PDT fundamentally possible. We developed potential therapeutic compositions consisting of a gas-transporting medium perfluorocarbon in which new fluorinated porphyrins were dissolved. The gas-transporting medium is the perfluorocarbon emulsion ‘Perftoranum’, an anti-hypoxic and anti-ischemic drug based on perfluorodecalin. Structural optimization of porphyrins aimed at improving their solubility in perfluorocarbon included the synthesis of derivatives with various fluoroalkyl substituents\textsuperscript{1}. The novel fluorinated porphyrins exhibited a low dark cytotoxicity (IC\textsubscript{50} > 50 µM). The red laser illumination (633 nm) of HCT116 colon carcinoma cells loaded with submicromolar concentrations of fluorinated porphyrins rapidly destructed tumor cells. This range of concentrations meets ‘dark-to-light’ requirements for development of anticancer photosensitizers. The photodamaging effect of fluorinated porphyrins was more pronounced with the perfluorodecalin emulsion than with the aqueous medium. The dark cytotoxicity of the emulsion remained low. The photoinduced cell death processed via a necrotic mechanism detectable on adhesive (HCT116) as well as suspension (K562 leukemia) cell lines. The photonecrosis developed within the first minutes after the start of cell illumination and was irreversible after the completion of exposure to light. Thus, novel fluorinated porphyrins dissolved in perfluorocarbon increased the photodamage of tumor cells while maintaining the low dark cytotoxicity. Our data provide evidence that hydrophobic porphyrins are promising for further development of anticancer drugs based on this chemical class.

\textsuperscript{1}Belyaeva E.V. \textit{et al.} Fluorine Notes, 2015, 5, 102.
MOLECULAR CO-CRYSTALS OF POLYFLUOROAROMATIC AMINES AND 18-CROWN-6: STRUCTURE, PROPERTIES, AND USING IN PRACTICE

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The development of various devices based on organic crystals requires an analysis of the methods and tools of supramolecular structures design. We have synthesized large groups of the uniform co-crystals of polyfluoroaromatic mono- and diamines with 18-crown-6 that allow studying the regularities of non-covalent interactions [1].

Co-crystals of diamines and crown ether of stoichiometry of 1:1 consist of the parallel 1D assemblies which have the repeating unit "diamine-crown". Structure of these supramolecular objects is provided by the intermolecular hydrogen-bonded synthon C\textsubscript{Crown} - O•••H - N\textsubscript{Arene}. Length of the unit \(l_U\) depends on the type of an aromatic framework (benzene, naphthalene, pyridine), location of the nitrogen atom in a heterocyclic ring (6,6'- and 6,6-diaminopyridines), nature, number and mutual arrangement of amino groups and substituents H, Cl, F, CF\textsubscript{3}. The associates crystallized from a solution and melt are found to have identical heat and melting point. In the group of meta-(het)arylenediamines associates there is a linear correlation between the specific melting heat \(\Delta H_U\) and the unit length \(l_U\): \(\Delta H_U = 475\pm35 - (23\pm2)l_U\); R = 0.954, SD = 5.7, n = 13.

Co-crystals of anilines and 18-crown-6 of stoichiometry of 2:1 also have 1D supramolecular structure with the repeating unit "amine-amine-crown". The structure of assemblies is supported by the two types of synthons: p-stacking of arenes and the hydrogen bonding mentioned above.

Architectures of co-crystals of diamines and 18-crown-6 of stoichiometry of 2:1 are more diverse. There are linear 1D structures with repeating unit "diamine-diamine-crown" in which polyfluoroarenes are linked via p-stacking or two equivalent synthons N\textsubscript{pyridine}•••H-N\textsubscript{amine}. Associates of polyfluorinated 2,6- and 2,4-diaminotoluenes form 2D supramolecular structures. Within the layer, each crown ether molecule is linked by hydrogen bonds with four molecules of arylenediamine, and each arylenediamine molecule is linked with two crown ether molecules, i.e. crown ether molecules serve as the network cross-points.

Effect of molecular recognition – selective co-crystallization of polyfluoroaromatic amines with crown ether – has been discovered and interpreted on the base of the dependence of co-crystal melting heats on the structure of 1D assemblies. This effect is used in the practice to separate the reaction mixtures of nonselective amination of polyfluoroarenes and to isolate high-purity products [2].

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AMMONIUM FLUORIDES IN RARE ELEMENTS TECHNOLOGY

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The most widespread fluorinating agent is hydrogen fluoride or fluohydric acid. Element fluorine is used for producing uranium hexafluoride. However, utilization of fluorine and hydrogen fluoride is complicated by high cost of these reagents and their high corrosive characteristics as compared to fabrication materials of chemical devices.

In recent years, utilization of ammonium fluorides as fluorinating agents is actively studied. In Russia research with ammonium fluorides are carried out at the Institute of Chemistry (Far-Eastern Division of Russian Academy of Science, Vladivostok), Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials named after I.V. Tananaev of the Kola Science Centre of the Russian Academy of Sciences, Tomsk Polytechnic University.

Ammonium fluorides (NH₄F, NH₄F ·HF) unlike fluorine and hydrogen fluoride have suitable physicochemical properties: under normal conditions they are solid materials. Fluorinating properties of ammonium fluorides are exhibited at elevated temperatures, especially in molten form in the temperature range from 160 to 240°C. The most important economic advantage of utilization of ammonium fluoride is its recoverability and multiple reuses.

The greatest economic benefit of utilization of ammonium fluoride results from implementing a technology for fabricating rare elements. Despite considerable reserves of mineral raw materials and high scientific and production competencies, Russia almost does not produce rare metals. Firstly, it can be attributed to the fact that existing manufacturing technologies were developed in the 60s of the XX century and, currently, are not competitive.

Tomsk Polytechnic University carries out a range of production research in the field of development and instrumentation of production of berillium, lithium, titanium, tungsten, and zirconium compounds. The technologies based on prior laboratory research evolve into design solutions and techno-economic justifications. At a pilot production semi-scale regimes of fluorinating mineral concentrates of berillium, tungsten, zirconium, titanium, lithium with ammonium fluorides are perfected. A basic fluorination device is rotating drum furnaces. For subliming and separating gaseous fluoride from resultants sublimers are used. Full regeneration cycle of ammonium fluoride and its return to the beginning of the process is organized.

Economic estimates suggest that production cost of processing from concentrate to pre-product (usually, metal oxide) is from 1 to 1, 5 thousand dollars per ton including capital construction costs, which is almost twice as less as the current cost of production.

The work was performed at the request of the Ministry of Industry and Trade of the Russian Federation, Tenir –Technology LLC, Scientific Production Association «Rare Metals of Siberia». 
SELECTIVE CARBOXYLESTERASE INHIBITORS BASED ON ALKYL 2-ARYLHYDRAZINYLIDENE-3-OXO-3-POLYFLUOROALKYLPROPIONATES AS PROMISING CO-DRUGS

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Carboxylesterases (CaE) are key enzymes of hydrolytic metabolism for major therapeutic agents that contain ester groups\textsuperscript{1}. The use of CaE inhibitors as co-drugs can considerably improve the therapeutic efficacy of known drugs and reduce their unwanted side effects\textsuperscript{2}. We found that 2-arylhydrazinylidene-3-polyfluoroalkyl-3-oxoesters of general formula

\[
\begin{align*}
\text{Alk} & \quad \text{O} = \text{N} \quad \text{R}^1 \\
\text{O} & \quad \text{N} \quad \text{X}
\end{align*}
\]

are new effective and selective CaE inhibitors that inhibit enzyme in the nanomolar range (IC\textsubscript{50} = 5–13 nM) in agreement with the results of molecular docking\textsuperscript{3}. Esterase profile analysis of the compounds showed that the CF\textsubscript{3}-containing ethyl and methyl esters exhibited much higher inhibitory activity and selectivity toward CaE in comparison with structural close butyrylcholinesterase and acetylcholinesterase. The leading compounds have low acute toxicity and low cytotoxicity that allows us to consider them as promising co-drugs for modulation metabolism of ester-containing pharmacological agents.

This work was supported by RFBR Project №14-03-01063.

\textsuperscript{1}Laizure S.C. \textit{et al.} \textit{Pharmacotherapy}, 2013, \textbf{33}, 210-222.
THE FLUORINATION OF PYRIDINE AND ITS DERIVATIVES IN THE PRESENCE OF TRANSITION METALS IN HIGHER OXIDATION STATES

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The growing interest to fluorinated pyridine and its derivatives is explained by the interesting and unusual physical, chemical and biological properties causing by presence of a strong electron-acceptor substituent (atom F) in aromatic ring. A large number of fluorine-heterocycles are a part of pharmaceutical drugs, plant protection products, etc. Fluorinated pyridine especially widely used as agrochemicals and in pharmaceutical industry. Pyridine with fluorine atom in third or/and fifth positions are often part of biologically active molecules. However, very often the formation of carbon-fluorine bond in such molecules is not selective and the synthesis of fluoropyridines still remains a challenge. Development of reliable synthetic methods allowing fast and regioselective introduction of fluorine in the pyridine ring still has great importance for seeking of new drugs and the markers for radiochemistry. In this work we propose new approaches for the fluorination of pyridine and its derivatives, 4-ethylpyridine and 2-phenylpyridine by available fluorinating reagents and transition metal salts under mild conditions in one stage without traditional additive of oxidant excess. Chemical and electrocatalytic oxidative fluorination of pyridine and its derivatives in the presence of nickel, cobalt and silver salts selectively primarily occurs in the ortho-position of pyridine ring.

Fluoride anions source does not affect on regioselectivity of fluorination, however, determines the yield of the final product. The dependence of regioselectivity of reaction from the nature of the metal-catalyst and method of synthesis (chemical or electrochemical) has been established. The mechanism of oxidative fluorination process has been proposed.

The work was financially supported by the Russian science Foundation (project No. 14-23-00016).
PARTICULARITY PRIMARY PEROXIDE DERIVATIVE SYNTHESIS FROM REACTION FLUORINATED CARBONYL COMPOUNDS WITH HYDROGEN PEROXIDE

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Peroxides resulted from the reaction of carbonyl compounds with HOOH are efficiently used in preparative organic synthesis and industry for many years. But at the same time synthesis of primary peroxide derivatives by the reaction of 1-hydroxy-1-hydroperoxides (HHP) is the subject of the discussions, because of their instability, however the investigation of properties of primary HHP has a great interest for understanding these reaction mechanism. For synthesizing different HHP synthesis we investigated the influence of fluorine atoms and fluoroalkyl groups, these groups have high electron-acceptor effect on the reactivity of aliphatic, cyclic and aromatic carbonyl compounds in reactions with HOOH, herewith we obtained HHP in high chemical yield (65-91%), whereas the hydrocarbon analogs of these compounds are not stable or don’t exist under usual conditions.

\[
\begin{align*}
R_F^3CH=O + HOOH & \rightarrow R_F^3CH(OH) – OOH \\
& \text{R}_F = CF_3(CF_2)_3, H(CF_2)_4, CF_3(CF_2)_5, H(CF_2)_6 \\
\text{n}(F_2C)|\text{C}=O + HOOH & \rightarrow \text{n}(F_2C)|\text{C}–\text{OOH} \\
& \text{n} = 4, 5 \\
\text{X-C}_6\text{Y}_4\text{CH}=O + HOOH & \rightarrow \text{X-C}_6\text{Y}_4\text{CH(OH)} – \text{OOH} \\
\text{Y} = \text{H} & \text{X} = \text{H}, 3-\text{F}, 4-\text{F}, 2-\text{CF}_3, 3-\text{CF}_3, 4-\text{CF}_3 \\
\text{Y} = \text{F} & \text{X} = \text{F}
\end{align*}
\]

The synthesized fluorinated HHP are stable under usual conditions, OH- and OOH- groups are involved in the reactions of acylation.

\[
\begin{align*}
\text{X-C}_6\text{Y}_4\text{CH(OH)} – \text{OOH+2(CH}_3\text{CO)}_2\text{O} & \rightarrow \text{X-C}_6\text{Y}_4\text{CH[OC(O)CH}_3] – \text{OO C(O)CH}_3 \\
\text{Reaction} \text{trifluorinearomatic HHP} & \text{with perfluorinealkylaldehyds proceeds unusually, giving not symmetrical 1,1\textsuperscript{\text{1}}-dihydroperoxides} \text{but perfluorinealiphatic HHP and aromatic aldehydes.}
\end{align*}
\]

It’s necessary to pay attention to great applicative potential of this investigation for different areas of the engineering, in particular in polymeric chemistry (composite material with unique properties)\textsuperscript{1}, synthesis of biologically active substances and etc.

\textsuperscript{1}Chapurkin V. V. et. al. Russ. J. Appl. Chem. 2015, vol.88, no.8, pp.1282-1287.
SYNTHESIS AND PROPERTIES OF PERFLUOROALKYL SULFONYL BROMIDES

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There are limited literature data pertaining to application of fluoroalkylsulfonyl bromides in the synthesis of organofluorine compounds\textsuperscript{1-4}. The goal of the given work is an expanding of the scope of practical application of perfluoroalkylsulfonyl bromides in organofluorine synthesis.

It is shown that fluoroaliphatic sulfonyl bromides 2a-f, including the compounds containing such functional groups as CF\textsubscript{2}=CFO-, ROC(O)-, FSO\textsubscript{2}- add smoothly to unsaturated compounds to give adducts 3a-f in preparative yields\textsuperscript{1}:

\[
\begin{align*}
R_F\text{SO}_2\text{Br} & \xrightarrow{\text{sun light, rt}} R_F\text{OC(O)CF}_3 \\
1a-f & \quad 2a-f \text{ (40-60\%) } \\
3a-f & \text{ (60-70\%)}
\end{align*}
\]

\begin{itemize}
\item \textbf{R\textsubscript{F}} =
\item a: -CF\textsubscript{2}CO\textsubscript{2}Et
\item b: -CF\textsubscript{2}CF\textsubscript{2}OCF=CF\textsubscript{2}
\item c: -CF\textsubscript{2}CF\textsubscript{2}OCF(CF\textsubscript{3})CO\textsubscript{2}Me
\item d: -CF\textsubscript{2}CF\textsubscript{2}OCF(CF\textsubscript{3})CF\textsubscript{2}OCF(CF\textsubscript{3})CO\textsubscript{2}Me
\item e: -CF\textsubscript{2}CF\textsubscript{2}OCF(CF\textsubscript{3})CF\textsubscript{2}OCF\textsubscript{2}CF\textsubscript{3}
\item f: -CF\textsubscript{2}CF\textsubscript{2}OCF\textsubscript{2}CF\textsubscript{2}SO\textsubscript{2}F
\end{itemize}

The examples of fluoroalkylsulfonyl bromides reactions with olefins performed both with the retention of SO\textsubscript{2}-group and accompanied by its reduction in the course of the reaction are discussed:

\[
\begin{align*}
\text{CF}_2\text{SO}_2\text{Br} & \xrightarrow{\text{sun light}} \text{CF}_2\text{OCOCF}_2\text{CF}_2\text{SO}_2\text{Br} & \xrightarrow{\text{PCl}_3} \text{CF}_2\text{SO}_2\text{Br} \\
30\% & \quad 60\%
\end{align*}
\]

\begin{itemize}
\item [\textsuperscript{1}] Huang W.-Y. et al. \textit{Chin. J. Chem.} 1992, 10(6), 544-548.
\item [\textsuperscript{4}] Tyutyunov A.A. et al. \textit{Fluorine notes}, 2015, 5(102).
\end{itemize}
ELECTROCATALYTIC FLUORALKYLATION OF VARIOUS CLASS SUBSTRATES. FROM CROSS-COUPLING TO C-H FUNCTIONALIZATION

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Fluoroalkyl groups can profoundly influence the properties of organic and organometallic molecules, and thus their applicability in pharmaceuticals, agrochemicals, and building blocks for organic materials and catalyst design has grown.\textsuperscript{1-2} Despite the importance of this substituent class, more general and reliable methods to incorporate fluoroalkyl groups into complicated molecules are needed.

The interest in electrochemical fluoroalkylation reactions is stirred by a number of factors: mild conditions (moderate temperature, ambient pressure), the possibility of closed-loop implementation with a small amount of the catalyst reactant that is repeatedly recycled, and the high environmental safety of the synthesis, especially in comparison with traditional organic chemistry techniques. Electrosynthesis is also useful in transition metal catalysis for generating the active form of the catalyst without the need to add external oxidizing or reducing agents.

That is why the goal of the work was to develop a simple one-step perfluoroalkylation method of different classes of organic compounds containing electrocatalytic metal complexes under mild conditions and establishment of regularities of the process.

As a result, an effective method of electrocatalytic fluoroalkylation different class of aromatic compounds was developed. The method has been tested with a variety of catalysts and metal anode. The regularities of cross-coupling reactions of organic halides consist in a linear dependence of the $\text{Ar-R}_2\text{F}$ product on the potential reduction of the complex catalyst and the principal value of copper anode to selectively produce a product that confirms the important role of the transmetalation step in the catalytic cycle. Implemented in electrocatalysis first reaction fluoroalkylation C-H aromatic and heteroaromatic compounds.

This experimental work was supported by the Russian Science Foundation № 14-23-00016 and Russian Foundation for Basic Research (Projects № 16-33-0088\_mol\_a, 16-03-00195, 16-33-50015\_mol\_nr).

\textsuperscript{1}Khrizanforov M.N. \textit{et al.} \textit{Dalton Trans.} 2015, \textbf{44}, 19674-19681.
IONIC REACTIONS OF FLUORINE-CONTAINING 1,2-OXI- AND THIIRANES


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Fluorinated 1,2-oxi- and thiiranes have been highly reactive compounds and important intermediates to synthesis of compounds with a wide spectrum of biological activity and technically useful properties. However the properties of the oxi- and thiiranes bearing at a third position a fluorine-containing substituent have been poorly studied. So a study of their chemical transformations is relevant.

The work presents reactivity of the fluorine-containing oxi- and thiiranes both reactions with N-, O-, Hal-nucleophiles and ring reduction (scheme).

Scheme

\[ \text{R}^F \text{XH} \rightarrow \text{R}^F \text{OH} \rightarrow \text{R}^F \text{CH} \rightarrow \text{R}^F \text{OH} \rightarrow \text{R}^F \text{XH} \]

\[ X = O, S \]
\[ \text{R}^F = \text{CF}_3, \text{F(CF}_2)_2 \text{CF}_3, \text{CF}_3 \text{CH}_2 \text{O}, \text{H(CF}_2)_2 \text{CH}_2 \text{O}, \text{H(CF}_2)_3 \text{CH}_2 \text{O}, \text{F(CF}_2)_6 \text{CH}_2 \text{O}, \text{F(CF}_2)_4 \text{CH}_2 \text{O}, \text{F(CF}_2)_4 \text{CH} = \text{CHCH}_2 \text{O}. \]

Obtained compounds were characterized by date of mass-, NMR-, IR-spectroscopy and elemental analysis.
TRIFLUOROACETYL NITRATE: SYNTHESIS, PROPERTIES, AND APPLICATIONS

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Trifluoroacetyl nitrate (TFAN) was synthesized by a reaction between N\textsubscript{2}O\textsubscript{5} and trifluoroacetic anhydride (TFAA) as well as from HNO\textsubscript{3} with a stoichiometric amount or excess of TFAA. We showed that TFAN could be generated in the presence of TFAA from any inorganic nitrate that did not exhibit redox properties. TFAN was characterized by \textsuperscript{19}F, \textsuperscript{14}N, \textsuperscript{15}N, \textsuperscript{13}C NMR and Raman spectroscopy. A totality of most intensive frequencies of compounds in the Raman spectra was established: 213, 314, 504, 599, 772, 891, 1279, and 1339 cm\textsuperscript{-1}. A shift of the compound (from –79 to –86 ppm depending on a solvent) in the \textsuperscript{14}N NMR spectra differed considerably from δ\textsubscript{N} N\textsubscript{2}O\textsubscript{5} (~ –60 ppm) and the \textsuperscript{19}F spectra fixed a TFAN signal in the region of –76.6 ppm (in TFA A and EtOAc) and –73.8 ppm (in CDCl\textsubscript{3}).

As evidenced by experiment, TFAN partially transforms to TFAA and N\textsubscript{2}O\textsubscript{5} (N\textsubscript{2}O\textsubscript{5} content ≈ 11 molar %) in the gas phase whereas the equilibrium in solutions shifts completely toward TFAN.

\[
\begin{align*}
\text{N}_{2}\text{O}_5 & \quad + \quad (\text{CF}_3\text{CO})_2\text{O} \quad \rightarrow \quad 2\text{NO}_2\text{OCOCF}_3 \\
\text{HNO}_3 & \quad + \quad (\text{CF}_3\text{CO})_2\text{O} \quad \rightarrow \quad \text{NO}_2\text{OCOCF}_3 \quad + \quad \text{CF}_3\text{COOH} \\
\text{MNO}_3 & \quad + \quad (\text{CF}_3\text{CO})_2\text{O} \quad \rightarrow \quad \text{NO}_2\text{OCOCF}_3 \quad + \quad \text{M}^+\text{CF}_3\text{COO}^-
\end{align*}
\]

Due to ready dissociation of TFAN at a point close to the room temperature (bp ~27 °C), this compound, both individually and in concentrated solutions, has explosive properties though it is safe in handling when diluted and at 0–5 °C.

A few nitronium salts were synthesized with 71–96 % yield from mineral acids and TFAN produced from TFAA and HNO\textsubscript{3}. Both the earlier known nitronium salts (NO\textsubscript{2}BF\textsubscript{4}, NO\textsubscript{2}CF\textsubscript{3}SO\textsubscript{3}, NO\textsubscript{2}FSO\textsubscript{3}, NO\textsubscript{2}HSO\textsubscript{7}, (NO\textsubscript{2})\textsubscript{2}S\textsubscript{2}O\textsubscript{7}, NO\textsubscript{2}ClO\textsubscript{4}) and novel compounds: (NO\textsubscript{2})[(CF\textsubscript{3}CO)SO\textsubscript{4}], (NO\textsubscript{2})[(CF\textsubscript{3}CO)S\textsubscript{2}O\textsubscript{7}], NO\textsubscript{2}IO\textsubscript{4}, NO\textsubscript{2}HSO\textsubscript{4} were prepared. The structure of (NO\textsubscript{2})[(CF\textsubscript{3}CO)SO\textsubscript{4}] was determined ab initio from powder X-ray diffraction data.

Most of nitronium salts were shown to dissolve readily in CF\textsubscript{3}COOH (TFA), being a convenient solvent for their NMR spectroscopic studies. TFAN solutions in TFA-free organic solvents were prepared by distillation of TFAA—HNO\textsubscript{3}—CH\textsubscript{2}Cl\textsubscript{2} and TFAA—NH\textsubscript{4}NO\textsubscript{3} mixtures, which allowed raising of nitronium salts yields and using of TFAN in nitration of the organic substrates sensitive to reaction media acidity. For instance, we performed selective nitration of [2.2]paracyclophane by TFAN in situ generated from anhydrous metal nitrates and TFAA and afforded 4-nitro-[2.2]paracyclophane with 62–77 % yield; its structure was established by single crystal X-ray analysis.

\textsuperscript{1}V. P. Zelenov, V. A. Tartakovskiy, S. S. Bukalov // A method for preparation of nitronium salts // RF Patent 2558115 S1, publ. 27.07.2015, appl. 23.05.2014.
THE RESEARCH OF BERYLLIUM CONCENTRATE HYDROFLUARINATION PROCESS

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The beryllium products consumption has increased and reached 400 tons in terms of metallic beryllium in 2015 year. Today in Russian Federation there are no factories, which realize beryllium raw materials processing and produce metallic beryllium and its compounds. In the same time on the Russian territory there is unique Ermakovskoe deposit, in the ores of which beryllium affiliates fluorite-phenacite-bertrandite metasomatites. Flotation concentrate which is produced by beneficiating of such ores has the following composition (table 1).

Table 1. The fluorite-phenacite-bertrandite concentrate (FPBC) composition, % mass.

<table>
<thead>
<tr>
<th>Compound</th>
<th>BeO</th>
<th>SiO₂</th>
<th>CaF₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, %</td>
<td>5.0</td>
<td>36.8</td>
<td>20.7</td>
<td>11.4</td>
<td>24.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>

The FPBC processing by classic sulfuric acidic scheme is complicated by following aspects: concentrate preliminary thermo-chemical activation stages lead-in is needed; the fluoride-ion, which goes into solution in the result of leaching, blocks full extraction of beryllium during the production of Be(OH)₂. This fact negatively results on beryllium make and region ecological situation afterwards waste solutions dumping.

To process FPBC effectively the alternative fluorine ammonium method has been developed. The essence of this method consists in hydrofluorination of FPBC in ammonium hydrofluoride (NH₄HF₂) liquor at 180-200 °C. The hydrofluorination process is described by following chemical equations:

\[ \text{Be}_2\text{SiO}_4 + 7\text{NH}_4\text{HF}_2 \rightarrow 2(\text{NH}_4)_2\text{BeF}_4 + (\text{NH}_4)_2\text{SiF}_6 + 4\text{H}_2\text{O}↑ + \text{NH}_3↑, \]  
\[ \text{Be}_4[\text{Si}_2\text{O}_7](\text{OH})_2 + 14\text{NH}_4\text{HF}_2 \rightarrow 4(\text{NH}_4)_2\text{BeF}_4 + 2(\text{NH}_4)_2\text{SiF}_6 + 9\text{H}_2\text{O}↑ + 2\text{NH}_3↑, \]  
\[ \text{Al}_2\text{O}_3 + 6\text{NH}_4\text{HF}_2 \rightarrow 2(\text{NH}_4)_3\text{AlF}_6 + 3\text{H}_2\text{O}↑, \]  
\[ \text{Fe}_2\text{O}_3 + 6\text{NH}_4\text{HF}_2 \rightarrow 2(\text{NH}_4)_3\text{FeF}_6 + 3\text{H}_2\text{O}↑, \]  
\[ \text{CaO} + \text{NH}_4\text{HF}_2 \rightarrow \text{CaF}_2 + \text{H}_2\text{O}↑ + \text{NH}_3↑, \]  
\[ \text{SiO}_2 + 3\text{NH}_4\text{HF}_2 \rightarrow (\text{NH}_4)_2\text{SiF}_6 + 2\text{H}_2\text{O}↑ + \text{NH}_3↑. \]

The thermodynamic calculations have shown that concentrate components (excluding CaF₂ and Fe₂O₃) react with NH₄HF₂ just at room temperature. There is no interaction between calcium fluoride and NH₄HF₂. The course of reaction with Fe₂O₃ initiates at 157 °C. The process of FPBC hydrofluorination is exothermal. The summary process caloric effect (Q) is 16,40 kJ/kg of concentrate at 157 °C. The experimental data shows that in static mode of operation the extraction rate of beryllium is about 97 % without preliminary activation stages. According to kinetic researches the FPBC hydrofluorination process is limited by diffusion of NH₄HF₂ to interaction surface. Dependences of reaction degree from time at 160-200 °C are described by Yander equation. The value of apparent activation energy of FPBC hydrofluorination process is 16,031 kJ/mol.

TRIFLUOROMETHYL-CONTAINING N, O-HETEROCYCLES BASED ON PERFLUORODIACETYL AND UREAS


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Cis-, trans-isomers of imidazolidines 2 were synthesized by the reaction of perfluorodiacetyl 1 with ureas. Significant influence of the nitrogen substituents of the imidazolidines 2 on the direction of the interaction with urea, the composition and the structure of the obtained compounds was found. In contrast to unsubstituted imidazolidine 2, which yields glycoluril 3 as a result of the reaction with urea, its monosubstituted analogs 2 form imidazooxazols 6 and hydantoins 5 under the same conditions. The reaction of N,N'-disubstituted imidazolidines 2 with urea is accompanied by the elimination of CF₃-group to give hydantoins 4.

\[
\begin{align*}
1 & \xrightarrow{\text{R}_1\text{NHCONHR}_2} \text{OH} \xrightarrow{i} \text{O} \\
2 & \xrightarrow{i, ii} \text{O} \\
3 & \xrightarrow{i} \text{O} \\
4 & \xrightarrow{i} \text{O} \\
5 & \xrightarrow{i} \text{O} \\
6 & \xrightarrow{i} \text{O}
\end{align*}
\]

2: \( R_1 = R_2 = H, \text{Me, Et, Ph}; R_1 = H, R_2 = \text{Me}; R_1 = H, R_2 = 4-\text{EtOC}_6\text{H}_4; R_1 = H, R_2 = \text{Ph} \);

3: \( R_1 = R_2 = H \);

4: \( R_1 = R_2 = \text{Me}; R_1 = R_2 = \text{Et}; R_1 = R_2 = \text{Ph} \);

5, 6: \( R_1 = H, R_2 = \text{Me}; R_1 = H, R_2 = 4-\text{EtOC}_6\text{H}_4, R_1 = H, R_2 = \text{Ph} \).

\( i: \text{NH}_2\text{CONH}_2, \text{dimethylacetamide (DMA)}, 160-165 \degree \text{C}; \)

\( ii: \text{DMA, 160-165 \degree C} \)

The work received financial support from the Ural Branch of Russian Academy of Sciences (projects 15-21-3-5, 15-21-3-6, 15-21-3-7).
THE EFFICIENT PATHWAY TO
4-(POLYFLUOROALKYL)PROPANE-1,2,3-TRIONE-2-OXIMES

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Oximes of fluorinated polyketones are useful reagents for organic synthesis. However, only a few examples of such compounds are known as common methods for their preparation are not available. In particular, there are no reliable methods for the synthesis of 2-hydroxymino-4-(polyfluoroalkyl)-propan-1,3-diones.1,2

We developed a simple and efficient approach to 1,2,3-alkanetrione-2-oximes 2a-d via nitrosation of lithium 4-(polyfluoroalkyl)-1,3-diketonates 1a-d with sodium nitrite in acetic acid. The targeted products formed with 65-92% yields. The starting precursors 1a-d technical purity can be used without loss of quality of target oximes. Products 2a-d were characterized by IR, 1H, 13C, 19F NMR spectroscopy, GC-MS, elementary analysis.

The molecular structure of oximes 2a (see pictured) and 2b have been determined by X-ray crystallography. The structures are characterized by non-planar placing of the functional groups and by the absence of the intramolecular H-bonds. On the other hand, benzoyl and oxime moieties interact through the intermolecular H-bonds. It should be noted that the benzoyl group is turned on the significant angle toward the plane of the 1,2-ketoxime moiety.

This research was supported financially by the Ural Branch of Russian Academy of Sciences (project № 13-3-033) and 211 Programme of the Government of the Russian Federation Agreement No. 02. A 03.21.0006.

1,2-EPOXY-PERFLUOROCYCLOHEXANE IN THE SYNTHESIS OF FLUORINE-CONTAINING POLYCYCLES COMPOUNDS


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1,2-Epoxy-perfluorocyclohexane (I) is accessible\(^1\) and perspective synthon to synthesize fluorinated heterocycles\(^2\).

It reacts with equimolar quantity of 3,3'-diaminobenzidine (II) giving new fluorine-containing diaminoarene - 4-(6,6,7,7,8,8,9-octafluoro-6,7,8,9-tetrahydro-phenazin-2-yl)-benzene-1,2-diamine (III).

The compound III is of the interest as a convenient precursor for synthesis of complex fluorine-containing heterocyclic systems with potential biological and luminescent properties. As a result of interaction of diaminoarene II with oxirane I and benzil new polycyclic compounds IV, V were synthesized. They were characterized by elementary analysis, IR, NMR \(^1\)H, \(^13\)C, \(^19\)F spectroscopy. The molecular structures of compounds III, IV have been determined by X-ray crystallography.

The absorption, emission on all excitation maxima and excitation on emission maximum spectra of CH\(_2\)Cl\(_2\) solution of compounds IV and V were obtained. The maxima for IV: \(\lambda_{\text{abs}}\) 277.5 and 353.0 nm, \(\lambda_{\text{ex}}\) 250.0 and 347.0 nm, \(\lambda_{\text{em}}\) 408.0 nm. The maxima for V: \(\lambda_{\text{abs}}\) 272.5 and 380.0 nm, \(\lambda_{\text{ex}}\) 260.0, 284.0 and 380.0 nm, \(\lambda_{\text{em}}\) 491.0 nm. The quantum yields of luminescence are 1.6 % (IV) and 38.0% (V). Quantum yields were estimated with 0.1 mol/L H\(_2\)SO\(_4\) solution of quinine sulfate as a reference\(^3\).

This research was supported financially by the Ural Branch of Russian Academy of Sciences (projects no. 15-21-3-5, 15-21-3-6).


\(^3\) Parker C. A. Photoluminescence of Solutions: with applications to photochemistry and analytical chemistry. – Amsterdam: Elsevier, 1968
SYNTHESIS AND TUBERCULOSTATIC ACTIVITY OF FLUORINE-CONTAINING 2-CYCLOALKYLIMINO-1,3-BENZOTHIAZIN-4-ONES

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6-Trifluoromethyl-8-nitro-1,3-benzothiazin-4-one (BTZ038), bearing 1,4-dioxa-8-azaspiro[4.5]dec-8-yl residue at position 2, was recently recognized as the perspective antitubercular agent, inhibitor of decaprenylphosphoryl-beta-D-ribose 2'-epimerase DprE1 (Rv3790), the enzyme responsible for the creation of arabinan in mycobacteria cells\textsuperscript{1}.

2-(4-Carbonylpiperazino)-6-trifluoromethyl-8-nitro-1,3-benzothiazin-4-ones also exhibited strong antitubercular activity\textsuperscript{2}.

Synthesis of 2-cycloalkylimino-1,3-benzothiazin-4-ones with different degree of fluorination of benzoring 4-6 has been realized through intramolecular cyclization of fluorine-containing \textsuperscript{N}-(cycloalkylimino-1-carbothioyl)benzamides 3, obtained by interaction of di- and tetrafluorobenzoylisothiocyanates 1 with cycloalkylimines 2. The evidence for the structures of benzothiazinones 4-6 is provided by their spectral data, including the \textsuperscript{1}H and \textsuperscript{19}F NMR-spectroscopy, as well as mass-spectrometry and the X-ray analysis.

The interrelation of the structure of compounds 4-6 and their activity towards Mycobacteriumtuberculosis\textsubscript{H\textsubscript{3}7}Rv has been analyzed. This work was supported by Russian Science Foundation (project 15-13-00077) and by the Ministry of Education of Russian Federation (project № 2458).


Fluorinated organic compounds have a remarkable record among modern medications. A substitution of hydrogen atoms for fluorine in bioactive molecules affects their properties due to both an enhancement of lipophilicity and changes in metabolism.

Thevinols (1a) and orvinols (1b), also well-known as Bentley’s compounds, are one of the main types of opioid receptor ligands. Some of them are used as analgesics or opioid antagonists both in veterinary and human medicine. So, fluorinated derivatives of compounds 1 are of great interest as the putative opioid ligands as well as valuable objects for study a structure-activity relationship in the thevinol/orvinol series.

We have elaborated a common method for preparation of C(21)-fluorinated compounds 3 that are structurally relative to alcohols 1 via either an addition reaction of the Ruppert-Prakash reagent (Me₃SiCF₃) to C(20) carbonyl derivatives 2 (R = H, CH₃) followed by a modification of the substituent at N(17) and/or O-demethylation of the methoxy groups at C(3) and C(6) or by the use of fluorinated ketone 2 (R’ = CH₃, R = CF₃) as the starting material. The last compound has been earlier reported by us. It reacts withorganometallic reagents directly furnishing alcohols 3 (R’ = CH₃) that can be further modified at N(17) and/or demethylated at C(3) and C(6).

Some of C(21)-fluorinated compounds 3 were found to exhibit the properties specific for opioid ligands.

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MODIFICATION OF SYNTHETIC ANALOGUES OF CURCUMIN WITH 3,5-DIMETHOXY-α-METHOXYCARBONYL-α-TRIFLUOROMETHYL-PARAmETHYLENEQUINONE

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Cyclic 1,5-diaryl-3-oxo-1,4-pentadienes (A) are considered as synthetic analogues of naturally-occurring compound Curcumin distinguished by pronounced anticancer activity\(^1\).

\[
A (X = CH_2, NH, NR_3)
\]

Among them, 3,5-bis(arylidene)-4-piperidones are of significant interest because heterocyclic NH group present in their molecules allows structural modification of dienone pharmacophore A with fluorine-containing electrophilic agents.

In this work we demonstrated that NH-3,5-bis(arylidene)-4-piperidones 1 readily react with previously described\(^2\) 3,5-dimethoxy-α-methoxycarbonyl-α-trifluoromethyl-para-methylenequinone 2 to form corresponding CF\(_3\)-derivatives 3 in high yields (75-85%).

\[
R = H, Alk, OAlk, Hal; \quad X = CH, N
\]

Phenolic OH group present in compounds 3 allows preparation of their water soluble forms and makes it possible to carry out further modification of their structures.

An in vitro screening of compounds 3 revealed that they high antitumor activity towards human malignant cell lines, such as PC3, HCT116 and MCF7, with IC\(_{50}\) values in the range of 2–5 \(\mu\)M, that surpassed, in some cases, that of Cisplatin and antitumor antibiotic Doxorubicin used as positive controls.


Reactions of perfluoroalkyl iodides with \(\alpha, \omega\)-diaminoalkanes in the presence or absence of elementary sulfur

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Perfluoroalkyl halides could be converted into the corresponding \(1H\)-perfluoroalkanes easily by several methods. The most widely used method is the base-catalyzed reduction of the iodides\(^1\) or the reduction with elemental zinc in methanol\(^2\).

We found that perfluoroalkyl-iodides (\(\text{CF}_3(\text{CF}_2)_n\text{I}\), \(n = 3, 5, 7, 9\)) react with \(\alpha, \omega\)-diaminoalkanes (\(\text{H}_2\text{N}-(\text{CH}_2)_n\text{NH}_2\), \(n = 2, 3, 4\)) at room temperature in the absence of any catalyst to afford the corresponding \(1H\)-perfluoroalkanes in good yields. This reaction proceeds under mild conditions with a 100% conversion of perfluoroalkyl-iodides. The \(1H\)-perfluoroalkane type products were easily isolated in a 70 - 80% yield using co-distillation with pyridine which gives a two-liquid phase system in the receiver, the lower one is the fluorous product (Fig. 1.).

However, a different reaction pathway was observed if a solution of elemental sulfur in ethylene diamine (or its homologue) was prepared first and then mixed with perfluoroalkyl iodides. Here, instead of formation of appropriate \(1H\)-perfluoroalkanes the complete degradation of the \(\sim\text{CF}_2\text{I}\) termini occurred yielding perfluoroalkylated amidine type heterocycles (Fig. 1.).

This multistep reaction involves the initial formation of \(N\)-(amino-alkyl)-perfluoroalkane-thioamides, some of them could be isolated and well characterized, which at somewhat increased temperature and longer reaction time are losing hydrogen-sulfide and forming the appropriate heterocycles. Under optimized reaction conditions some thioamides were obtained in 97% isolated yield, while the corresponding nitrogen heterocycles in good to excellent yields using different \(\alpha, \omega\)-diaminoalkanes and perfluoroalkyl-iodides with elementary sulfur (Fig. 1.).

Fig. 1. Novel and Effective Functionalizations of Commercially Available Perfluoroalkyl Iodides.

The research was supported financially by NKFIH (OTKA NN 117633).

\(^1\) J.L. Howell et. al. J. Fluor. Chem. 1995, 72, 61-68.
IMPROVED SYNTHESSES OF FLUOROUS AZIDES AND AMINES

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The introduction of $R_{fn}$-groups ($R_{fn} = C_{n}F_{2n+1}$) into organic molecules is a simple way to prepare fluorophilic compounds. Fluorous azides and amines are important building blocks for the synthesis of fluorous molecules\textsuperscript{1}. Their synthesis usually involves several steps starting from perfluoroalkyl alcohols, halides or sulfonates. The fluorous phase affinity of these compounds mostly controlled by the length of the fluorous chain ($n$ in $R_{fn}$); however the reactivity of these molecules depends on the number of methylene spacers between the highly electron withdrawing perfluoroalkyl substituent and the functional group.

The synthesis of fluorous azides $[R_{fn}(CH_{2})_{m}N_{3}, (n = 4, 6, 8, 10; m = 1 - 4)]$ was accomplished in good yield from the appropriate perfluoroalkyl-alkyl halide or sulfonate (Fig. 1). It is worthy to note that these azides were isolated by steam distillation on multigram scale (0.5 – 100 g). No explosion or thermal decomposition was observed during their isolation and purification by distillation at 16 mm Hg.

\begin{equation}
\begin{split}
Q\leftarrow\text{CF}_{2}\_n\text{CH}_{2}\_mX & \xrightarrow{\text{NaN}_{3}, \text{DMSO}} \text{CF}_{2}\_n\text{CH}_{2}\_mN_{3} \\
Q &= \text{H, F} \\
\text{n} &= 4, 6, 8, 10 \\
\text{m} &= 1, 2, 3, 4 \\
X &= \text{Cl, Br, I, -OMs, -OTf, -OBs, -OTs}
\end{split}
\end{equation}

Fig. 1. Synthesis of fluorous azides

Hydrogenation and deuteration of the azides provided the appropriate fluorous amines (R-NH$_2$, R-ND$_2$) in quantitative yield (Fig. 2). These reactions were optimized in a flow reactor system (H-Cube by ThalesNano). We attempted to find the optimal conditions (99+\% conversion by highest flowrate) by varying the catalyst (Pd/C, Pd(OH)$_2$, Pt/C, Rh/C, Ru/C, Ti, Raney-Ni), and the reaction conditions (pressure, temperature, flowrate and concentration of the reactant).

\begin{equation}
\begin{split}
Q\leftarrow\text{CF}_{2}\_n\text{CH}_{2}\_mN_{3} & \xrightarrow{\text{cat. H}_2 / \text{D}_2, \text{H-Cube}} \text{CF}_{2}\_n\text{CH}_{2}\_m\text{NH}_2 \\
\text{Fig. 2. Reduction of fluorous azides}
\end{split}
\end{equation}

The research was supported financially by NKFIH (OTKA NN 117633).

THE NEW METHOD OF SYNTHESIS TRIMETHYLSILYL-, ALLYL AND HALOGENBENZEN DERIVATES.

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Polyfluorinated aromatic acid derivates found wide range application in organic synthesis as starting materials for introduction polyfluorinated aromatic part in different molecules. Compounds containing pentafluorophenyl fragment, used in dermaceutics, agrochemistry, medicine chemistry, electrontransport devises, polygraphy, light-signal diodes, LCD-s, fluorine biphase ligandes, as well as for creation different functional functional materials. We developed the new route for preparing polyfluoroarylsilanes by decarboxylation corresponding acides.

We developed new method for preparation different polyfluoroarylhalogenides.

\begin{align*}
\begin{array}{c}
\text{R'}'\text{COOH} \rightarrow \text{R'}'\text{COOK} \ + \ \text{ClSi(Me}_3\text{)}_3 \rightarrow \text{R'}'' \text{Si(CH}_3\text{)}_3 \\
\text{ClSi(Me}_3\text{)}_3 \rightarrow \text{R'}'\text{COOSi(CH}_3\text{)}_3
\end{array}
\end{align*}

при $\text{R'}' = \text{H}; \ \text{R'}'' = \text{H}; \ \text{R'}''' = \text{H}$

при $\text{R'}' = \text{COOH}; \ \text{R'}'' = \text{Si(CH}_3\text{)}_3; \ \text{R'}'''' = \text{COOSi(CH}_3\text{)}_3$;

We developed new method for preparation different polyfluoroarylhalogenides.

\begin{align*}
\begin{array}{c}
\text{R'}'\text{COOH} \rightarrow \text{R'}'\text{COOK} \ + \ \text{R-Hal} \rightarrow \text{R'}'' \text{Hal} \\
\text{Hal} = \text{Cl, Br, I}
\end{array}
\end{align*}

$\text{R} = \text{Cl, CCl}_3, \text{Br, I, BrCCl}_2\text{CCl}_2, \text{C}_2\text{Cl}_5$

при $\text{R'}' = \text{H}; \ \text{R'}'' = \text{H}$

при $\text{R'}' = \text{COOH}; \ \text{R'}'' = \text{Cl, Br, I}$

By this way, we applied for produsing allylbenzene derivates.
SYNTHESIS OF 2-(POLYFLUOROARENESULFONYL)-ETHANOLS FROM POLYFLUOROARENES

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The desired 2-(polyfluoroarenesulfonyl)-ethan-1-ols seem to be good precursors of the (ethylenesulfonyl) polyfluoroarenes – monomers and building blocks, however, little is known about properties of such compounds. For these reasons we have realized their synthesis from the available perfluoroarenes. One way was based on interaction of perfluoroarenes 1\textsubscript{a,b} with potassium hydrosulfide to obtain thiols 2\textsubscript{a,b}. Then the thiols were alkylated by 2-chloroethan-1-ol and sulfides 3\textsubscript{a,b} obtained were treated by excess of hydrogen peroxide in acetic acid to afford sulfones 4\textsubscript{a,b} in high yield.

Scheme 1. i. KSH, HOCH\textsubscript{2}CH\textsubscript{2}OH – DMF, 40\textdegree C; ii. ClCH\textsubscript{2}CH\textsubscript{2}OH, K\textsubscript{2}CO\textsubscript{3}, DMF, 20-25\textdegree C; iii. H\textsubscript{2}O\textsubscript{2} (30%), HOAc, 20-25\textdegree C;

Another way to 2-(polyfluoroarylsulfanyl)-ethanols was based on the reaction of perfluoroarenes 1\textsubscript{a,b} with 2-(sulfanylethane)-1-ol. However, in some cases it was complicated by introduction of 2 or 3 sulfanylethanol groups into the perfluoroarene with the formation of compounds 5 or 7. Hydrogen peroxide also turned out to be effective for oxidation of sulfides 5 and 7 to sulfones 6 and 8.

Scheme 2. i. HSCH\textsubscript{2}CH\textsubscript{2}OH, K\textsubscript{2}CO\textsubscript{3}, DMF, 20-25\textdegree C, ii. H\textsubscript{2}O\textsubscript{2} (30%), HOAc, 20-25\textdegree C

More examples of perfluoroarene transformations in the reactions discussed will be presented, some problems of preferable aromatic nucleophilic substitution of fluorine in polyfluoroarenes will also be considered.

This study was carried out under a financial support of Russian Foundation of Basic Research (project 15-03-08869а).
EFFECT OF POTASSIUM AND CESIUM FLUORIDES ON THE NUCLEOPHILIC PROPERTIES OF POLYFLUOROARYLZINC COMPOUNDS IN THE REACTIONS WITH POLYFLUOROARENES

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Reactions of polyfluoroarylzinc compounds with perfluoroarenes lead to the preparation of polyfluorobiaryls in 20-79 yields\(^1\). The low yields of polyfluorobiaryls in a number of reactions may be the result of the low nucleophilicity of polyfluoroarylzinc compounds. In this regard, we have started to use potassium and cesium fluorides to enhance the nucleophilicity of polyfluoroarylzinc compounds.

Reaction of C\(_6\)F\(_5\)ZnX (X = Cl, C\(_6\)F\(_5\)) with hexafluorobenzene at 120-130\(^\circ\)C (30 h) practically did not proceed. In a similar process, addition of KF or CsF to these reagents lead to the formation of the mixture of perfluorinated biphenyl, \(p\)-terphenyl, \(p,p'\) -quaterphenyl.

Similar results were obtained in the reactions of C\(_6\)F\(_5\)ZnX (X = Cl, C\(_6\)F\(_5\)) with ethyl pentafluorobenzoate. Practically no reaction proceeds in the absence of KF or CsF, whereas in the presence of KF or CsF polyfluorinated derivatives of biphenyl and \(p\)-terphenyl contained ethylcarboxylate group were obtained.

The effect of KF and CsF on other reactions of polyfluoroarylzinc compounds with polyfluoroarenes was also studied. A possible mechanism of the effect of these salts to enhance the nucleophilicity of polyfluoroarylzinc compounds will be discussed.


This study was performed under financial support by the Russian Foundation for Basic Research (project № 15-03-08869a).
SYNTHESIS OF IODOPOLYFLUOROARENES FROM POLYFLUOROARYLZINC COMPOUNDS AND I₂

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Iodopolyfluoroarenes are of interest as compounds for liquid crystals and reagents for cross-coupling reactions with use of palladium catalysts (eg, Sonogashira, Hiyama, Stille reactions).

We have used polyfluoroarylzinc compounds for the synthesis of iodopolyfluoroarenes. Earlier polyfluoroarylzinc compounds have been obtained from perfluoroarenes and Zn in DMF in the presence of catalytic amounts of SnCl₂.

Reactions of polyfluoroarylzinc compounds with iodine afforded iodopolyfluoroarenes in good yields.

Interaction of 1,4-dibromo-2,3,5,6-tetrafluorobenzene with Zn in DMF in the presence of catalytic amounts of SnCl₂ leads to the formation of p-tetrafluorophenylenedizinc bromide. The treatment of this reagent by iodine gives 1,2,4,5-tetrafluoro-3,6-diiodobenzene.

Perfluorobiaryls were first used for the formation of organozinc compounds which were then converted to the iododerivatives of perfluorobiaryls in the reactions with iodine.

This route has also been applied to obtain other iodopolyfluoroarenes.

This study was performed under financial support by the Russian Foundation for Basic Research (project № 15-03-08869a).

UNUSUAL REACTION OF BIS(DIMETHYLAMINO)METHANE WITH HEXAFLUOROPROPENE

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It is has been shown that the reactions of bis(dimethylamino)methane (1) with different electrophiles such as carboxylic acids, acyl chlorides etc. result in the formation of iminium salts that use extensively in the reactions of electrophilic substitution as synthetic equivalent of formyl cation\textsuperscript{1,2}.

We have found that 1 acts as nucleophile in the reaction with highly electrophilic hexafluoropropene (2) to give adduct 3 in preparative yield:

\[
\begin{align*}
\text{Me}_2\text{NCH}_2\text{NMe}_2 & \quad \text{CF}_3\text{CF} = \text{CF}_2 \\
1 & \quad 2 \\
\rightarrow & \\
\text{CF}_3\text{CF} & \quad \text{CF}_2\text{NMe}_2
\end{align*}
\]

The adduct 3 is thermally stable and its reactivity is similar to the reactivity of Yarovenko’s and Ishikawa’s reagents that allows to use it as fluorinating agent in relation to O-nucleophiles:

\[
\begin{aligned}
\text{ROH} & \quad \text{MeCN, 50-70°C} & \quad \text{RF} \\
\rightarrow & \quad 50-60\% \\
\text{R} = n\text{C}_4\text{H}_9, n\text{C}_6\text{H}_{13} & \quad \text{CO}_2\text{Et}
\end{aligned}
\]

\textsuperscript{1}H. Bohme et al., \textit{Chem. Ber.}, 1958, 91, 340-345.
\textsuperscript{2}H. Bohme et al., \textit{Chem. Ber.}, 1970, 103, 104-111
SUBSTITUTION HALOGEN ATOM ON FLUORINE IN CONJUGATED SYSTEMS

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We developed the method of synthesis fluorine-containing compounds aromatic line from halogen substitution benzene derivatives in the presence of potassium fluoride under tetraalkylguanidium fluoride - catalyzed system at polar aprotic solvents.

\[ \text{Hal}_n \text{R} + n \text{KF} \xrightarrow{\text{cat, solv, } \Delta t} \text{F}_n \text{R} \]

\( R = \text{CF}_3, F \) \( n = 1, 2, 3, 5 \) \( \text{Hal} = \text{Cl}, \text{Br}, \text{I} \)

This method of synthesis fluorinated aromatic derivatives was applied for unsaturated compounds aliphatic line.

\[ \text{CCl}_2=\text{CCl}-\text{CCl}=\text{CCl}_2 + \text{KF} \xrightarrow{\text{cat, solv, } \Delta t} \text{Cl}_{2-n}\text{CF}_n=\text{CCl}-\text{CCl}=\text{CF}_n\text{Cl}_{2-n} \]

\( n = 1, 2 \)

\[ \text{CCl}_2=\text{CCl}_2 + \text{C}_2\text{Cl}_6 + \text{KF} \xrightarrow{\text{cat, solv, } \Delta t} \text{CF}_3 - \text{CCl}_3 \]
THERMOLYSIS OF SILVER 2-HYDROPERFLUORO-3-METHYL CROTONOATE

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Earlier it was shown that thermal decomposition of silver \(\alpha,\beta\)-unsaturated perfluorocarboxylates of general formula \(R_F\text{CF}=\text{CFCO}_2\text{Ag}\) (\(R_F = i-C_3F_7;\ t-C_4F_9\)) (1) resulted in formation of corresponding perfluoro-\(\alpha\)-dienes in 80-85% yield\textsuperscript{1}.

In the given work it is established that in contradiction from carboxylates 1 thermolysis of silver 2-hydroperfluoro-3-methylcrotonoate (2) leads to the formation of complex mixture of compounds in which along with the expected 1,1,1,6,6,6-hexafluoro-2,5-bis(trifluoromethyl)-2,4-hexadiene (3)\textsuperscript{2,3} there are the products of further transformation of diene 3 – tetrakis(trifluoromethyl)butatriene (4)\textsuperscript{4,5}, 1-perfluoropropen-2-yl-2-(2-hydrohexafluoro-i-propyl)acetylene (5) and 1,2-bis(perfluoropropen-2-yl) acetylene (6).

\[
\begin{align*}
\text{CF}_3\text{CF} = \text{CHCO}_2\text{Ag} & \quad (2) \\
\Delta & \quad -\text{CO}_2 \\
\text{CF}_3\text{CF} = \text{CH} - \text{CH} = \text{C} \left( \text{CF}_3 \right)_2 & \quad (3) \\
\text{CF}_3\text{CF} = \text{C} = \text{C} = \text{C} \left( \text{CF}_3 \right)_2 & \quad (5) \\
\text{CF}_3\text{CF} = \text{C} = \text{C} = \text{C} = \text{CF}_2 & \quad (6)
\end{align*}
\]

The mechanism of the reaction is discussed.

\textsuperscript{4}Morken P.A. et al. Synthesis, 1994, 969.
SYNTHESIS OF BICYCLIC SULFIDES WITH SPIRO FRAGMENTS
BASED ON 2,2-DIFLUORO-2-CHLOROTHIOACYL CHLORIDE

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Synthesis of the corresponding thioacylfluorides from benzyl-(1,1,2,2-tetrafluoroethyl) sulfide and 2-bromo-1,1,2,2-tetrafluorobenzyl sulfide by acid cleavage with phosphorus pentoxide has been shown earlier. In a similar manner, we synthesized 2,2-difluoro-2-chlorothioacyl chloride (1) from benzyl-2-chloro-1,1,2-trifluoroethyl sulfide with a yield of 90%. The reaction mixture was heated to 150-180°C. The vapors of the product formed at this temperature are condensed in a regular water-cooled condenser, collected in an ice-cooled liquid collector, and can be further used without additional purification (content of the main substance being at least 95%).

\[
\text{ClCF}_2\text{CFCI} \overset{\text{P}_2\text{O}_5}{\longrightarrow} \text{ClCF}_2\text{CCI} (1)
\]

The product was used to study the [4+2] cycloaddition reactions with spirocyclic dienes: spiro[2.4]heptadiene-4,6 and spiro[4.4]nonadiene-1,3. Both reactions are stereospecific and give rise to endo isomers of the corresponding 3-(difluorochloromethyl)-3-chloro-2-thiaspiro(bicyclo[2.2.1])hept-5-en-7,1'-cyclo-alkanes (2, 3) with the yield of both products of ~90%. Stereospecificity of the reactions is caused by exclusively spatial reasons, namely, the shielding effect of the cyclopropyl and cyclopentenyl moieties that hinders the exo orientation of the bulky CF₂Cl group compared to the reaction between this thioacyl chloride and cyclopentadiene. The reactivities of the two spirocyclic dienes differ significantly. Thus, complete cycloaddition of spiro[2.4]heptadiene-4,6 takes place at 0°C, while the reaction with spiro[4.4]nonadiene-1,3 occurs only at 20°C.
SYNTHESIS OF LOW-MOLECULAR FLUORINE-CONTAINING IMIDAZOLES

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A new synthetic protocol for the synthesis of 1,4,5-trisubstituted imidazoles containing fluoroalkyl and fluoroaryl groups has been developed using van Leusen reaction.

The authors are grateful to the Russian Foundation for Basic Research (grant No. 16-33-00349/16), to the Ministry of Education and Science of the Russian Federation (State program No. 426).
SYNTHESIS OF LUPANE TRITERPENOID-2-PERFLUOROACYLCYCLOALKANE-1,3-DIONE HYBRIDES WITH POLYMETHYLENEDIAMINE LINKER

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The hybridization of bioactive natural and unnatural compounds is one of the most promising approaches for the design of new leading structures as a bioactivity of some novel hybrids (sometimes also referred as conjugates) often is above an activity and selectivity of an action of parent compounds. In recent years an interest to natural lupane triterpenoids and their derivatives grows up significantly because of high cytotoxicity of betulinic acid towards a number of tumor cell lines. For an introduction of pharmacophore fragments of 2-perfluoroacylcycloalkane-1,3-diones into structure of pentacyclic lupane triterpenoid hybrides, we have been developed an approach using an polymethylenediamine linker. An approach is based on an ability of enol derivatives of 2-perfluoroacylcycloalkane-1,3-diones to react with N-nucleophiles by a mechanism of vinylogous substitution with forming endocyclic enamine derivatives.

By a treatment of betulonic acid with excess of (COCl)_2, chloride acid was synthesized and was introduced into a reaction with polymethylenediamines in the presence of Et_3N in chloroform to obtain monoamides. An interaction of 3-methoxy-2-perfluoroacyl-2-cyclohexen-1-ones with equivalent amount of amides and 3-chloro-2-perfluoroacyl-2-cyclopenten-1-ones with double excess amount of amides in chloroform resulted in betulonic acid hybrides. Betulinic acid hybrides were prepared by reduction of compounds under an action of NaBH_4 in isopropanol.

This work was realized as a part of jointed investigations of NAS Belarus and RAS Siberian branch (grant X15CO-001).

The percentage of fluorine-containing pesticides in the total amount of chemical plant protection products is constantly growing due to the high efficiency of their action. The introduction of fluorinated substituents into composition of obviously known pharmacophore heterocyclic compounds usually leads to enhancement of their biological activity. Thus the synthesis of fluorine-substituted derivatives of 1,2-azoles in the series of isothiazole and isoxazoles is of great interest since these compounds are actively used as bioactive products of different activity spectrum. The ability of some isothiazoles to increase pesticides action is of particular importance because they reduce the rate of pesticides consumption and allow to overcome the pest insects resistance to them.

Anilide 4,5-dichloroisothiazole-3-carboxylic acid and its 4- fluorophenyl phenyl ether were found to increase in several times the action of the pyrethroid insecticide cypermethrin against larvae and adults of the Colorado potato beetle and fleas with adding 3-10%. New fluorine-containing derivatives are perspective for their study in mixtures with insecticides of pyrethroid and neonicotinoid series against pest insects and vectors of highly dangerous infections pathogens. Fluorine-containing amines can also form salts with ferrocenecarboxylic acids which have even higher biological activity.

The work was financially supported by BRFFR (project № X15CO-006) and SB RAS (grant of SB RAS № 4).
SYNTHESIS AND PROPERTIES OF FERROCENYLPERFLUOROALKYLAZOLES

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Incorporation of ferrocene moiety into organic compounds leads to different biological activity which is associated with abnormal biodegradation of ferrocene compounds. Moreover ferrocene derivatives of heterocycles were shown to display pronounced antitumor activity in combination with low toxicity, which was shown either in vitro or in vivo, in models of transplantable solid tumors \textsuperscript{1}.

At the same time the introduction of fluorine or perflourinated alkyl substituents into biologically active compounds is an important method of synthesis of potential drugs.

In this work we used as a ferrocenylalkylating agents 1-ferrocenyl-1-trifluoromethyl-2,2,2-trifluoroethanol (1) which can be easily produced from ferrocene and hexafluoroacetone and 1-(1,1,1,3,3,3-hexafluoro-2-chloroprop-2-yl)ferrocene produced by the reaction of 1 with thionylchloride\textsuperscript{2}.

Earnmarked ferrocenylperfluoroalkylazoles were synthesized by two methods: interaction of 1 with \textit{N,N}-carbonyldiimidazole and its thionyl analogues as well as nucleophilic substitution of chlorine in 2 with corresponding heterocyclic anions.

The \textit{in vivo} study of acute toxicity and anti-tumor activity of 1-(1,1,1,3,3,3-hexafluoro-2-ferrocenylprop-2-yl)imidazole (3) in mice solid tumors model (carcinoma Ca-755) was carried out. Compound 3 was shown to have an antitumor effect against carcinoma Ca-755, causing growth inhibition at 80\% compared with control (10th day of tumor incorporation)\textsuperscript{3}. The observed carcinoma Ca-755 sensitivity to compound 3 while good tolerability of the compound by animals points on desirability for further in-depth study of a pharmacological action mechanism and anticancer properties of this type compounds.

\textsuperscript{1} A.A.Simenel et al, Appl. Organomet. Chem. 2008; 22, 276.
\textsuperscript{3} S. M. Igumnov et al., RF Patent № 2533823
6-FERROCENYL-4-TRIFLUOROMETHYL-2(H)-PYRIDAZIN-3-ONES- NEW LIGANDS FOR CYCLOPALLADATION

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Cyclopalladium derivatives of ferrocene are widely recognized as effective catalysts for a lot of reactions in organic chemistry (Heck reaction, Suzuki reaction etc.). In this regard, the search for new ligands for cyclopalladation is very important. To solve this task, we used three-component reaction, recently discovered by us\(^1\), in the result of which 6-substituted-4-trifluoromethyl-2-phenyl-2H-pyridazin-3-ones are obtained, and transferred it to metallocene compounds.

Indeed, boiling of acetylferrocene with corresponding hydrazine and methyl trifluoro-

\[
\begin{align*}
\text{AcONa} + \text{Na}_2\text{PdCl}_4 & \rightarrow \text{PdCl}_2 + \text{AcOH} + \text{H}_2\text{O} \quad (1) \\
\text{Fe} + \text{NH}_2\text{NH}_2 & \rightarrow \text{Fe-NH}_2\text{NH}_2 \quad (2) \\
\text{F}_2\text{C} = \text{O} & \rightarrow \text{F}_2\text{C} = \text{O} \quad (3)
\end{align*}
\]

pyruvate in toluene in the presence of CH\(_3\)CO\(_2\)H leads to formation with high yield of 2-substituted 6-ferrocenyl-4-hydroxy-4-trifluoromethyl-4,5-dihydro-2H-pyridazin-3-ones 4, which are lately dehydrated to target ligands 5. To obtain effective catalysts 6, aspects of cyclopalladation of 6-ferrocenyl-4-trifluoromethyl-2H-pyridazin-3-ones are studied 5.

This work was financially supported by RFFI (project 14-03-00467)

\(^1\) Dyachenko V.I. et al. Novel tree-component reaction as a route to the synthesis of 4-trifluoromethyl-pyridazin-3-ones Thesis of 7th All-Russian conference “Fluorine Chemistry”, Moscow, Russia, 2006, O-06.
FERROCENYLALKYLATION OF FLUORO-CONTAINING HETEROCYCLES

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Fluorine has become an essential element for drug industry. Trifluoromethyl group is one of the most popular pharmacophore group.\(^1,2,3\) Three fluorine atoms affect adjacent groups in molecule, increasing for example its acidity. Being the most lipophilic among all known groups, it provides target molecule transport into organism. It is also known that electron withdrawing substituents increase potential drugs’ metabolism.\(^4\)

Ferracene-modification of heterocycles permits us to produce compounds with various biological activity.\(^5,6\) The presence of trifluoromethyl group in benzimidazole allows to slightly carry out its alkylation with different hydroxyalkylferrocenes in biphasic aquatic-organic system under the catalysis by 48% HBF\(_4\) (scheme 1).

\[
\begin{array}{c}
\text{OH} \\
\text{Fe} \\
\text{R} \\
\end{array}
+ \begin{array}{c}
\text{N} \\
\text{Fe} \\
\text{R}_1 \\
\end{array}
\xrightarrow{\text{HBF}_4, \text{CH}_{2}C\text{Cl}_2, H_2O}
\begin{array}{c}
\text{Fe} \\
\text{R} \\
\end{array}
\]

\(R=H\) (a), CH\(_1\) (b), C\(_2\)H\(_3\) (c), C\(_3\)H\(_7\) (d), i-C\(_2\)H\(_7\) (e), C\(_4\)H\(_7\) (f)
\(R_1=\text{CF}_3, \text{CHF-CF}_3\)

\textbf{Scheme 1}

Structures of ferrocenylalkylation products confirmed by mass-spectrometry, NMR-spectroscopy methods and elemental analysis data.

\textit{This work was supported by the Russian Foundation for Basic Research (project No 16-33-60163 mol\_a\_dk).}

NOVEL FLUORINATED PORPHYRAZINE PIGMENTS AS THE EFFICIENT AGENTS OF PHOTODYNAMIC THERAPY AND OPTICAL INTRACELLULAR VISCOSITY SENSORS

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Herein, we report a new red-emitting viscosity-sensitive porphyrazines \textbf{I} and \textbf{II} (Figure 1) that is suitable in prospect for quantitative measurements of intracellular viscosity in a large dynamic range. We also demonstrate a new approach to PDT, based on fluorescence lifetime measurements of these porphyrazine dyes.\textsuperscript{1} PDT in cells using porphyrazines is accompanied by cell death and a significant viscosity change, as measured by its fluorescence quantum yield and lifetime.\textsuperscript{2} Thus we demonstrate that photoinduced changes in viscosity could be used as a new diagnostic tool during PDT treatments and could be indicative of the treatment outcome.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.8\textwidth]{fig1.png}};
\end{tikzpicture}
\end{center}

\textbf{Fig. 1. Molecular structures of porphyrazines I and II.}

It should be noted that the disadvantage of \textbf{I} is very low red emission intensity in a non-viscous environment. That prevents porphyrazine \textbf{I} high efficacy as PDT agent. We modified the structure of porphyrazine by a variation of aryl substituents in the porphyrazine peripheral frame. The introduction of \textit{p}-fluorobenzoyloxy substituents into benzene rings framing the macrocycle provides a multiple increase in a quantum yield of red fluorescence as well as the decrease of minimum dye concentration causing the photoinduced cell death (about one order of magnitude less than that for porphyrazine \textbf{I}, whilst porphyrazine \textbf{II} demonstrates the same sensitivity of the fluorescence parameters to viscosity as porphyrazine \textbf{I}.

This work is supported by RFBI (Contract № 15-02-05468 and 16-34-60117)

\textsuperscript{2}T. Forster and G. Hoffmann, Z. Phys. Chem.- Frakfurt 1971, 75, 63
DEVELOPMENT OF FLUORINE-18 LABELED BENZOTHIAZOLE DERIVATIVES SYNTHESIS, POTENTIAL DIAGNOSTIC AGENTS FOR BREAST CANCER IMAGING BY PET

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The development of new radiotracers for positron emission tomography (PET) has a great impact on the further method formation and its use in clinical and preclinical studies. The substituted benzothiazoles (BT) represent a class of compounds with selective and effective inhibition of aryl hydrocarbon receptor (AhR) that is expressed by several types of breast cancer cells. Among them 2-(3,4-dimethoxyphenyl)-5-fluorobenzothiazole (PMX 610) exhibited very potent (GI50 < 0.1 nM) and selective in vitro antiproliferative properties in human breast cancer. Based on this BT scaffold we recently introduced 2-(3,4-dimethoxyphenyl)-6-(2-[18F]fluoroethoxy)benzothiazole ([18F]FEDMBT), a fluoroethylated analogue of PMX 610, labeled with [18F] (T1/2=110 min). Also we were interested in preparing “true analog”, 2-(3,4-dimethoxyphenyl)-5-(2-[18F]fluoro)benzothiazole ([18F]FDMBT). This is a challenging task, considering the difficulty to introduce [18F]-label in non-activated position of aromatic ring via nucleophilic substitution. In this work we intended to develop efficient automated synthesis methods that can be used in the preclinical trials of these new radiotracers.

The synthesis of [18F]FEDMBT and [18F]FDMBT was accomplished via direct nucleophilic substitution of the leaving groups in the precursor structures in presence of kryptofix 2.2.2 and tetrabutylammonium salt respectively (see scheme). Novel solid-phase extraction (SPE) method for [18F]FEDMBT purification on disposable cartridges tC18 Plus (Waters) was elaborated. With this approach the radiotracer was obtained in high radiochemical yield of 60% (decay-corrected) and radiochemical purity >99% within 40 min synthesis time. The synthesis was fully automated using TracerLab FX N Pro synthesis module (GE HealthCare, USA). [18F]FDMBT radiofluorination yield was up to 30%, the work is now in progress to develop the corresponding SPE purification method.

This study was supported by RFBR grant 15-54-52026/16.

1Chen CL et al, EJNMMI, 2015, 42, Suppl.1, S481
NEW METHOS OF SEVOFLURANE SYNTHESIS

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1,1,1,3,3,3-hexafluoro-2-(fluoromethoxy)propane (Sevoflurane, CAS 28523-86-6 RN) is an effective and safety inhalational anaesthetic widely used in medicine due to its fast onset and offset.

1,1,1,3,3,3-hexafluoro-2-(fluoromethoxy)propane hasn’t been produced in Russia even though the existing domestic methods of its synthesis. Our company has applied its many years’ experience in ultrapure chemicals production and halogen exchange synthesis of fluorinated compounds to 1,1,1,3,3,3-hexafluoro-2-(fluoromethoxy)propane synthesis. In the result we have developed and patented new method of 1,1,1,3,3,3-hexafluoro-2-(fluoromethoxy)propane synthesis via reaction of 1,1,1,3,3,3-hexafluoro-2(chloromethoxy)propane with Potassium fluoride anhydrous in presence of phosphonium or guanidinium salts. The target product is distilled from reaction zone as far as synthesized. The synthesis itself is performed in the inert diluent that does not react but makes easier the interchange of oil and distillation of the final product.

The approved method allows synthesizing the target product with the output up to 85% and purity up to 98%. During this work we have studied the mechanism of halogen exchange of this reaction and forces that influence the output and purity of raw sevoflurane. We made complete identification of 1,1,1,3,3,3-hexafluoro-2-(fluoromethoxy)propane impurities and worked out effective methods of its distillation that allows to produce compound with purity of 99,999+% . In the result of these we have developed initial data and Perm Chemical Company have started the projecting on the basis of halogen exchange site of workshop with capacity of 20 MT per year of 1,1,1,3,3,3-hexafluoro-2-(fluoromethoxy)propane. Company “MEDISORB”, have finished preclinical trials of our samples and have started clinical studies.

1 Igumnov S.M. et al. RF Patent №2368597
2 Bodyagin M.B.. RF Patent application №2005107467
3 Deryabin A.A. et al. RF Patent №2479566
NEW APPROACH TO POLYFLUOROCHLOROBENZENES’ SYNTHESIS

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Hexafluorobenzene and its derivatives like pentafluorophenol, pentafluoropyridine and others have wide application in different fields. They are commonly used in microelectronics, nuclear industry, in syntheses of drugs and crop protection chemicals, as well as in R&D. Until recently the main raw material for industrial production of hexafluorobenzene was hexachlorobenzene. But its production has been prohibited by Stockholm Convention on POP. In this connection the new methods of synthesis of perhaloginated benzenes containing one and more atoms of Fluorine with general formula C_6F_nCl_{6-n} where n=1-5 become quite actual. These compounds are precursors of hexafluorobenzene and are not included into the list of restricted chemicals.

Our company have developed and patented the new method of these compounds synthesis\(^1\). The main idea of this method is the use of fluorinated benzenes as starting substances; by their chlorinating by N-chloramides in strong acids media the target perhaloginated benzenes can be obtained:

\[
\begin{align*}
\text{C}_6\text{F}_n\text{H}_{6-n} + \left[N\text{Cl}_k\right] &\rightarrow \text{C}_6\text{F}_n\text{Cl}_{6-n} + \left[H\text{N}_k\right] \\
\text{C}_6\text{Cl}_{6-n} + \left[N\text{Cl}_k\right] &\rightarrow \text{C}_6\text{F}_m\text{Cl}_{6-m} + \left[H\text{N}_k\right]
\end{align*}
\]

\(n = 2-4, k = 1-3,\)

\([\text{Cl--N}]_k\text{--R} – \text{trichloroisocyanuric acid, hexachloromelamine, N-cholrosuccinamide, N,N-dichlorocarbamide, 1,3-dichloro-5,5-dimethylhydantoin}\)

There is another way of synthesis when less expensive chlorinated benzenes are partially fluorinated with Chlorine exchange by Potassium fluoride anhydrous in presence of interchange catalyst with further chlorination by N-chloroamide in strong acids media (in the case of exchange of more than three atoms of Hydrogen by Chlorine partially fluorinated benzenes should be initially chlorinated by Chlorine in presence of Fe):

\[
\begin{align*}
\text{C}_6\text{Cl}_{6-n}\text{H}_n + \text{mKF} &\rightarrow \text{C}_6\text{F}_m\text{Cl}_{6-m} + \left[\text{Cl--N}_k\text{--R}\right] \\
\text{C}_6\text{Cl}_{6-n}\text{H}_n + \text{Cl}_3\text{FeCl}_3 &\rightarrow \text{C}_6\text{F}_m\text{Cl}_{6-m} + \left[\text{Cl--N}_k\text{--R}\right]
\end{align*}
\]

\(n = 2-3, m = 2-3, k = 1-3,\)

\([\text{Cl--N}]_k\text{--R} – \text{trichloroisocyanuric acid, hexachloromelamine, N-cholrosuccinamide, N,N-dichlorocarbamide, 1,3-dichloro-5,5-dimethylhydantoin}\)

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\(^1\) Deryabin A.A et al., RF patent №2577863
NON-RIGID METHYLENE DERIVATIVES OF POLY(TRIFLUOROMETHYL)FULLERENE $C_5C_{70}(CF_3)_8$

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Design of novel materials with desired molecular structure and electronic properties are the key for fabrication of effective organic electronic devices. Fullerene derivatives are prospective materials for such application due to their electronic conductivity and possibility of fine tuning of electronic band structure via specific arrangement of addends and insertion of various molecular fragments. For example, we showed that difluorocarbene addition to $C_{60}$ results in homofullerene $C_{60}(CF_2)$ with enhanced electron affinity due to unprecedented annulenic structure.$^1$ Recently we synthesized two valence isomers of $C_{70}(CF_2)$ where CF$_2$ moieties have cyclopropanated and annulenic configurations (so-called "closed" and "open" isomers)$^2$ The valence isomers of $C_{70}(CF_2)$ demonstrates different electrochemical behavior and electron affinities. Furthermore, reversible electron-driven interconversion between cyclopropanated and annulenic configurations was experimentally proved by means of in situ ESR spectroelectrochemical studies. These results stimulated us to performed studies of fullerenes derivatives where such interconversion provokes significant changes in the π-conjugated system and, therefore, structure of boundary molecular orbitals.

Novel methylene and difluoromethylene derivatives of poly(trifluoromethyl)fullerene $C_5C_{70}(CF_3)_8$ were obtained by the cycloaddition reaction of diazomethane and carbene :CF$_2$. High selectivity of the fullerene cage methylation is predetermined by orienting effect of CF$_3$ groups with near-equatorial addition pattern. Two products, $C_5C_{70}(CF_3)_8[CF_2]$ with [5,6]-open configuration ($r_{C-C}=2.09$ Å) and $C_5C_{70}(CF_3)_8[CH_2]$ with [5,6]-closed configuration ($r_{C-C}=1.69$ Å), were isolated and their structures were reliably determined by single crystal X-ray analysis and NMR spectroscopy (Fig. 1). The unexpected effects of the attachment of CX$_2$, $X=\text{F and H}$, moiety to fullerene cage on its structural and electronic features are interpreted by means of quantum chemical calculation performed at the DFT level of the theory.

![Fig. 1](image_url)

Fig. 1 Annulenic (a) and cyclopropanated (b) configuration of C(CX$_2$)C moieties of $C_5C_{70}(CF_3)_8[\text{CX}_2]$, X=F and H, respectively.

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MOLECULAR AND ELECTRONIC STRUCTURE OF INDIVIDUAL HIGHER TRIFLUOROMETHYLATED [70]FULLERENES

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Trifluoromethylated fullerenes are of interest for studying their molecular and electronic properties due to a large structural diversity of this family of fullerene derivatives with varying number of addends and addition patterns. In particular, electrochemical behavior of a number of individual lower trifluoromethylated fullerenes $C_{70}(CF_3)_{2-12}$, being comparatively easier isolated and purified, are yet investigated by Popov A.A. and co-workers.¹ Here we report electrochemical properties of a variety of individual isomers of higher trifluoromethylated derivatives $C_{70}(CF_3)_{12-20}$.

A mixture of higher trifluoromethylated fullerenes $C_{70}(CF_3)_{12-20}$ was synthesized according to standard procedure.² Contrary to previous works,³,⁴ here we report another strategy for HPLC separation of the obtained mixture including utilization of several HPLC columns with different stationary phases. Thereby, individual isomers of $C_{70}(CF_3)_{12}$, $C_{70}(CF_3)_{14}$, $C_{70}(CF_3)_{16}$ (4 isomers), $C_{70}(CF_3)_{18}$ (5 isomers) and $C_{70}(CF_3)_{20}$ (2 isomers) were isolated in sufficient quantities. Notably, structures of three novel compounds: two isomers of $C_{70}(CF_3)_{18}$ and one isomer of $C_{70}(CF_3)_{16}$, were determined by single-crystal X-ray diffraction analysis. Molecular structures of previously characterized compounds: $C_{70}(CF_3)_{20}$,³ $C_{70}(CF_3)_{18}$ (2 isomers)³,⁴ $C_{70}(CF_3)_{12}$,² and $C_{70}(CF_3)_{14}$,² were also confirmed by means of single-crystal XRD studies.

Electrochemical properties of the obtained individual isomers of higher trifluoromethylated [70]fullerenes were studied by means of cyclic voltammetry. Most of investigated compounds exhibited reversible one-electron reduction. Similar to lower trifluoromethylated fullerenes,¹ the values of first reduction potential, and therefore electron affinity, of studied $C_{70}(CF_3)_{12-20}$ are significantly dependent on addition pattern of CF₃ groups and in a less degree on number of addends. Energies of frontier molecular orbitals of compounds under study were estimated using electrochemical and electronic spectra data.

The work was supported by Russian Foundation for Basic Research (grant no. 15-03-07665).

⁴ Ignat’eva D.V. Chem. Commun. 2006, 2463–2465
INTERACTION COTTON ALKALOIDS WITH HIGHLY ELECTROPHILIC FLUORINE-CONTAINING ALKENES

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One of the areas of modern organic chemistry is the modification of natural compounds for the attachment of useful qualities, used to create pharmaceutical and agrochemical preparations.

It is known that such conversion of the basic structures by polyfluoroalkyl group introduction, for example the CF$_3$-group as a part of building block, can lead to significant changes in the properties of the obtained fluorine-containing compounds. Cotton alkaloid, gossypol and its isomers, widely used in medicine to treat a number of diseases of viral nature, were selected as an object of the research in our work. Earlier, under investigation of the approaches to the synthesis of trifluoromethyl derivatives of salicylic aldehydes, were obtained the fluorinated nitrochromenes $^{1}$. Using this approach for the natural compounds of the ($\pm$) gossypol it was shown that their interaction with 3,3,3-trifluoromethyl-1-nitropropen leads to the corresponding isomers with the structure comprising the fragments of nitrochromen $^{2}$. In turn, the reaction of ($\pm$) gossypol with 3,3,3-trifluoromethyl-2-nitrobuten-2 in the presence of Hunig’s base ((i-Pr)$_2$NEt) was obtained the corresponding (hydroxy)(trifluoromethyl)nitrochroman.

Carrying out the model reactions under similar conditions with the participation of a wide range of salicylic aldehydes has allowed significantly optimize the conditions and to simplify the selection of final polyfluorinated synthons with good yields.

The investigation of cytotoxic activity of the compounds synthesized in the Blokhin Cancer Center showed their high activity in biological assays and expressed cytotoxicity in the concentration range adopted for the modern anticancer drugs.

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$^{2}$ Gusev D.V. et al., *Eurasian Patent № 015364*
SYNTHESIS AND RESEARCH OF FUNGICIDAL ACTIVITY 2-(2-PYRIDYL)-4- HYDROXYL-6- TRIFLUORIDEMETHYLINDOLE

\[ \text{CF}_3 \text{O}_2 \text{N} \text{O}_2 \text{N} \text{CH}_3 + \text{K}_2\text{CO}_3, \text{NMP, 70 }^\circ\text{C, 17 h} \rightarrow \text{CF}_3 \text{O}_2 \text{N} \text{N} = \text{N} \text{CH}_3 \]  

\[ \text{CF}_3 \text{O}_2 \text{N} \text{N} = \text{N} \text{CH}_3 + \text{BuOH}-1/\text{CH}_3\text{COCl, reflux, 38-44 h} \rightarrow \text{CF}_3 \text{O}_2 \text{N} \text{CH}_3 \]  

Interest to chemistry of indoles is determined by the fact that condensed heterocyclic compounds make a great range of substances, which possess diverse bioactivity.

Previously we have developed a method of synthesizing the indole series compounds containing a hydroxy group, with different aryl substituents in the second position from 1,3,5-trinitrobenzene and recognize their fungicidal activity against phytopathogenic fungi and funguses, relatively pathogenic to a human. It was found that these compounds possess fungicidal activity, in many cases exceeding standard triadimefon. Increasing solubility of pharmaceutical products is often of great importance in their prospects. So we synthesize hydroxyindole 6, that knowingly possesses greater solubility, than initial aryl substituting group. It was found that synthesis comes with some side reactions on each step. However we managed to separate and identify sought 6.

It's tests on fungicidal activity \textit{in vitro} by well-known procedure towards to plant pathogenic fungi of different taxonomic species: \textit{Sclerotinia sclerotiorum} (S.s.), \textit{Fusarium oxysporum} (F.o.), \textit{Fusarium moniliforme} (F.m.), \textit{Bipolaris sorokiniana} (B.s.), \textit{Rhizoctonia solani} (R.s.) showed that it is a match to the corresponding nitrated derivative, and in some cases even exceeds the standard triadimefon.
HIGHLY EFFICIENT COPPER (I) BASED CATALYTIC SYSTEM IN RADICAL ADDITION OF HALOTHANE TO OLEFINS: READILY AVAILABLE SYNTHETIC ROUTE TO TRIFLUOROMETHYL-SUBSTITUTED CYCLOPROPANES

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Cyclopropanes was found as a basic structural element in a wide variety of naturally occurring compounds and in a number of physiologically active substances. Moreover, many derivatives have been prepared to test the bonding features of this class of highly strained cycloalkanes, and to study the mechanism of enzymes action, and inhibition processes\textsuperscript{1}. In our previous works we suggest two step procedures for the creating a wide variety of derivatives of small carbocycles from readily available starting materials or reaction intermediates\textsuperscript{2}. Particularly, sequential Cu(I) catalyzed atom transfer radical addition (ATRA) to unsaturated substrate and next reductive cyclopropanation of 1,3-dihalides via metals (Zn/Cu couple).

The trifluoromethyl group has become increasingly importance for improving/modification of bioactivity or for creating of new fluorine - containing drug candidates. In this aspect elaboration of the readily available synthetic route to trifluoromethylated cyclopropanes is challenging task\textsuperscript{3}.

According to results of our last investigations we have developed simple and available catalytic system: [CuBr/Imide of natural tartaric acid (reducing agent-chiral auxiliary)/DMSO (ligand-cosolvent)], showing high efficiency in ATRA reactions. In this report we present a new approaches of application this catalytic system in utilization of halothane to fluorine - containing cyclopropane derivatives.

![Fig.1. Utilization of halothane for creating of trifluoromethylated cyclopropanes](image)

Sequential steps: 1) ATRA, \( R = \text{benzyl or cyclohexyl} \); 2) reductive 1,3-cyclopropanation.

Substrates: a) styren, overall yield 87 \% (GLC); b) (R)-(+-)-Limonene, overall yield 72 \% (GLC).

This work was supported by The State Committee of Science MES RA, in the frame of the research project № SCS 15Ap.


\textsuperscript{2} Mikaelyan A.R. Russian Journal of Organic Chemistry. 2010, \textbf{46}(11), 1662-1666

ELECTROPHILIC ACTIVATION OF 1-TRIFLUOROMETHYL-2-BROMO- AND 2,3-DIBROMOALLYLALCOHOLS IN CF₃SO₃H

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In this paper we studied the reactions of mono- and dibromosubstituted CF₃-allyl alcohols (1, 2) with arenes in Bronsted superacid CF₃SO₃H. Under the reaction conditions, monobromo alcohols 1a-c produce allylcations represented by two resonance forms A and B. Both forms A and B react with the arenes and provide two regioisomers 3a-l and 4a-l with a 37-95% total yield.

The interaction dibromo-substituted alcohols 2a-d with arenes with CF₃SO₃H leads to the formation of 2,4-diaryl-3,4-dibromo-1,1,1-trifluorobut-3-enes 5a-h with 54-87% yields.

The E- and Z-configurations of the compounds were confirmed by 3-5 HH, HF-NOESY NMR, X-ray diffraction studies.

The research was supported financially by Russian Foundation for Basic Research (Project No. 16-33-00504).
P-33

ELECTROPHILIC REACTIONS OF 3-BROMO- AND 3,4-DIBROMOSUBSTITUTED 4-ARYL-1,1,1-TRIFLUOROBUT-3-ENE-2-ONES IN SUPERACIDS

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Organofluorine compounds have widespread applications in different areas of chemistry, physics, biology, medicine, material science and nanoscience. This diversity is provided by peculiar set of fluorine atom properties: its strong electronegativity, chemical inactivity and lipophilicity. Introduction of a CF₃ group into organic molecules may increase their metabolic activity and bioavailability dramatically.

Present study considers behavior of 3-bromo- and 3,4-dibromo-1,1,1-trifluorobut-3-ene-2-ones with different substituents in the aryl ring in superacids. It was found that mono- and dibromo-CF₃-enones 1a-f and 2a-g at low temperatures in FSO₃H undergo cyclizations forming 2-bromo-1-trifluoromethyl-1H-inden-1-ols 3a-f and 2,3-dibromo-1-trifluoromethyl-1H-inden-1-ols 4a-g. Bromosubstituted indenols 3a,c,e are able to react with benzene in the presence of CF₃SO₃H with formation of 2-bromo-1-trifluoromethyl-1H-indenes 5a-c. Dibromosubstituted indenols 4a,b,d,e,g in the same conditions undergo a reaction with two molecules of benzene giving 2-bromo-3-trifluoromethyl-1,1-diphenyl-1H-indenes 6a-e.

Structures of obtained compounds were verified by NMR spectroscopy data (¹H, ¹³C and ¹⁹F) and Xray diffraction data.

The study was performed with financial support of Russian Foundation of Basic Research (project №16-33-00504).
SYNTHESIS OF FLUORINATED 1,3-HEXAHYDROPYRIMIDINES BY MANNICH TYPE REACTION

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Hexahydropyrimidine derivatives are biologically active compounds exhibiting a wide range of pharmacological properties: cytotoxic, antibacterial, antiviral, anticonvulsant and antiarrhythmic. Introduction of fluorine in the molecule structure often leads to increase lipophilicity and metabolic stability and significantly increase the biological activity of the compound. The main methods of synthesis of fluorinated heterocyclic compounds are either direct introduction of fluoroorganic substituents into heterocycle or build cycle using as starting components fluorinated compound.

This paper presents a one-pot method of preparing fluorinated hexahydropyrimidines, based on the reaction of 1,3-dicarbonyl compounds (ethyl 4,4,4-trifluoroacetoacetate, 1,1,1-trifluoro-2,4-pentanedione, 1,1,1,5,5,5-hexafluoroacetylacetone) with formaldehyde and hydrochloride ester of natural l-amino acids by Mannich type reaction. Carrying out the reaction in the presence of AcONa·3H₂O in acetate buffer (pH 4) at a molar ratio of CH-acid: formaldehyde: amine: AcONa·3H₂O = 1: 15: 2: 2 leads to novel 1,3-hexahydropyrimidine derivatives with 30-70% yields. When using the hydrochloride ethyl ester l-tyrosine is observed unusual direction of interaction leading to the formation of the trifluoroacetate 5-(ethoxycarbonyl)-1,3-bis[2-ethoxy-1-(4-hydroxyphenyl)-2-oxoethyl]-3,4,5,6-tetrahydropyrimidin-1-ium.

The preliminary screening of cytotoxic activity of the 1,3-hexahydropyrimidines on cell lines HEK293, Hep G2, Jurkat in vitro was carried out. The data showed that these compounds prospects for further study as the antitumor agents.

This work was supported by Russian Science Foundation (project №14-33-00022).
INTERACTION OF 3-POLYFLUOROALCOXYPROP-1-ENES WITH BENZOIC ACID

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Numerous fluorine contained compounds are useful in various branches of industry as a greases, working fluids, detergents etc.

The present work aims to estimate the main dependences of interaction between polyfluorinated alkoxypropenes (PFAP) and benzoic acid.

The PFAP were prepared by the reaction of allylchloride or allylbromide with corresponding polyfluoro alcohols (telomeres \( n = 1 \) – 3) in aqueous alkali media:

\[ 3-(2,2,3,3\text{-tetrafluoropropoxy})\text{-prop-1-ene, 3-(2,2,3,3,4,4,5,5-octafluoropentoxy})\text{-prop-1-ene and 3-(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluorohexoxy})\text{-prop-1-ene.} \]

\[ \text{H(CF}_2\text{CF}_2)_n\text{OH} + \text{HlgCH}_2\text{=CHCH}_2\text{OCH}_2\text{(CF}_2\text{CF}_2)_n\text{H} \rightarrow \text{CH}_2\text{=CHCH}_2\text{OCH}_2\text{(CF}_2\text{CF}_2)_n\text{H} \]

We found, that only PFAP (\( n = 2, 3 \)) reacts under boiling (3 – 10 h) with benzoic acid in the presence of catalytic amounts of \( \text{H}_2\text{SO}_4 \) to give benzoic esters of polyfluoroalkoxyalkanols.

\[ \text{COOH} + \text{CH}_2\text{=CHCH}_2\text{OCH}_2\text{(CF}_2\text{CF}_2)_n\text{H} \rightarrow \text{COCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{(CF}_2\text{CF}_2)_n\text{H} \]

\[ \text{где } n = 2, 3. \]

In the case of 3-(2,2,3,3-tetrafluoropropoxy)-prop-1-ene (\( n = 1 \)), having respectively low boiling point (110-112°C), no reaction occur.

The structures of benzoic esters were estimated by the data of UV, IR, NMR \(^1\text{H}\) and \(^19\text{F}\) spectroscopy.
THERMAL REACTIONS OF 6-SUBSTITUTED OCTAFLUOROINDAN-5-THIOLS WITH TETRAFLUOROETHYLENE

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Polyfluoroarenes containing benzenothiophene skeleton are studied in a small degree. Synthesis and some reactions of polyfluorodihydrobenzo[b]thiophens are described \(^1\). Along this line, the thermal reactions of 6-substituted octafluoroindan-5-thiols with tetrafluoroethylene (TFE) are interesting too. In these reactions, the formation of compound containing of polyfluorobenzenothiophene skeleton could be expected.

Indeed, we have shown that 6-bromo- and 6-chlorooctafluoroindan-5-thiols react with TFE at 425-625ºC in a flow system to give mainly dodecafluoro-2H,3H,5H,6H,7H-indeno[5,6-b]thiophene (1) along with tetradecafluoro-1,2,3,5,6,7-hexahydro-s-indacene (2) (Scheme 1). 6-Bromoderivative by reaction with TFE at 625ºC affords compounds 1 and 2 in yields 55% and 8% respectively.

\[ \text{Scheme 1} \]

\[
\begin{align*}
\text{F} & \quad \text{F} \quad X \quad \text{SH} \\
\text{CF}_2=\text{CF}_2 & \quad \rightarrow \\
425-625^\circ \text{C} & \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{S} \\
& \quad 1, 38-55\% \\
& \quad 2, 4-8\%
\end{align*}
\]

Compounds 1 (33%) and 2 (3%) were also synthesized from bis(6-bromo-5-pertorindanyl)disulfide.

The copyrolysis 6-thiomethoxyoctafluoroindan-5-thiol (3) with TFE at 420ºC resulted in the reactions mixture which is contained practically no compound 2. This has allowed us to isolate from the reaction mixture the individual arene 1 and its structure was confirmed by elemental analysis, molecular weight, \(^{19}\)F NMR spectrum and X-ray analysis (Scheme 2).

\[ \text{Scheme 2} \]

\[
\begin{align*}
\text{F} & \quad \text{F} \quad \text{SCH}_3 \quad \text{SH} \\
\text{CF}_2=\text{CF}_2 & \quad \rightarrow \\
420^\circ \text{C} & \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{S} \\
& \quad 1, 18\%
\end{align*}
\]

Ways of reactions involving the intermediate formation of radical \(\sigma\)-complexes are considered.

\(^1\)Platonov V.E. et al. J. Fluorine Chem. 1995, 75(1), 41-49.
SYNTHESIS OF POLYFLUORINATED OXACALIXARENES – MACROCYCLIC POLYPHENYL ETHER.

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Oxacalixarenes is one of the new platforms for the design of molecular receptors. It has been demonstrated that the presence of electron-withdrawing groups enhances the possibility of formation of oxacalixarenes complexes with anions. We have proposed the use of polyfluoroaromatic building blocks for the synthesis of polyfluorinated oxacalixarenes. Fragment «3+1» coupling approach using polyfluoroaromatic compounds and bisphenol containing three fragments of tetrafluororesorcinol gives in good yield the perfluorinated tetraoxacalix[4]arenes.

In one-pot approach the interaction of perfluoro-m-xylene with tetrafluororesorcinol gives in good yield the tetraoxacalix[4]arenes, but the reaction with resorcinol produce the cyclooligomeric mixture of polyfluorinated oxacalix[n]arenes (n>4).

The structure of polyfluorinated oxacalixarenes established on the basis of spectral and x-ray data.

The authors thank the RFBR for financial support within the framework of scientific project No. 15-03-08869.
REACTIONS OF DIFLUORINATED PHOSPHONIUM SALTS INDUCED BY LIGHT

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Previously we showed the possibility of formation of difluorinated phosphonium salts from aldehydes and PDFA.

\[
\begin{align*}
\text{R}^1 & \text{Me}_3\text{SiO} \text{F}_2 \text{PPh}_3 \text{O} \text{R}^1 \\
\text{Cl} & \text{C} \text{H}_2\text{C} \text{H}_2\text{Cl} \\
\text{PDFA} & = \text{Me}_3\text{SiCl} \\
\text{PDFA} & = \text{Me}_3\text{SiCl}
\end{align*}
\]

In this work we demonstrated the interaction of the resulting difluorinated phosphonium salts with silyl enol ethers to give fluorofurans in high yields. Process takes place in two stages in one pot. The last step was carried out using a photocatalyst and ultraviolet light.

We have also demonstrated that difluorinated phosphonium salts react with alkenes using Hantzsch ester and visible light.

\[
\begin{align*}
\text{Me}_3\text{SiO} & \text{PPh}_3 \text{Cl} \\
\text{Irrpy} & (0.5\%) \\
\text{propylene oxide} & \text{400 nm LED, rt, 4 h} \\
\text{TsOH, } & \Delta, 30 \text{ min} \\
\text{R}^1 \text{ R}^3 & = \text{aryl} \\
\text{R}^2 & = \text{H, alkyl}
\end{align*}
\]

This work was supported by the Russian Science Foundation (project 14-13-00034).

FUNCTIONALIZED N-(DIFLUOROMETHYL)PYRAZOLES

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Modern synthetic strategies towards new biologically active compounds is focused on elaboration of the low-molecular weight functionalized building blocks useful for the pharmacophore-based drug design. Introduction of the fluorine atom to these building blocks noticeably modifies their properties and, consequently, provides a series of new properties to the target molecules.

In continuation of our research on the field of the fluorinated pyrazole derivatives, we developed a simple and versatile route to \( \text{N-difluoromethylation of 3-methylpyrazole} \) and elaborated an efficient procedure of the resolution of two isomeric products. A series of highly reactive building blocks were synthesized by functionalization of pure isomers of pyrazole bearing a methyl group at position 3 or 5 (on Scheme only 1,3-substituted isomers are shown). These building blocks have potent applications in the rational synthesis.

Structures of all synthesized compounds were confirmed by multinuclear NMR spectroscopy, IR spectroscopy, and microanalysis data, the purity of the compounds was monitored by LC/MS.
SYNTHESIS OF 5-OXO-5,6,7,8-TETRAHYDRO-4H-CROMONES BASED ON PYRAZOLYLCARBOXALDEHYDES BEARING POLYFLUORINATED ALKYL SUBSTITUENTS

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Polyfunctionalized chromones have found wide applications as biologically active substances; they are also extensively used in organic synthesis. A number of efficient approaches to access chromone derivatives with a certain combination of the substituents are known. One of these routes is a one-pot three-component condensation of aldehydes, malononitrile, and 1,3-dicarbonyl compounds. The efficiency of this method strongly depends on the choice of the proper reaction conditions, which, in turn, depend on the properties of an aldehyde component. Based on this method, we studied the possibility to involve pyrazolylcarboxaldehydes bearing the fluorinated alkyl groups (with one, two, and three fluorine atoms) at different positions of the cycle in this condensation (some examples are given on Scheme). We succeeded to develop conditions allowing high-yield synthesis of the target products bearing all mentioned above fluorinated alkyl substituents. More than 50 compounds were synthesized.

![Chemical structures](attachment:Scheme.png)

Structures of all synthesized compounds were confirmed by multinuclear NMR spectroscopy, IR spectroscopy, and microanalysis data, the purity of the compounds was monitored by LC/MS.
REACTION OF POLYFLUOROARENETHIOLS WITH PBr$_5$, PBr$_3$ + Br$_2$ AND Br$_2$. PREPARATION OF BROMOPOLYFLUOROARENES.

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It is found that the reactions of pentafluorobenzenethiol (1) with PBr$_5$, a mixture PBr$_3$ and Br$_2$ to form bromopentafluorobenzene (2) proceed easier than the reaction with Br$_2$ (Scheme 1).

Increasing the amount of Br$_2$ and the reaction time increased the yield of compound 2 (Scheme 2).

Analogously, 1-bromo-2,5-dichloro-3,4,6-trifluorobenzene (6) and 1-bromo-2,4,5-trichloro-3,6-difluorobenzene (7) were obtained from 2,5-dichloro-3,4,6-trifluorobenzenethiol (4) and 2,4,5-trichloro-3,6-difluorobenzenethiol (5) when the latter compounds were heated with Br$_2$. The formation of dibromoderivatives in these cases is observed in small quantities according to the $^{19}$F NMR, GC-MS and GLC (Scheme 3).

6-Bromo- and 6-chlorooctafluoroindan-5-thiols (8 and 9) are reacted with bromine to give 5,6-dibromo-octafluoroindan (10) and 5-bromo-6-chlorooctafluoroindan (11) (Scheme 4).

The reasons for the difference between PBr$_5$ and Br$_2$ as brominating reagents and the proposed pathways of bromination process will be discussed.

This study was carried out under a financial support of Russian Foundation of Basic Research (project 15-03-08869a).
ОСОБЕННОСТИ ПРИСОЕДИНЕНИЯ К СТЕРЕОИЗОМЕРНЫМ
5,5,6-ТРИФТОР-6-ТРИФТОРМЕТИЛ-
БИЦИКЛО[3.2.1]ГЕПТ-2-ЕНАМ

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На примере циклоаддуктов гексафторпропилена и циклопентадиена 1a,1b
показано, что присоединение тех или иных регентов к этим энзо- и эндо- CF3-
содержащим бициклогептенам в зависимости от условий реакции характеризуется
различной регио- и стереоспецифичностью. Так, свободнорадикальное присоединение
gалогенов приводит только к цис-энзо-диагогенидам (для ClF-региоспецифично). При
присоединении в ионных условиях в случае эндо-CF3-циклоаддукта 1а реализуется только
цис-энзо-присоединение, а в случае эндо-CF3-циклоаддукта 1б – только транс-
присоединение (для BrF-региоспецифично), например:

Присоединение трифторметилгипофторита (в присутствии HgF2)
стереоспецифично, но не региоспецифично: из каждого бициклогептена 1а и 1б
образуется по два возможных цис-энзо-CF3O- и F-содержащих аддукта. Еще менее
специфично реализуется присоединение трифторметилйодида (в присутствии перекиси
бензола). По данным хроматомасс-спектрометрии образуется смесь 16 изомерных
аддуктов – по 8 из каждого бициклана. Основное содержание смеси составляют продукты
энзо- CF3-присоединения: две трудно разделимые пары цис/транс – региоизомеров на
основе 1а и два аддукта на основе 1б, выделенные в индивидуальном состоянии, а
именно:

Полученные фторсодержащие бициклогептаны оценены как бактериостатики (in
vitro) и ратициды (in vivo). Установлено, что во всех случаях цис-аддукты активнее транс-
аддуктов, а эндо-CF3-содержащие стереоизомеры активнее энзо-CF3-содержащих.
INTERACTION OF PYRIMIDINE BASES
WITH FLUORINATING AGENTS

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Among the derivatives of nucleic acid components fluorinated pyrimidines and nucleosides, with their geometrical structures most close to those of antimetabolite molecules, are of considerable practical interest.

5-R substituted uracil derivatives (R=CH\textsubscript{3}, F, Br), and 6-azouracil are dissolved easily in anhydrous hydrogen fluoride thus making it possible to fluorinate those substances either with elemental fluorine (30-100% concentration) within temperature range (-)30 to (+) 5°C, or with fluorine derivatives (chlorine monofluoride, nitrile fluoride).

The interaction results in the addition of those reagent fragments by the multiple 5,6 bond of pyrimidine molecule to produce fluorinated 5,6-dihydrouracys with quantitative yield. In the case of 6-azouracil fluorination the only reaction product is 5-fluoro-6 azouracil.

The substances separated from anhydrous hydrogen fluoride solution and treated with some nucleophile agents (water, organic acids) form new functional 5-fluorosubstituted uracil derivatives difficult to prepare otherwise.

The structure of thus produced substances is investigated by the methods of IR, UV, NMR (\textsuperscript{1}H and \textsuperscript{19}F) spectroscopy.

The availability of 5,6-difluoro-5,6-dihydrouracys opens the way to the synthesis of various fluorinated pyrimidines.
SYNTHESIS AND PROPERTIES OF 2-HYDRO-1,1,1,2,4,4,5,7,7,8,8-
UNDECAFLUORO-5-TRIFLUOROMETHYL-8-SULFONYL FLUORIDE-
3,6-DIOXAOCTANE

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Modern science and current technology development assume wide use of nanotechnologies, and nanomaterials. The latter include membrane-catalytic systems based on perfluorinated monomers. One of the most well-known and widely applied perfluorinated sulfomonomers is perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonyl fluoride

\[
\text{CF}_3 \quad \text{FSO}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}=\text{CF}_2
\]

Even the earliest studies on the synthesis of vinyl ethers via the pyrolysis of the corresponding salts of perfluorinated carbonic acids and their derivatives have shown that some monohydrogenated by-products are formed, in our case it is

\[
\text{CF}_3 \quad \text{FSO}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCFHCF}_3
\]

2-hydro-1,1,1,2,4,4,5,7,7,8,8-undecfluoro-5-trifluoromethyl-8-sulfonyl fluoride-3,6-dioxaoctane. The substance results from the reaction of an intermediate in the pyrolysis of perfluorocarbonic acid alkaline salts in the presence of water or another solvent containing active hydrogen in its molecule.

\[
[\text{FSO}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCFM}] \rightarrow \text{FSO}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCFHCF}_3
\]

The mechanism of formation is offered, and the properties of the substance are discussed, this being a hardly separated impurity in the industrially produced monomer.
VINYLIDENE FLUORIDE COPOLYMERS AND PROSPECTS OF THEIR APPLICATION

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Polymers and copolymers of a vinylidenfluoride (VDF) are known for a set of valuable technical properties which distinguish them from other representatives of fluoroplastics group. Polyvinylidenfluoride (PVDF) competes convincingly on a number of parameters with polytetrafluoroethylene.

VDF is highly attractive monomer actively participating in copolymerization reactions with other fluoro-olefins offering one of effective ways of fluoropolymers product line expansion. VDF polymers appeared also very convenient model which has been used when studying interrelation "composition – synthesis – property".

As a result of carrying out series of investigational studies data on influence of end groups type on the thermal stability of VDF polymers, their rheological and dielectric parameters were obtained, optimal composition and parameters of polymerization process carrying out defined and methods of tailor-made synthesis of the VDF polymers suitable for specific designation created and in practice implemeented.

Processes for a big group of VDF based polymers are developed, such as:

- special type of modified PVDF which crystal structure is capable to be formed under certain conditions mainly in to β-form, allowing the piezoelements with improved characteristics (piezoelectric modulus up to \( d_{31} = 20 \times 10^{-12} \text{ C/N} \));

- VDF copolymers with trifluoroethylene which composition and preparation conditions provide the primary maintenance of a β-form at a synthesis stage;

- VDF copolymers with tetrafluoroethylene with given composition and MWD for extrusion to thin-walled products: tubes, hollow fibers for gas-separation membranes;

- new soluble VDF copolymers with perfluordioxolane having selective gas-liquid permeability.
STUDY OF FLUOROPOLYMER COMPOSITES PREPARATION
PROCESS SPECIFICITIES

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Creation of the new fluoropolymer composite materials (CM) is one of the main fluoroplastics development directions now. Various compositions on the basis of PTFE which have allowed to overcome his disadvantageous features as cold flow, small hardness and wear resistance are well-known. For melt-processible fluoropolymers (FP) the development of compositions is complicated by special requirements to fillers. The high thermal stability of fillers and their compatibility with FP powders or granules, and also their ability to formation of homogeneous melts with a high melt flow index, Tensile and resistance to thermal and mechanical degradation is necessary. The new developments have allowed to prepare a number of perspective CMs.

One of interesting FP for new CM is TFE copolymer with ethylene. Thanks to contents of hydrogen-containing units –CH\textsubscript{2}–CH\textsubscript{2}– in macromolecule ETFE, which for cross-linking necessary radical nucleation under irradiation provide, this copolymer was the most suitable for creation of CM with the use of radiation technology. Various crosslinking agent (CA) used for crosslinking process efficiency upgrading were studied: allyl esters of polycarboxylic acids, allyl cyanurates, etc. Triallyl isocyanurate (TAIC) was the most effective one. As a result of researches conditions were found which have allowed to exclude largely the competing, undesirable TAIT homopolimer formation reaction.

The problem requiring technical solutions is the big weight of cable networks in aircraft and space equipment objects. For the purpose of insulating layer mass decrease a pore-forming additive containing composition on the basis of F-4MB with use of a physical foaming method is developed. Conditions are studied and the parameters determined which the necessary amount and the size of pores and also uniform gas distribution in polymer melt provide. Taking into account the high melt viscosity a blowing process regulator providing an optimum of polymeric and gas phase volume ratio in an insulating layer was chosen.

Studies on optimization of formulations and preparation parameters for fluoropolymeric pigment masterbatches needed for coloring of wire isolation, film materials, coatings and fibers are undertaken. New compounds (colors) suitable for FP coloring taking into account destructive processes with evolution of HF, initial monomers and decomposition products of technological additives at high fluoropolymer processing temperatures are investigated.
FLUORINATED POLYURETHANES, SYNTHESIS AND PROPERTIES

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Fluorinated polyurethanes are novel materials with a unique set of features such as mechanical strength and high chemical stability. Fluorinated fragments added to the macromolecule bring about high hydro- and oleophobic properties and, in a number of cases, it is possible to ensure a good low-temperature behavior.

It is known that the insertion of fluorinated fragments into the macromolecule sometimes entails a dramatic drop of the polymer glass transition temperature. Therefore we endeavored to synthesize new poly- and oligourethanes that would incorporate a fluoropolyether ingredient in the diol constituent both in the polymer backbone and in the side chain. A conceptual approach to the synthesis of such polymers is given in the scheme:

\[
\text{HOCH}_2 - R - \text{CH}_2\text{OH} + \text{OCN} - R' - \text{NCO} \rightarrow [ - \text{R} - \text{CH}_2\text{O} - \text{C} - \text{NH} - R' - ]_n
\]

\[
R = \text{CFOCF}_2\text{CFO(CF}_2\text{O)}_6\text{OCFCF}_2\text{OCF} - ; \text{C}_3\text{F}_7\text{OCFCF}_2\text{OCFCF}_3\text{N} \text{CH}_2 \text{CH}_2 \text{CH}_2
\]

\[
\text{CH}_2[(\text{CF}_2\text{O})_d(\text{CF}_2\text{CF}_2\text{O})_{3,46}\text{CH}_2] + \text{CF}_3\text{O}[(\text{CF}_2\text{O})_d(\text{CF}_2\text{CF}_2\text{O})_{3,46}\text{CH}_2]
\]

It has been established that the non-catalyzed polyaddition reaction runs quite smoothly both in solvents and in the melt. Contact angles for polymers wetted with water achieved 100-117°, which is indicative of their rather high hydrophobicity. The characteristic viscosity of fluorinated polyurethanes was 0.13 dl/g in hexafluorobenzene. The temperature of the decomposition onset was 240°C and the glass transition temperature was as high as –143°C.
TELomerization and SoteLOmerization
galOgenolefinov

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Processes of radical telomerization of ethylhalogenolefylne under the influence of a fluoroxyfluoromethane (FOTFM) in the presence of solvents have been studied, and also at temperatures when reagents are in different aggregate states in the continuous and periodic modes. Consistent patterns and essential differences were found, allowing to create and improve technologies of receiving a row fluoro-chloro-containing of liquids and oils, unique on heatphysical and dielectric properties, common for all described reactions, with a high chemical and thermal stability in the wide range of temperatures have been determined.

Unlike the threefold ‘monomer-initiator-telogen’ systems where each reagent carries out a single function, in the halogenolefin-FOTFM systems, the latter serves at the same time as the initiator, and telogens: that makes one of features of the process. For synthesis with system of heterogeneous reactions it is difficult to establish localization and to define slow stages of multistage polymerization. The presented examples allow to conduct process at sub-zero temperatures when initial monomer is in a liquid state with pressure below atmospheric. A comparison of the factors and products received at such synthesis allow to define some of these parameters.

Telomerization of trifluorochlorethylene, a tetrafluoretylene, a trifluorbrometylene, a trifluoroxytrifluoretylene and a hexafluoropropylene and under the influence of FOTFM was carried out at presence the pergaloid of solvents, the structure of the received telomers was controlled on the basis of data of spectroscopy NMR$^{19}$F. At the continuous modes of polymerization the possibility of regulation of molecular mass of the formed products by a variation of temperature and a ratio is shown "olefin- FOTFM", and also optimization of the dynamic mode of the reactionary device. In case of the periodic mode (possible for some of the given processes) it is possible to control degree of a telomerization, changing only one parameter – the speed of the initiator input. All received telomers don't support in the structure C-H of the communications and atoms of carbon connected more than with one atom of chlorine and also nonlimiting C=C of communications and, unlike the similar polymers received in other ways have linear structure. Thanks to these features the received final products surpass the known foreign and domestic analogs in a number of indicators: are steady against effect of the main and strong mineral acids at the room temperature, don't react with fluorine and trifluoride of antimony, and remain stable at temperatures up to 250°C.

In the Perm branch "RSC "Applied Chemistry" installation is created for receiving via telomerization method (in the periodic mode) of the fluorochlorocarbon oils and greasings with performance of up to 10 tons per year, the products have passed tests with positive results. The technology has been further optimized and technology of continuous telomerization has been developed.
DIFLUOROCYCLOPROPANATED POLYNOBORNESES: SYNTHESIS AND PROPERTIES

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Modification of double bonds in polynorbornenes obtained by ring-opening metathesis polymerization (ROMP) opens the possibility to increase their chemical stability and supply other new important properties. At the same time, only hydrogenation of metathesis polynorbornenes (MPNB) has been studied in sufficient details. Other methods of MPNB modification are poorly described in the scientific literature. It is known that introduction of fluoro-containing substituents or bulky SiMe\textsubscript{3} groups as the side chains in the MPNB significantly increase their gas-separation properties\textsuperscript{1}

In this work we studied difluorocyclopropanation (FC) of unsubstituted polynorbornene (PNB) and poly(5-trimethylsilylnorbornene) (PNBSi) in order to study gas-separation and other properties of modified polymers.

Initial PNB and PNBSi were synthetized by ROMP of norbornene and 5-trimethylsilylnorbornene in the presence of 1\textsuperscript{st} generation Grubbs’ catalyst, Cl\textsubscript{2}(PCy\textsubscript{3})\textsubscript{2}Ru = CHPh. The FC of polymers was carried out by the action of difluorocarbene formed during sodium chlorodifluoroacetate thermolysis in methyl benzoate media at 185 °C (scheme). In order to decrease side reactions of polymer scission and cross-linking the antioxidant - 2,2’-methylenebis(6-tert-butyl-4-methylphenol) was added into reaction medium.

\[
\begin{array}{c}
\text{F} & \text{F} \\
\text{R} & \text{SiMe}_3
\end{array}
\begin{array}{c}
\text{ClF}_2\text{CCOONa, 185 °C} \\
\text{PhCOOMe} \\
\text{- NaCl, CO}_2
\end{array}
\begin{array}{c}
\text{F} & \text{F} \\
\text{R} & \text{SiMe}_3
\end{array}
\]

where R = H; SiMe\textsubscript{3}

The conditions supplying almost complete FC of C=C bonds in PNB were found and high molecular weight polymers with good film-forming properties were synthesized. A strong influence of bulky SiMe\textsubscript{3} groups on the FC process was observed. Obtained polymers were characterized by \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F, \textsuperscript{29}Si – NMR, IR spectroscopy, GPC and DSC methods. It was shown that introduction of difluorocyclopropane fragment in MPNB increased their glass transition temperature and considerably influenced gas-separation properties. For example, PNB gas permeability for oxygen increased in 2 – 2.5 time.

This work was supported by Russian Science Foundation (grant № 14-19-01362).

\textsuperscript{1}Finkelshtein E, Bermeshev M., Gringolts M., et al., Russ. Chem. Rev. 2011, 80, 341.
ELECTRICALLY CONDUCTIVE COMPOSITIONS BASED ON FLUORO-ORGANOSILICON BINDER FOR FORMING A LOW DENSITY COATING ON RADAR STRUCTURES

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Developed coating compositions based on gradient coatings fluoro-silicone binder (varnish FT-32L, 42, KO-945) using the electrically conductive fillers. The measurement results of the amplitude-frequency characteristics of the absorption of electromagnetic radiation (EMR) from the weighting characteristic of the coatings at least 4kg/m\textsuperscript{2} on a metal substrate with low density fillers in the wavelength range of 1-3.75 cm showed values of -20 dB. Chemical and physical methods of modifying layered graphite compounds of various sizes, shapes, and fillers of low density fillers silicon oxides synthesized in developing radar absorbing coatings compositions. Nanotubes, graphene structure with a high specific surface area and the clusters with ferromagnetic metals, fillers lower density silicon oxide with conductive properties are obtained under thermal and microwave heating stimulated. Colloidal suspensions based on organic binders and synthetic fillers have allowed receiving paint formulations for radar absorbing coatings.

Impregnation of the tissue samples, paper, foam or other dielectric materials based on conductive bonding PTFE and silicone bonding materials made with different levels of surface electrical conductivity of 5 to 300 ohms. The compositions of inks used in instrument for protection against electromagnetic radiation effects.

To shield the devices from EMR effects applied coatings with the highest values of specific volume resistance: - 1 \texttimes 10\textsuperscript{-3} - 5 \texttimes 10\textsuperscript{-5} ohm-cm (90 parts by weight of silver, 10 mass.ch perchlorvinyl resin); 10\textsuperscript{-3} ohm-cm (77 parts by weight of carbonyl nickel NPK-1); 5.2 \texttimes 10\textsuperscript{-5} ohm-cm (85 parts by weight of graphite in the composition with ED-20 and the silver solution).

It was found that at lower than with other types of graphite-filled polymer component of thermoexpanded graphite TEG reached high conductivity composites samples.

Two technological approach of combining the polymer component with the TEG were considered: 1 mixture of polymer component (on rollers, pressing) with the TEG, which was obtained by thermal expansion of the modified graphite (MG). 2 mixing the polymer component with the MG, and thermal expansion of the composition (obtained preform was compressed or is rolled on rollers with a variable gap). The PTFE powder was used as the polymer component. The level of electrical conductivity of the material depends on the technology of its manufacture. TEG sample conductivity (thickness d = 3 mm, volumetric density \(\gamma = 140 \text{ g} / \text{l}\)) was equal to \(\sigma = 1.5 \times 10^2 \text{ S} \text{ cm}^{-1}\), and after the rolling mill at such a sample with a variable gap to a graphite foil (d = 0.4 mm, \(\gamma = 1100 \text{ g} / \text{l}\)) was equal to the conductivity \(\sigma = 1.5 \times 10^3 \text{ S} \text{ cm}^{-1}\).

The work was supported by the Presidium of the Russian Academy of Sciences (program I.1P).
INVESTIGATION OF NEW CLASS OF AMPHIPHILIC OLIGOMERS - FLUOROALKYL-TRIMETHYLSILANES; DETERMINATION OF CHAIN LENGTH BY THE THERMOGRAVIMETRIC AND MASS-SPECTROMETRY METHODS

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Amphiphilic oligomers X(C\textsubscript{2}F\textsubscript{4})\textsubscript{n}R, with X=H, F, Cl with sufficiently long perfluorinated chain (n>4) and hydrophilic end group R, are considered the most promising compounds for anti-icing coatings. The hydrophobic chain facilitates removal of the drops of supercooled water, while the hydrophilic end group enables strong bond with the surface.

Our prior reports presented a new method for radical polymerization of tetrafluoroethylene (TFE) in solution, which produces oligomers with chain length distribution (mean n from 4 to 20) and various end groups. Films of these oligomers can show superhydrophobic behavior with nanoscale roughness. The latter arises due to formation of a supermolecular framework from the rigid rod oligomers that interact via hydrogen bonding between the end groups.

Radiation-induced radical polymerization of tetrafluoroethylene (TFE) in solutions of trimethylsilanes (tetramethylsilane Si(CH\textsubscript{3})\textsubscript{4} (TMS), ethyl trimethylsilane C\textsubscript{2}H\textsubscript{5}Si(CH\textsubscript{3})\textsubscript{3} (ETMS), chloro trimethylsilanes ClSi(CH\textsubscript{3})\textsubscript{3} (CTMS) produces oligomers with the general formula R(C\textsubscript{2}F\textsubscript{4})\textsubscript{n}X where R=CH\textsubscript{2}Si(CH\textsubscript{3})\textsubscript{3}, C\textsubscript{2}H\textsubscript{4}Si(CH\textsubscript{3})\textsubscript{3}, Si(CH\textsubscript{3})\textsubscript{3}, in TMS, ETMS, CTMS respectively, X=H,Cl. The end groups and the molecular mass distribution were determined by the thermogravimetric (TG, DTG and DTA) measurements and mass-spectrometry methods.

With increasing TFE concentration in the range 0.4 – 1.3 M, 1.2 – 2.7 M, 0.13 – 0.7 M in TMS, ETMS, CTMS respectively, the resulting chain length increases, accompanied by a transition from homogeneous to colloidal solution and to gel of the polymerization products. At the top of the aforementioned TFE concentration range, the chain length reaches n=10-12.

The experimental data including DTG curves and mass spectra presented above demonstrate that (1) the chain length of the oligomers produced by radical polymerization can be controllably increased by increasing the initial concentration C\textsubscript{0} of tetrafluoroethylene precursor; (2) in homogeneous solutions, the chain length is n=3–5, close to that obtained by synthesis of individual chemical compounds; (3) in gels formed upon polymerization of TFE in the TMS, ETMS, CTMS solutions with C\textsubscript{0} ~ 1 M, the chain length reaches the maximum value of n=10-12. The presented results demonstrate a strategy for controlling not only the chain length, but also structure of the product phase from dilute colloidal solutions to structured gels. Altogether, these findings open new possibilities for the design of poly-functionalized coatings.

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CROSS-LINK EVALUATION OF PERFLUORORUBBER
ACCORDING TO FTIR DATA

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Among the functional groups used in perfluororubbers, the most known cyano group (nitrile)\(^1\). Depending on the type of cure agent bis-ortho-aminophenols-AF (BOAF) or perfluorodiimidoylamidine (DPIA) the curing proceeds by formation of benzoxazole or triazine cross-links\(^2\). However, the quality of cured rubbers is determined only indirectly via a set of physical and mechanical characteristics.

FTIR-spectroscopy method applied to thin films of perfluororubber compositions allows additionally monitoring of curing process, also to make evaluation of the degree of cross-linking.

The presence of overtone CF in the range of 2200 - 2650 cm\(^{-1}\) from the main signal allows to use relative areas of the absorption bands and to neglect variable thickness of the films studied.

Using of model compounds, identical to heterocycles, formed during vulcanization process, make possible to establish the quantitative relationship between the mass of a model compound and corresponding relative area of the absorption band. The relations are described by linear equations with correlation coefficient R\(^2\) equal at least 0.99. The structure and purity of the synthesized model compounds were proved by NMR \(^1\)H and \(^{19}\)F data.

Evaluation of cross-link level according to FTIR data allows to find the exact ratio of the components and thermal curing modes.

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STUDY OF PROCESSES MELT SPINNING SYNTHETIC YARNS CONTAINING NANOPARTICLES OF IRON, STABLE TELOMERS POLYTETRAFLUOROETHYLENE

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Modern textile materials must have specific properties that are required in a particular sphere of human activity, as well as to be able to change them in the right direction of a person under the influence of the external environment, ie, to produce a response. Textile materials with such qualities are named the so called “intelligent” textiles and they are widely used for military and space industry. Mountain-climbers, sportsmen, people working in extreme conditions use clothes made of those textile materials. The main aim is to create the materials which have the properties such as: antibacterial qualities, electroconductivity and fine physico-mechanical characteristics.

The synthetic yarns get useful qualities by introducing the metal nanoparticles into a polymer melt. Nowadays this method is the most perspective and economically-grounded. It does not require essential changes of technological conditions and the use of additional modified equipment. The following equipment was used for studying the melt spinning process and orientation exhaustion: CFPB-1 and OCB-1 test benches. Thanks to this equipment it is possible to create the synthetic yarns with new qualities and perfect the technology of their production. The present work is one of the stages of research purpose at the creation of yarns with special properties.

The purpose of this work was to study the effect of iron nanoparticles stabilized telomers polytetrafluoroethylene (PTFE) in the melt spinning process and the physical and mechanical properties of polypropylene filaments.

Polypropylene yarns were melt spinning on CFPB-1 test bench. The temperature of spinning yarns in working areas was: T₁ equals 130 (degrees centigrade) (preheating zone), T₂ equals 220 (melting zone), T₃ equals 220 (stabilization zone), T₄ equals 220 (heating zone of a formed plate). The speed of the forming disks was 100 meters per minute and was defined by technological reasons and constructional peculiarities of the test bench. These parameters remained constant during the experiment.

Iron nanoparticles stabilized polymers of polytetrafluoroethylene was applied to the polypropylene granules before spinning yarns.

The concentration of PTFE telomer in polypropylene filaments was 0.2 - 0.7% iron nanoparticles 0.01 - 0.035%. We studied the effect of the composite filler on the physico-mechanical properties of polypropylene filaments, their biocidal and electrical resistance.
MORPHOLOGICAL FEATURES OF THE HYPERFINE FLUOROCARBON COATING FORMED ON POLYMERIC MATERIALS FROM SUPERCRITICAL CO2 CO-SOLVENT

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The problem with polyester textile materials giving high hydrophobicity is a serious scientific and practical interest. For hydrophobizing, usually used for coating the fibrous material substances with low surface energy that can significantly reduce the surface energy of the fibrous substrate. The greatest effect may be obtained by using fluorinated hydrocarbons. Hydrophobic effect is achieved by producing on the surface of the textile substrate nanoscale coatings with low surface energy, which follows the micro-relief structured surface forming fabric yarns.

In this work modification of polyester (PET) fabric preparation Forum® (ultrafine polytetrafluoroethylene - PTFE) in solution of SC-CO2 (20 MPa, 90 ° C) supplemented with co-solvents (methanol, ethanol, butanol) in an amount of 5% and 10 without cosolvents . The characteristics of surface hydrophobicity and specific content repelling agent after modification. In detail the features of the surface morphology of the coating formed on the PET film from solutions Forum® preparation in SC-CO2 with the addition of co-solvent by the method of atomic force microscopy.

The surface of samples modified in the presence of a co-solvent, acquires, as compared with the original film, a pronounced roughness. The calculation of the surface energy and its dispersive and polar components of the modified PET film. Formation of coatings based on PTFE ultrafine polyester film on the surface leads to a significant reduction of its surface energy. The greatest decrease is observed in the case of modifying PET film from among pure CO2 and SC-adding it in 10% methanol. In these cases, the maximum reduction is achieved by the water absorption of the tissue samples.

The results correlate well with those works¹,² in which the method of molecular dynamics shows a different form of existence of co-solvents in the medium sverhkritickego fluid (alcohol distributed in the amount of monomers and hydrogen-bonded dimers). When the need for materials with hydrophobic PES additives cosolvents possible selection agent and maintaining its concentration gtdrofobnosti parameters.

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THE CORRELATION OF TETRAFLUOROETHYLENE TELOMERES SUBLIMATION RATES WITH MOLECULAR MASS

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The tetrafluoroethylene (TFE) telomers sublimation kinetics was investigated using a gravimetric method at a residual pressure 0.13 Pa and temperatures 40 – 320°C. The rate constants and activation parameters of fluorotelomer sublimation were calculated. Molecular mass of TFE telomers was determined using thermomechanical spectroscopy data. It is shown that in the interval $10^3 < M_N < 10^5$ the activation energy of the process increases linearly with the molecular mass of telomers.

To describe the kinetics of sublimation of a mixture of fluorotelomers of different lengths, a mathematical model of polychronous kinetics was suggested. This model assumes that the material consists of a large number of fractions, the sublimation of which is described by a kinetic equation for the first order reaction with the activation energy $E$. The continuous spectrum of the activation energy distribution $P(E)$ corresponds to the sublimation of the total mass of the test mixture. A method is proposed for determining the monotonous integral distribution function of the mass fraction of telomers on the activation parameters of the sublimation $P(E)$ (and hence on the molecular mass). It is based on solving the inverse problems using the stable optimal integral representations method.

The correlations found are used to determine the molecular-mass distribution (MMD) of tetrafluoroethylene telomers prepared through $\gamma$ irradiation of monomer solutions in acetone. It is shown that the synthesis conditions (the pressure of the monomer in the reactor) significantly affect the value of the molecular mass and the function of MMD generated telomers. When the pressure increases from 1 to 2.5 ATM. the bimodal function of MMD replaced by the monomodal one: the peak related to the fluorotelomers of low molecular mass disappeared and the peak corresponding to higher values of the MM is shifted towards higher values.

Fig. 1. DTG curves of TFE telomers sublimation obtained for $P(E)$ and MMD calculation. The pressure of TFE in the reactor is 1 (1); 1.7 (2) and 2.5 ATM. (3).

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OPTICAL PROPERTIES AND STABILITY BORON FLUORIDE COMPLEXES OF DIPYRROMETHENE

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Using a variety of optical devices in modern technology makes it necessary to explore the photonics of new organic luminophores. One of the most perspective compounds for this purpose are boron fluoride complexes of dipyrromethene (BODIPY) which have already established themselves as active laser media and used for this purpose a number of commercial firms\textsuperscript{1} However, necessary to carry out the search for new more perspective compounds in this series to create on their basis of materials for fluorescent probes, markers, sensors. For the successful application of BODIPY complexes need to systematic study of spectral-luminescent, lasing, photochemical properties and establishing their connection with the features of the complex structure, which is the purpose of this work.

As objects of this study are selected new boron fluoride coordination complexes of dipyrromethene with ligands of different structures (Figure 1).

Figure 1. Structures and notations of investigated complexes

Alkyl-substituted boron fluoride complexes of dipyrromethene upon excited at longer wavelengths show good emissivity ($\gamma_{fl} = 0.8-1$) and generate stimulated emission with efficiency up to 75%, which allows us to recommend them for use as the basis for the laser-active media.

Introduction halogen atom in structure BODIPY lead to decrease fluorescence quantum yield greatly due to the increase intersystem crossing, as evidenced by the presence of the phosphorescence in frozen solutions. The dependence of the intensity of the phosphorescence from the gas mixture (quenching in oxygen atmosphere, increase under argon) show that the halogen-substituted BODIPY complexes can use as materials for oxygen sensors.

For practical applications in a variety of optical devices necessary to know the stability of the complexes in the ground and excited states. It is shown that alkyl and halogen-BODIPY have low probability for the dissociation complexes of in neutral proton solvents. For the good dissociation requires a very acidic environment, which is consistent with the statement of the high photochemical stability of a class of laser dyes alkyl-BODIPY in ethanol\textsuperscript{2}.

The work was supported by the Russian President's grant (NSH-7166.2016.2).

\textsuperscript{1}Loudet A. et al. Chem. Rev. 2007, 107(11), 4891-4932.
P-57

(CO)POLYMERS 1- TRIFLUOROMETHYL-1-FERROCENYL-2,2,2-TRIFLUOROETHYL METHACRYLATES AND DIACRYLATES, SYNTHESIS AND PROPERTIES

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We developed a method of synthesis of monomers containing ferrocene - 1-ferrocenyl-1-trifluoromethyl-2,2,2-trifluoroethyl esters of (meth) acrylic acid 1a, b, 2a, b, obtaining their homo- and copolymers, and subsequent creation based on them upon exposure high temperatures (500-1000 °C) pyrocarbon composites doped with nanoparticles of zerovalent iron (Fe⁰).

Pyrocarbon matrix composites produced contains in its composition Fe⁰ nanoparticles with the average size of 50 nm (Figure 1). It is composed of carbon in a state sp²-hybridization, 80% of which is of disoriented graphite. The magnetization of these materials 59 G cm³ / g.

Study SEM pyrocarbon matrix obtained in a high vacuum of composite materials containing iron nanoparticles, shown that it has a porous, well-branched 3D-structure (Fig. 2).

Fig. 1. The structure of the nanocomposite "core-shell matrix" (TEM method).
Fig. 2. Structure of highly porous nanocomposite (SEM method).

In addition to the study of fundamental phenomena occurring during the formation of composite materials data searched applied aspects of their use in nanotechnology (photonics, radioabsorption, targeted drug delivery, etc.).

The work was supported by the Presidium of the Russian Academy of Sciences (program 1.35P).
CONJUGATES OF WATER-SOLUBLE POLYMERS WITH TETRAKIS-(HEXAFLUOROACETYLACETONATE)GADOLINIUM AND PORPHYRAZINE FOR BIMODAL FLUORESCENCE/MAGNETIC RESONANCE DIAGNOSTICS OF TUMORS

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Novel materials which are promising as the potential agents for two independent modalities of non-invasive diagnostics of tumors (fluorescent and magnetic-resonance bioimaging) had been developed. Chelate complex tetrakis(hexafluoroacetylacetonate) gadolinium (1) was synthesized and used as a magnetically active component. Tetra-(4-fluorophenil)tetracyanoporphyrazine (2) was used as a fluorescent component.

Water-soluble polymers (polymer brushes (3), oligosiloxane (4) and polyethylene glycol (M = 6000) were used as solubilizers forming a conjugates of a water-insoluble gadolinium complex with porphyrazine. The effect of the solubilizing agent on the gadolinium relaxation properties was investigated.

The prepared conjugates are found to be potentially good T\textsubscript{2} contrast agents. Their transverse relaxivity r\textsubscript{2} significantly higher than the longitudinal relaxivity r\textsubscript{1}, and significantly higher than these values for the standard contrast agents which are widely used in clinical diagnostics (Magnevist and Primovist). This work was supported by RFBR (project № 15-02-05468-a).
GAS TRANSPORT PROPERTIES OF HEXAFLUOROPROPYLENE AND TETRAFLUOROETHYLENE COPOLYMERS

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Perfluorinated polymers form unique class of polymeric materials due to combination of various properties (low surface and cohesive energies, high chemical resistance, low electrical conductivity, high refraction index, etc.). A few of them can be successfully applied in gas separation because many perfluorinated polymers are semicrystalline and, hence, have low gas permeability. In this work, synthesis of new perfluorinated copolymers and investigation of their physicochemical and transport properties are considered.

The copolymers (copoly-HFP-TFEs) of hexafluoropropylene (HFP) and tetrafluoroethylene (TFE) with intrinsic viscosity $[\eta] = 0.62$ and 1.099, respectively, were synthesized by radical polymerization of HFP and TFE at 280°C and 12 kbar with partial ratio of the comonomers 5:3 and 3:1. However, actual ratios of the comonomers in bulk polymers according to $^{19}$F NMR were equal to 0.92:0.08 and 0.95:0.05 respectively. The copolymers are amorphous, soluble in common perfluorinated solvents (perfluorodimethylcyclohexane, perfluorotoluene, perfluorobenzene) and have sufficient film-forming properties. According to DSC analysis, copoly-HFP-TFEs have glass transitions at 150-160°C. The densities of the copolymers determined by hydrostatic method are as high as 2.02 and 2.01 g/cm$^3$.

Permeability ($P$) and diffusion ($D$) coefficients of He, H$_2$, O$_2$, N$_2$, CO$_2$, CH$_4$ were measured by Daynes-Barrer method on Baratron barometric setup in the temperature range of 20-50°C. The upper stream pressure varied in the range of 1-3 atm, the downstream pressure was up to 12 Torr. Each polymer film was prepared by casting its 2 w/w% solution in perfluorotoluene on a cellulose support and subsequent removal after evaporation of the solvent. Then, the films were annealed according to the following protocol (heating (5°C/min) up to 110°C, keeping for 3 h at this temperature, 130°C (3 h), 140°C (1.5 h), 160°C (1 h), 170°C (2 h) and subsequent cooling to the ambient temperature). Gas transport properties were determined for as cast and annealed samples of the copolymers.

Annealing procedure results in a compactization of the samples so that the permeability coefficients of light gases (He, H$_2$) lower slightly while the permeability and diffusion coefficients of larger penetrants are reduced significantly by a factor of 3-10 for different gases. On Robeson diagrams (ideal separation factor vs. permeability of more permeable gas) for He/CH$_4$, CO$_2$/CH$_4$, H$_2$/CH$_4$, N$_2$/CH$_4$ the data for copoly-HFP-TFEs lie on common lines formed by other perfluorinated polymers, locating in the middle position near Hyflon AD60 and polyhexafluoropropylene PHFP. Diffusion coefficients of gases in copoly-HFP-TFEs are lower than those in AF1600 by a factor of 1-1.6 but are comparable and slightly higher than diffusion coefficients of gases in Hyflon AD60, PHFP and Cytop. The same is true for solubility coefficients of gases calculated as $P/D$ ratio. Thus, new perfluorinated copolymers of HFP and TFE were synthesized by radical polymerization at high pressure and temperature. The copolymers were shown to have moderate level of gas sorption, diffusivity and permeability among other perfluorinated polymers available, but at the same time they have quite favorable combination of permeation and ideal separation factors for gas pairs containing hydrocarbons.
THE METHOD OF HYDROGEN FLUORIDE OBTAINING FROM AN AQUEOUS SOLUTION OF HEXAFLUOROSILICIC ACID

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Almost all industrial fluorine compounds are produced using anhydrous hydrogen fluoride (AHF) or fluorine, produced from AHF.

An industrial production of AHF is based on the sulfuric acid decomposition of high-quality natural calcium difluoride CaF\textsubscript{2} (fluorspar). Required grade fluorspar reserves are exhausted in Russia, so fluorspar have to be imported. Therefore, the development of methods for AHF obtaining from other fluorine-containing materials, including man-made, is an urgent task.

Considerable amount of aqueous solution of hexafluorosilicic acid (HFSA) is formed at production of phosphate fertilizers using fluoroapatite containing silicon dioxide. Currently, the HFSA is neutralized and solid fluorides are placed on sludge fields.

The amount of fluorine circulating in the fluoroapatite processing is about several million tons per year. Therefore, aqueous solutions of HFSA are useful to consider as a fluorine-containing raw material in the development of new technologies for production of AHF.

The authors of this report have developed a scientific basis of a two-stage method of AHF obtaining with aqueous solutions of HFSA using as a raw material. In the first stage, the interaction of aqueous solution of HFSA with ammonia or ammonia water gives ammonium polyfluoride (APF) NH\textsubscript{4}F·nHF. In the second stage, PFA is gasified with the formation of gas-phase ammonia and hydrogen fluoride. This mixture is fed for the catalytic decomposition of ammonia on the elements.

The catalyst should not change its properties in the presence of hydrogen fluoride in the second stage of the process. The GIPH-55\textsuperscript{1} catalyst consisting generally of fluorides of chrome and magnesium conforms to this requirement. Experimental research shows that the measured rate of dissociation of ammonia is about 0.1 mole\textsubscript{NH\textsubscript{3}}·c\textsuperscript{-1}·m\textsuperscript{-3} in temperature range of 450–550°C with a pressure of 0.1 MPa.

Thus, the proposed method can be considered as a basis for the development of industrial technology of AHF obtaining with HFSA using as a raw material.

\textsuperscript{1}E. Z. Golosman. Domestic developers and manufacturers of catalysts. Chemistry in Russia. 2001, N 2.
Perfluoroorganic compounds (PFOC) are promising as components of aqueous emulsions artificial hemococonaler, currently used in medical practice. When choosing PFOC as blood substitutes, the determining factor, along with the vapor pressure, is the stability of emulsions. Analysis of the stability of fine emulsions of PFOC in aquatic environment was conducted using data on the intermolecular interactions (IMI) at the interface. A quantitative measure of the IMI in the liquid can serve as the density of cohesion energy, \( C_i = \Delta_i E / V_m \) (\( \Delta_i E \) - cohesive energy, \( V_m \) - molar volume). At temperatures significantly below the critical, the cohesive energy is calculated by the formula based on the enthalpy of vaporization, \( \Delta_vapH \), at a temperature \( T \)

\[
\Delta_i E = \Delta_vapH - RT
\]

where \( R \) - universal gas constant.

The following table shows the values of the density of cohesion energy, \( C \), calculated for PFOC based on certain values enthalpy of vaporization measured calorimetrically in this work for six PFOC, namely perfluorodecaline (PFD), perfluoroindane (PFI), perfluoro-N-(4-methylcyclohexyl) piperidine (PMCP), perfluorothreebutylamine (BAF-3), perfluorodibutyl ether (\( \text{C}_4\text{F}_9\text{O} \)) and perfluorodiamyl ether (\( \text{C}_5\text{F}_{11}\text{O} \)). Errors \( \Delta_vapH \) measurement is \( \leq 0.5 \% \). For comparison, the value of \( C \) is also calculated for decaline - hydrocarbon analog of perfluorodecaline (PFD). Density of the liquid required for the calculation of \( C \), defined in this study with an accuracy of \( \leq 1 \cdot 10^{-4} \) g / cm\(^3\).

**Table.** Vaporization enthalpies, densities of cohesion energy and molar volume of PFOC

<table>
<thead>
<tr>
<th>Compound</th>
<th>PFD</th>
<th>PFI</th>
<th>PMCP</th>
<th>BAF-3</th>
<th>(( \text{C}_4\text{F}_9\text{O} ))</th>
<th>(( \text{C}<em>5\text{F}</em>{11}\text{O} ))</th>
<th>Decaline</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta_vapH ), kJ/mol</td>
<td>45.8±0.1</td>
<td>42.05±0.1</td>
<td>61.8±0.9</td>
<td>60.3±0.1</td>
<td>40.7±0.1</td>
<td>49.53±0.1</td>
<td>53.5</td>
</tr>
<tr>
<td>( C \cdot 10^{-4} ), kJ/m(^3)</td>
<td>18.0</td>
<td>18.1</td>
<td>19.2</td>
<td>16.2</td>
<td>14.3</td>
<td>15.1</td>
<td>32.9</td>
</tr>
<tr>
<td>( V \cdot 10^{-4} ), m(^3)/mol</td>
<td>2.40</td>
<td>2.19</td>
<td>3.30</td>
<td>3.58</td>
<td>2.67</td>
<td>3.12</td>
<td>1.55</td>
</tr>
</tbody>
</table>

As can be seen from the table, examined PFOC have a number of distinctive features compared to their hydrocarbon counterparts: high values of molar volume and low enthalpy of vaporization, and the density of cohesion energy, due to the peculiarities of the intermolecular interactions in the liquid.

Among the studied compounds PFD and PMCP have the highest values of the density of cohesion energy, \( C \). The obtained values of the density of cohesive energy PFOC are in a good agreement with the experimental literature data on reduction dispersity of their emulsions from Ref\(^1\), a namely the stability of PFOC emulsions is proportional to the increase of the density of cohesion energy, \( C \).

\(^1\) Kabalnov A.S. et al. Colloid. J. 1986, 8(1, 2), 27-32, 393-394.
THERMODYNAMIC INVESTIGATION OF PERFLUOROCARBONS – PERSPECTIVE ARTIFICIAL BLOOD

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Perfluoroorganic compounds (PFOC) are chemically inert that find ever increasing applications in biology and medicine as perfluorocarbon blood substitute emulsions and perfusion environment. The thermodynamic data of PFOC are scarce.

The standard vaporization enthalpies, $\Delta_{vap}H$, of seven perfluorocarbons, namely cis- and trans- perfluordecaline (PFD), perfluoro-N-(4-methylcyclohexyl) piperidine (PMCP), perfluorothrebutylamine (BAF-3), perfluorothreepropylamine (PAF-3), perfluoroocetyl bromide (PF-octylBr) и perfluorodibutyl ether $(C_4F_9)_2O$ were determined using Wadso and Calvet calorimeters. Using Sventoslavsky ebulliometer, temperature dependences of vapor pressure, $p_s$, for these eight perfluoroorganic compounds were determined. The densities of their liquids were determined by picnometrically.

The new method of calculation of oxygen capacity of liquid PFOC, $\varphi_{O_2}$, based on the definition of the enthalpies of vaporization, $\Delta_{vap}H$, the vapor pressures, $p_s$, and densities in dependence on the temperature is proposed.

In Table given vaporization enthalpy, $\Delta_{vap}H^0$, vapor pressure, $p_s$, calculated oxygen capacity, $\varphi_{O_2}(1)$ and experimental oxygen capacity, $\varphi_{O_2}(2)$ for seven studied perfluoroorganic compounds.

Table. Vaporization enthalpies, vapor pressures and oxygen capacities of PFOC

<table>
<thead>
<tr>
<th>Compound</th>
<th>PFD - cis</th>
<th>PFD - trans</th>
<th>PMCP</th>
<th>BAF-3</th>
<th>PAF-3</th>
<th>PF-octylBr</th>
<th>$(C_4F_9)_2O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_{vap}H^0$, kJ/mol</td>
<td>45.5±0.5</td>
<td>44.8±0.5</td>
<td>56.6±0.2</td>
<td>58.9±0.8</td>
<td>46.9</td>
<td>47.7±0.3</td>
<td>39.3±0.4</td>
</tr>
<tr>
<td>$p_s$, Pa, at 37°C</td>
<td>15.6</td>
<td>17.3</td>
<td>0.81</td>
<td>1.71</td>
<td>14.7</td>
<td>13.8</td>
<td>82.2</td>
</tr>
<tr>
<td>$\varphi_{O_2}(1)$, cm³/100ml</td>
<td>40.3</td>
<td>41.1</td>
<td>40.0</td>
<td>41.9</td>
<td>47.4</td>
<td>46.6</td>
<td>51.2</td>
</tr>
<tr>
<td>$\varphi_{O_2}(2)$, cm³/100ml</td>
<td>40.3¹</td>
<td>42 ¹</td>
<td>-</td>
<td>40¹</td>
<td>46.5¹</td>
<td>-</td>
<td>51¹</td>
</tr>
</tbody>
</table>

The obtained values of oxygen capacity, $\varphi_{O_2}(1)$, of PFOC are in a good agreement with the experimental literature data, $\varphi_{O_2}(2)$, from Ref.¹ Among the studied compounds PAF-3 and $(C_4F_9)_2O$ have the highest values of oxygen capacity.

ELECTROMETRIC WAY OF DETERMINATION OF MICROCONCENTRATION OF FLUORIDE IONS

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The safety and durability of the NPP technological equipment depends on the content of $F^-$ ions in water nuclear power plant coolant. The concentration of these ions in process waters should not exceed $6.4 \text{ mkg/dm}^3$. When determining their needs express, non-destructive testing method. To solve this problem potentiometric method selected. As the ion-selective electrode is used commercially available fluoride selective electrode ISE-F-01. To ensure its operation in the range microconcentrations investigated various background electrolyte additives - hydrochloric, sulfuric, nitric acids and formic and acetic acids and salts thereof.

To ensure satisfactory metrological characteristics ISE-F-01 at concentrations ranging from $10^{-7}$ to $10^{-4}$ M $F^-$ ions in waters glubokoobessolennyyh water treatment plants (WTP) as a supporting electrolyte is necessary to use acetic acid at a concentration of 0.001 to 0.1 M. this provides a pH $= 3.5 \pm 0.5$ units, which is in the optimal range in terms of the state of the supporting electrolyte and the concentration of fluoride ions.

The influence of various interfering ions on the basic metrological characteristics fluoride selective electrode ISE-F-01. Established maximum allowable concentrations of interfering ions that cause no interfering effect on the stability and reproducibility of the measurement electrode readings. In the study of $Fe^{3+}$ cations effect the metrological characteristics ISE-F-01 show that the concentration of iron cations is equal to $70 \text{ mkg/dm}^3$, significantly affects the function of a fluoride electrode.

It is found that with increasing deviation of acidity in this range decreases pH: from 88 to 30%. Therefore, to determine microconcentrations $F^-$ ions is preferable to use an acidic environment of pH $= 2.2$.

In the study of the effect of acidity on the metrological characteristics of the electrode it is shown that an increase in pH (from 2.2 to 7.5 units.) ISE-F-01 loses its sensitivity, which is associated with poisoning the surface membrane of lanthanum hydroxide. Best metrological characteristics electrode microconcentrations range obtained when used as a supporting electrolyte - 0.1 M HCl. The comparative measurement method was introduced, and the results show that the proposed method makes it possible to ensure the reliability of the measurements.

The developed method makes it possible to create on its basis a continuous automatic installation to determine microconcentrations $F^-$ ions in dynamic conditions (in a continuously flowing solution).

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SYNTHESIS AND LUMINESCENCE PROPERTIES OF YTTERBIUM- AND ERBIUM-DOPED CALCIAL FLUORIDE MATERIALS FOR BIOMEDICAL IMPLEMENTATION

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Inorganic fluorides are used in many different areas of modern technology including the relatively novel area of photodynamic cancer diagnostics and therapy. One of the limiting factors for their application in this field is the fact that the excitation frequencies of the biologically active substances used in the aforementioned diagnostics and therapy belong to the spectrum interval, where human tissues are not sufficiently transparent, so medical procedures cannot be carried out at the depth exceeding a few millimeters. Up-conversion luminophores can be a solution for this problem, for they allow convert near-infrared pumping radiation, where tissues of living organisms are transparent, to the radiation in the visible part of the spectrum, where biologically active substance absorb irradiation. At the present moment, such luminophores as Yb$^{3+}$:Er$^{3+}$-co-doped fluorides are considered to be the most prospective materials for photodynamic cancer diagnostics and therapy. However, use of these materials is limited by their relatively low quantum yields. Therefore, the target of our present study was synthesis and investigation of physical and chemical properties of ytterbium- and erbium-doped calcium fluoride as well as determination of the optimal ratio for the aforementioned dopants. We used co-precipitation from aqueous solutions method to synthesize our specimens, and we utilized ammonium fluoride and HF as fluorinating agents in our syntheses. The most efficient technique for the preparation of fluorite-type solid solution precipitates included simultaneous dropwise addition of the aforementioned fluorinating agent solution and corresponding aqueous metal nitrates in the reactor initially filled up with double-distilled water. This method allowed us to synthesize samples with up-conversion luminescence energy yield of 3.11 % (HF was used as a fluorinating agent; Fig. 1).

This work was partially supported by RFBR 15-32-21152-mol-a-ved grant.
SYNTHESIS OF SrF₂:Yb:Er AND SrF₂:Yb:Tm LUMINOPHORES

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Interest in inorganic fluoride-based up-conversion luminophores significantly grew up over last several years due to the broad area of implementation of these materials as well as fluoride matrix advantages over the other compounds. Rare earth-doped alkali and alkaline earth fluorides are the most prospective materials among aforementioned inorganic luminophores, for they exhibit relatively high efficiency, possess short phonon spectra and have capability to form solid solutions with rare earth activators with broad concentration intervals. Varying the rare earth dopants result in luminophores of different colors, and there were many papers about making white light by combining Yb³⁺/Er³⁺/Tm³⁺ ions in the luminophore via their simultaneous introduction in the matrix. However, energy yield of such white-light up-conversion luminescence is very low (about 1%) due to the complexity of selecting the optimal material composition and non-linear correlation between luminescence intensity and pumping power; and such low energy yield limits application of said luminophores because of their price. Also, in contrast with NaYF₄, rare earth doped SrF₂ has been studied quite insufficiently.

Therefore, the purpose of our study was synthesis of Sr₁₋ₓ₋ᵧYbₓErᵧF₂₊ₓ₊ᵧ and Sr₁₋ₓ₋ᵧYbₓTmᵧF₂₊ₓ₊ᵧ powders, preparation of SrF₂:Yb:Er and SrF₂:Yb:Tm mixtures, and investigation of the physical and chemical properties of these specimens, including their luminescence.

In our study, we used co-precipitation from aqueous solution technique: we added dropwise 0.08 M aqueous strontium and rare earth nitrates to 7% excess of 0.16 aqueous NH₄F in order to obtain Sr₁₋ₓ₋ᵧYbₓErᵧF₂₊ₓ₊ᵧ and Sr₁₋ₓ₋ᵧYbₓTmᵧF₂₊ₓ₊ᵧ samples with various content of the rare earth dopants.

X-Ray diffraction characterization of Sr₁₋ₓ₋ᵧYbₓErᵧF₂₊ₓ₊ᵧ and Sr₁₋ₓ₋ᵧYbₓTmᵧF₂₊ₓ₊ᵧ precipitates indicated that all specimens contained only one fluorite-type phase with face-centered crystal lattice (obtained X-ray diffraction patterns were also used for calculation of unit cell parameters and sizes of coherent scattering domains). Particle size before and after thermal treatment has been determined by scanning electron microscopy (SEM). Luminescence spectra of Sr₁₋ₓ₋ᵧYbₓErᵧF₂₊ₓ₊ᵧ and Sr₁₋ₓ₋ᵧYbₓTmᵧF₂₊ₓ₊ᵧ samples and their mixtures were recorded with the use of 974 nm laser pumping, and these spectra were also used for determination of chromaticity coordinates in the corresponding chromaticity diagrams. As a result of our study, we were able to develop the synthesis protocol for preparation of SrF₂-based energy-efficient and thermally stable up-conversion luminophores as well as adjust luminescence color pattern for these specimens by varying their component ratios.

This work was partially supported by RFBR 16-32-00654-mol-a and RFBR 15-32-21152-mol-a-ved grants.
SYNTHESIS OF Sr$_{1-x}$R$_x$F$_{2+x}$ (R = Er, Yb) NANOPOWDERS WITH FLUORITE STRUCTURE FROM CITRATE SOLUTIONS

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Synthesis of rare earth-doped alkaline earth metal nanofluorides, that possess unique luminescent spectrum properties, is one of the most important areas in the modern materials science for photonics. Surfactant organic molecules, being added to the reaction mixture, control nanoparticle growth and prevent their agglomeration by stabilizing the surfaces of the aforementioned nanoparticles. One of such organic surfactants is citric acid (H$_3$Cit). It has been widely used to modify surfaces of nanofluorides when the latter were precipitated from aqueous nitrate and/or chloride solutions. However, there has been no data in the literature regarding the use of rare earth and alkaline earth citrates as precursors in precipitation from water solution technique.

We have studied the influence of various conditions on the particle shape, size and agglomeration of fluorite-type Sr$_{1-x}$R$_x$F$_{2+x}$ (R = Er, Yb) nanopowders, when the latter were co-precipitated from citrate solutions. We have found that R:Cit and Sr:Cit initial component ratios, pH values, starting citrate solution concentrations, type of fluorinating agent (HF or NH$_4$F solutions), and order of reagent addition affect the aforementioned particle size and morphology as well as phase composition of the precipitates.

Sr$_{1-x}$R$_x$F$_{2+x}$ (R = Er, Yb) nanopowders synthesis is a complicated procedure because Er, Yb and Sr ions form various composition complexes in aqueous citric acid. Er and Yb complexes are more stable than Sr complexes, but stability of said complexes depends on pH value and anion concentration. Formation of citrate complexes leads to precipitation of two-phase specimens (SrF$_2$ and amorphous Er or Yb citrate complex; the latter forms R$_2$O$_3$ under thermal decomposition) under the certain conditions. Nevertheless, we were able to determine conditions for the preparation of the single phase fluorite-type Sr$_{1-x}$R$_x$F$_{2+x}$ nanoparticles (ca. 5 nm diameter; Fig. 1).

All synthesized samples were characterized by X-ray diffraction, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM).

Fig. 1. Sr$_{0.935}$Yb$_{0.065}$Er$_{0.015}$F$_{2.065}$ TEM image.
POLYFLUORINATED β-DIIMINATES OF PALLADIUM, SYNTHESIS AND CRYSTAL STRUCTURE.

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The chelating ability of polyfluorinated β-diimine, which methods for synthesis were developed in the laboratory of organofluorine compounds of INEOS RAS, has been studied. Several types of palladium diiminate complexes have been prepared.

The composition and structure of all prepared compounds have been confirmed by NMR spectroscopy, mass spectrometry and X-ray analysis.

The conditions for preparing each type of complexes, their interconversion and spectral characteristics are discussed.
FLUORINE-CONTAINING ORGANIC SOLVENTS
IN A TITANIUM-TANTALUM NIOBATE TECHNOLOGY

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The performance of fluorine-containing organic solvents in extraction of niobium and tantalum from titanium-tantalum niobate mineral raw materials, such as loparite, perovskite, plumbomicrolite, and pyrochlore, which decomposition occurs at high temperatures (t >100°C), during more than 10 h, at high material flows, and reagent and power consumptions, is discussed. At the same time, decomposing in a heterogeneous “solid-organic solvent” system, where the aqueous reaction medium is substituted for an organic reagent (the solvometallurgy method), takes lower temperatures and allows not to dissolve the initial mineral product totally, but to selectively transfer the target component to the organic phase. In this work, the non-aqueous solvent was a high-molecular monoatomic aliphatic alcohol, 1-octanol, containing hydrofluoric acid, which plays the part of a both decomposing and complexing reagent affording to isolate, already at the decomposition stage, the niobium and tantalum fluorocomplexes from insoluble fluorides, including those of the uranium and thorium series, incorporated into the minerals’ structure. The sequence of operations in the titanium-tantalum niobate process, involving a nonaqueous fluorine-containing solvent based on hydrofluoric extracts of aliphatic alcohols, can be represented in the following way: 1 – production of a nonaqueous solvent by saturating the n-octanol, or another monoatomic alcohol, or a mixture including steric isomers ROH (R=C₆-C₈) with hydrofluoric acid to obtain an extract containing 130-150 g/L HF; 2 – a solvometallurgy process, i.e. interaction between titanium-tantalum niobate and a hydrofluoric extract at 20±2°C during 0.5-1.0 h, yielding a collective niobium and tantalum extract and an insoluble fluoride cake, at a total isolation of uranium and thorium radionuclides; 3 – producing from the extract of either a niobium and tantalum mix or individual oxides of rare refractory metals containing 96-99% niobium and tantalum; 4 – sulphatization of the insoluble fluoride cake followed by aqueous extraction of radionuclides from the sulphatic mass. The obtained target products represented niobium and tantalum pentoxides containing impurity elements at a level of <2⋅10⁻⁴ - 5⋅10⁻² wt.% and a collective oxide concentrate containing >99% of the Nb and Ta sum, which can be applied as precursors in manufacture of niobium and tantalum fluoride salts further processed for metal powders.
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PRODUCING METALLIC TITANIUM FROM FLUORIDE-CHLORIDE MELTS

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Currently an increasing scientific and industrial interest is the search for alternative method of production of metallic titanium, to replace the expensive Kroll process, which was developed in 1946. The main objective in the development of alternative process – reducing the number of stages or by complete replacement or by combining separate operations. Such alternative projects as Ginatta-process and FFC-process are most known. Ginatta process based on the reduction of TiCl₄ in molten NaCl. This project was built a pilot plant with a capacity of about 7 tons/year. The temperature of melting salts is 950°C, current intensity 50 kA, the resulting precipitates contained 0.059% oxygen and 0.0566% chlorine. After a few years, the project was stopped because of the impossibility of solving engineering problems. The main problem was to create a membrane to prevent back oxidation of titanium. Other famous project FFC-process, is developed in 2000 at faculty of materials science of the Cambridge university. The TiO₂-cathode are placed at CaCl₂ salt fusion. Electric current is passed through fusion of salts. By the electrolysis the formation of the active metal ions of calcium, which, in turn, chemically restores dioxide. To obtain 1 kg of titanium is consumed 20 kWh of energy, the temperature of the process 950°C. The price of Ti-powder depends on a method of synthesis and on the cost of initial reagents. Therefore the majority of the developed projects are connected with processing of dioxide of the titanium as most available chemical. We are developing a process based on the electrolytic production of titanium metal powder from molten salts KF-KCl-K₂TiF₆-TiO₂. For commercial production of the metal composition of the electrolytic bath must contain at least 2-4% of the recovered TiO₂. For the purpose of increasing the solubility of titanium dioxide in an equimolar mixture of KCl-KF introduces K₂TiF₆. It is established that at the mix concentration of 15-20% K₂TiF₆ solubility of TiO₂ is 2-8% in the range of temperatures 650-750°C. The synthesized cathodic deposit contains the titanium powder and salt fusion in which electrolysis process carried out. The number of the allocated titanium depends on many factors. The main factor is cathodic density-direct current. This factor influences not only an exit on current, but also the size of particles. A study was conducted on the influence of the current density in the range of 0.2-2.0 A/cm² on the morphology of the precipitate. Granulometric analysis showed that the size of the obtained particle powder is in the range 200 µm-10 µm. If current density is increased, then the quantity of large particles increases. Process of electrolysis was carried out in the argon atmosphere. The anode was produced from graphite.

MICROSTRUCTURAL ANALYSIS MnS – YF₃ SYSTEM

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Literature data on the character of phase equilibria in MnS – YF₃ system. Earlier, data were obtained on the nature of the interaction at subsolidus temperatures MnS – LnF₃ (Ln = La, Ce, Gd¹, Er²) systems. Yttrium is in subgroup IIIB and shows affinity properties with rare earth elements. According to the ionic radius of yttrium is located between dysprosium and holmium. At system MnS – YF₃ were synthesized samples containing 90, 66.6(6), 50, 33.3(3), 20, 10 mol. % YF₃. According to data X-ray diffraction in samples are present two phases – MnS and YF₃. The phase separation of alloy occurs in all samples (Fig. 2c). Full of of alloy into 2 component does not occur, which is confirmed by microstructural analysis (MSA). The microstructure of samples of different composition in the part the rich MnS is identical (Fig. 1a, 2a). The main part is occupied by large crystals of light-colored MnS, intergrain area clearly visible. The grain of phase YF₃ dark color are located in two variants: the crystals dispersed all over the surface of sample and the crystal of intergrain in the area between the grains of MnS. At the part of the rich YF₃ (Fig. 1 b, 2 b) in some places there is a dendrites structure of MnS grains, but most of the sample occupy separate, needle-like crystals of MnS. Physico-chemical characteristics of the components, the presence of phase separation in the system do not imply the formation of homogeneous areas on the basis of MnS and YF₃.

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MnS – MnF₂ SYSTEM

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MnS – MnF₂ system studied by microstructural analysis (MSA). Melting of the samples predetermined composition was performed in the graphite crucible in an inert atmosphere, exposure to high frequency induction.

MSA of the samples system leads to the conclusion about the type of interaction between the eutectic MnS and MnF₂. At MSA of samples containing 3, 6, 10, 15, 20, 25, 33.3 (3) 50 66.6(6), 75, 80 in reflected light is observed only two phases - light crystals MnS and dark MnF₂. In samples containing 3, 6 mol. % MnS from the melt primary crystallize MnF₂ grain. In intergrain area crystallized eutectic. But MnS grains are present in two variations: small and slightly larger. A sample of composition 10 mol. % MnS as close to the eutectic. Near the center of crystallization eutectic grain is a point and expenses (like fireworks) to the edges, becoming slightly more elongated. The following samples the primary crystals are MnS. The characteristic dendritic MnS crystal structure is observed in samples containing 15 to 25 mol. % MnS. At contents MnS more than 50 mol. % skeletal structure is not observed, only scattered grain visible. In the samples of compositions 1: 2, 1: 1, 2: 1 there is a change of the eutectic area compared with other samples. In addition to with classic fine-grain-size eutectic clearly observed rather large grain of dark color (MnF₂). In the sample composition of 75 mol. % MnS eutectic mixture of fine-grain-size (type of "fingerprint") is presented and present the primary grain MnS.

![Image of microstructure](image.png)

Fig. 1. Photo of the microstructure of sample MnS – MnF₂ system, crystallized from the melt

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RESEARCH OF COMPLEX FORMATION OF FLUORIDE ZIRCONIUM IN AMMONIUM FLUORIDE SOLUTION

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Compound of fluoride zirconium is a breakdown product of ammonium heptafluorozirconate \( (\text{NH}_4)_3\text{ZrF}_7 \), at a temperature from 380°C to 410°C, in zirconium dioxide fluoride technologies.\(^1\)

Method of complex formation of fluoride zirconium in ammonium fluoride solution is being of practical interest.

Series of experiments in interaction dependence of degree fluorination from time and working temperature have been conducted for determination of optimum conditions process off fluoroammonium complex formation in ammonium fluoride solution is being of practical interest.

In this experiment was used a product with content: \( (\text{NH}_4)_3\text{ZrF}_7 - 96.05 \% \), \( (\text{NH}_4)_2\text{SiF}_6 - 0.53 \% \), \( (\text{NH}_4)_2\text{TiF}_6 - 0.3 \% \), \( \text{AlF}_3 - 1.78 \% \), \( \text{FeF}_3 - 1.54 \% \).

Quantity of ammonium fluoride was took according to stoichiometry which needs for complex formation of fluoride zirconium:

\[
\text{ZrF}_4 + 3\text{NH}_4\text{F} = (\text{NH}_4)_3\text{ZrF}_7
\]

Obtained product filtered, mother liquid – ammonium fluoride solution, fixed residue – soluble fluoroammonium zirconium complex dissolved in the water overloading in order to separate soluble compound from fluoride zirconium residue.

Degree fluorination defined with the help of insoluble residue.

Transformation \( \text{ZrF}_4 \) in solution occurred on 70 % within 5 minutes even at room temperatures (20°C), which is evidence of high response speed reaction of formation fluoroammonium zirconium complex.

Fluorination degree linearly increases with increasing of temperature.

The greatest complex formation with high degree of extraction zirconium in solution was under 80 °C within 30 minutes. Degree of extraction zirconium in solution was increased 98 % under 60°C from 40 to 50 minutes.

Obtained results can show operating conditions for processing of complex formation of fluoride zirconium in ammonium fluoride solution: operating temperature is from 60°C to 80°C, process life is not less than 30 minutes.

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THE ACYLATION OF METHYL POLYFLUOROALKYL KETONES

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Halogen anhydrides and anhydrides of polyfluorocarbonic acids, $R_F^eCOHal$ and $(R_F^eCO)_2O$ ($Hal = Cl, F,$ and $R_F^e = XCF(CF_2)_n$ in case of $X = H, Cl, F$ and $n = 0-7$) have been found to form corresponding fluorinated trialkyl ammonium $\beta$-diketonates by reaction with methyl polyfluoroalkylketones in the presence of two equivalents of tertiary amines.

$$R_F^eCOHal + CH_3COR'_F + 2R_3N \rightarrow + NR_3HHal$$

These reactions were treated by mineral acids, corresponding fluorinated $\beta$-diketones were formed with more than 75% yield.

$$R_F^eC(CH_2CR'_F)HNR_3 + H_2SO_4 \rightarrow R_F^eCCH_2CR'_F + R_3N^+H_2SO_4$$

1,1-Difluoroacetone, acetone, pinacolone, and acetophenone was not acylated under the same conditions to form corresponding trialkyl ammonium $\beta$-diketonates that was probably due to their reduced CH-acidity in comparison with methyl polyfluoroalkyl ketones. In this case, mainly alternative process occurred, i.e. interaction of tertiary amines with acylating agents that in particular was described in the case of formation of $\beta$-diethylaminovinyl perfluoroalkyl ketones by reaction of perfluoroacetyl chlorides and thiethyl amine$^3$. 

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ABNORMAL ELECTROCHEMICAL BEHAVIOR OF $\omega$-BROMOOXAPERFLUOROCARBOXYLIC ACIDS

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Earlier it was shown that product composition of $\omega$-halogencarboxylic acids Hal$_n$H$_{2n}$CO$_2$H (Hal = F, Cl, Br) anodic oxidation depends on the length of their hydrocarbon chain: the formation of $\alpha,\omega$-dihaloalkanes was observed only for higher homologues ($n = 4 \div 10$ depending on the nature of halogen)$^1$

We have established that in series of $\omega$-bromooxaperfluorocarboxylic acids BrC$_2$F$_4$OCF(CF$_3$)$_2$CO$_2$H ($n = 0\div3$) anodic oxidation of two lower homologues ($n = 0, 1$) is also characterized by abnormal electrochemical behavior. Under the conditions of Kolbe electrosynthesis complex product mixture was formed in which no Kolbe dimers have been detected (GC-MS). At the same time in the case of $1$ ($n = 1$) the intermediate generation of $\omega$-bromoperfluoroalkyl radical was proved by preparation of Kolbe cross-dimer BrC$_2$F$_4$OCF(CF$_3$)$_2$OCF(CF$_3$)$_2$ (50% yield) by the anodic cross-coupling reaction with CF$_3$CO$_2$H. Electrooxidation of higher homologues of acids $1$ ($n = 2, 3$) results in the formation of Kolbe homodimers in 80-85% yields.

Most probably the different electrochemical behavior of acids $1$ is connected with different adsorption energy of electrochemically generated radicals at the anode material that is favoured by donor-acceptor interaction of ethereal oxygen atoms with anode$^2$ and inhibited by steric hindrance imposed by side CF$_3$-groups. In the case of higher homologues of acids $1$ the influence of steric factor becomes dominating that leads to the migration of radicals into the electrolyte bulk and formation of dimerization products.

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CALORIMETRIC INVESTIGATION OF THERMOCHEMICAL PROPERTIES OF HEXAFLUOROPROPYLENE OXIDE OLIGOMERS

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This work continues systematic investigation of thermochemical properties of fluoroorganic compounds, which is carried out at Luginin’s Laboratory of Thermochemistry. It is devoted to determine the enthalpies of formation of dimer and trimer of hexafluoropropylene oxide, which are fluoroanhydrides of perfluoro(2-methyl-3-oxa)hexanoic and perfluoro(2,5-dimethyl-3,6-dioxao)nonanoic acids. The choice of object of research is caused by its application in organic synthesis and need of technological calculations of relevant processes.

There are no literary data on thermochemical properties of hexafluoropropylene oxide oligomers. The enthalpies of formation of perfluoro(2-methyl-3-oxa)hexanoic and perfluoro(2,5-dimethyl-3,6-dioxao)nonanoic acids were determined in thermochemistry laboratory early. Its energies of combustion in oxygen at 298.15 K were measured in calorimeter with a rotating platinized bomb and used to calculated the standard enthalpies of formation of these compounds in liquid state.

The purity of samples of dimer and trimer of hexafluoropropylene oxide is 99.99 and 99.92 mass.% (GLC analysis) correspondently.

The determination of dimer and trimer of hexafluoropropylene oxide enthalpies of formation was produced by solution calorimetry method. The enthalpies of reactions of dimer and trimer of hexafluoropropylene oxide and perfluoro(2-methyl-3-oxa)hexanoic and perfluoro(2,5-dimethyl-3,6-dioxao)nonanoic acids with aqueous solution of NaOH (0.927 M) were measured at 298.15 K in hermetically sealed swinging calorimeter with an isothermal coat. Titanium calorimetric vessel was paraffined to defend it from reactions of system components. Temperature rise in each run was measured by copper resistance thermometer. Thermometric sensitivity of circuit was \(-3 \times 10^{-5} \text{K}\). The energy equivalent of calorimeter was determinated by electric technique.

The enthalpies of formation of dimer and trimer of hexafluoropropylene oxide in liquid state were calculated on basis of experimental data and the reliable literary data on enthalpies of formation of NaF and NaOH solutions. Beside that the contribution from the \([-\text{CF}_2\text{OCF}(_3)\text{-}]\) group in enthalpies of formation of studied compounds was calculated and formula for the estimation of enthalpies of formation non-investigated hexafluoropropylene oxide oligomers was proposed.

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THE ELECTROCHEMICAL ACTIVITY OF PLATINUM AND PALLADIUM ANODES IN THE CONDITIONS OF ELECTROSYNTHESIS OF PERFLOROOKTILBROMIDE

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Electrochemical synthesis of gas transfer substance perfluorooktilbromide PFOB, that based on perfluorononyl acid (FNA) and NaBr has features. Polarization studies of all current-voltage dependences in water acetonitrile solution of NaBr on electrochemically activated platinum or palladium anode an one-electron oxidation of ion Br wave have showed. The current decline after reaching the "critical" value of "zero charge potential" $E_{cr}$ have been observed. It is related to the fact that the mechanism of electrochemical desorption for bromine molisation by this anode potential $E_A$ decline is replaced on the heterogeneous recombination mechanism:

$$
\text{when } E_A < E_{eq}: \text{Br}^- + \text{Br}^* \rightarrow \text{Br}_2 + \varepsilon,
$$

$$
\text{when } E_A > E_{eq}: \text{Br}^* + \text{Br}^* \rightarrow \text{Br}_2.
$$

Coverage of the Br atoms on a palladium surface compared to platinum at more positive anodic potentials (respectively 3.0 V and 2.6 V) is observed. Apparently, the more pronounced the anode material ability to chemosorb the electrically neutral particles (atoms, molecules and their dimers, as well as radicals), the less likely cross-condensation and is more likely the condensation of identical particles. It occurs at the same potential, when the surface concentration of particles the required value reaches.

Critical potential of the Kolbe synthesis beginning $E_{cr}$, share an area with a more plausible mechanism of electrochemical desorption on energetically heterogeneous anode surface (area of lower polarization) and the area with a more likely mechanism of direct condensation. The direct condensation of perfluoroalkyl radicals as a result of FNA molecular dimers discharge on energetically smooth homogeneous anode surface occurs.

The problem of PFOB obtaining with significant anode deterioration and instability of the platinum electrochemical characteristics is connected. It is with a weak perfluorinated acids anions chemisorption on platinum and platinum tendency to induce a Kolbe-dimerization associated. Thus, the electrochemical desorption reaction mechanism for based on FNA acidelectrochemical PFOB synthesis can be assumed:

$$
\text{Br}^- \rightarrow \text{Br}_{ads}^+ \varepsilon;
$$

$$
\text{CF}_3(\text{CF}_2)_7\text{COO}^- \overset{\text{Br}_{ad}^+ \text{Br}_{ad}^+}{\text{Br}^*} \rightarrow \text{CF}_3(\text{CF}_2)_7\text{Br} + \text{CO}_2^+ \varepsilon.
$$

The process in a solvent MeCN:HzO = 1:1 on platinum or palladium anode was carried out. In the case of the platinum anode using, especially in the initial (“induction”) period of electrolysis, the product a number of FNA acid Kolbe dimer contains.

The induction period by a prior, before switching on the current, introducing into the electrolyte of PFOB additives can be prevented. This technique depolarizes the anodic process of the FNA anions discharge and as atomic bromine and neutral perfluorinated Kolbe dimer the formation and accumulation in the anode space prevents. In this case the gas transfer superstructures formationsynergistic effect seems to be crucial.

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STUDIES ON THE MECHANISM OF ELECTROCHEMICAL FLUORINATION

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By now the optimization of conditions for electrochemical fluorination followed empirical rules developed during long-term experience. The treatment of the electrochemical fluorination mechanism varied depending on the researcher1.

In order to determine the electrochemical fluorination mechanism we investigated the nickel anode behaviour in various solutions of liquid hydrogen fluoride /4, 5/. The fast galvanostatic pulse method was applied to obtain anode charging curves on nickel in acetic acid, pyridine or water dissolved in hydrogen fluoride, as well as in anhydrous HF. It is shown that fluorine ion discharge is the only electrochemical process that occurs at potential values corresponding to electrochemical fluorination. The slowest step of electrochemical fluorination is the starting materials diffusion to the anode surface and withdrawal of the reaction products from it.

To test this hypothesis we studied experimentally the competing reactions in the process of electrochemical fluorination of a mixture of two substances that differ in structure. In the process of electrochemical fluorination of CH3COF/(C4H9)3N mixture during the study period of electrolysis (142Ach /l) the predominant reaction was that of CH3COF fluorination.

In our experiment on electrochemical fluorination (ECF) of C8H17SO2F/(C3H7)3N mixture at the first step we observed mainly ECF of C8H17SO2F, while that of (C3H7)3N was suppressed. Apparently, the adsorption of C8H17SO2F on the anode surface is stronger than that of (C3H7)3N. For C8H17SO2F the most dramatic reduction of its concentration in electrolyte is observed at the first step of electrolysis, and then it slows down. Obviously, after substitution of one or more hydrogens with fluorines in C8H17SO2F the molecule adsorption capacity changes to become at least comparable with that of (C3H7)3N.

Those results confirm that diffusion of starting materials to the anode surface and withdrawal of the reaction products from it performs as the slowest step of electrochemical fluorination. It means that the electrochemical process rate is determined by diffusion limitations at the anode surface, and active stirring of electrolyte is necessary in the reaction zone, i.e. close to the electrode stack.

Starting from those results we developed universal electrolysers with current load of 2 and 30 kA that allow the production of different classes of fluorochemicals using the same hardware.

SYNTHESIS OF ETHYL ESTER OF PERFLUOROISOBUTYRIC ACID

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According to the published data [1] electrochemical fluorination (ECF) of substances with iso-structured carbonic chain results in the formation of products both with unchanged skeleton and with normal-structured skeleton, i.e. a parallel isomerisation process takes place.

We investigated the preparation of ethyl ester of perfluoroisobutyric acid by the reaction between ethanol and a crude product (mixture of liquid electrolysis products) resulting from ECF of isobutyric acid, or a crude product resulting from ECF of ethyl ester of isobutyric acid.

ECF of isobutyric acid may be presented by equation (1):

\[
\text{iso -C}_3\text{H}_7\text{– COOH} + 10\text{HF} \overset{18\text{e}}{\rightarrow} \text{iso-C}_3\text{F}_7\text{–COF} + 9\text{H}_2 + \text{OF}_2 \quad (1)
\]

ECF of ethyl ester of isobutyric acid may be presented by simplified equation (2):

\[
\text{iso -C}_3\text{H}_7\text{–COOC}_2\text{H}_5 + 8\text{HF} \overset{20\text{e}}{\rightarrow} \text{iso-C}_3\text{F}_7\text{–COF} + 10\text{H}_2 \quad (2)
\]

The synthesis of ethyl ester of perfluoroisobutyric acid by the reaction between ethanol and perfluoroisobutyric-acid fluoride may be represented by equation (3):

\[
\text{iso – C}_3\text{F}_7\text{–COF} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{iso–C}_3\text{F}_7\text{–COOC}_2\text{H}_5 \quad (3)
\]

The analysis of reaction products revealed that further to the target substance (perfluoroisobutyric acid ethyl ester) the electrolysis process, both in the case of isobutyric acid ECF, and in the case of isobutyric acid ethyl ester ECF, results in the formation of ethyl ester of n-perfluorobutyric acid.

The iso-product/n-product ratio 2:1 makes it possible to assume simultaneous occurrence of ECF process according both to the fluorination reaction with retention of the initial carbon chain structure and that with isomerization of the initial carbon chain.

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METHOD FOR PRODUCING
PERFLUORO(3-METHOXYPROPIONYL FLUORIDE)

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We developed a method for the production of perfluoro(3-methoxypropionyl fluoride) (CF$_3$OCF$_2$CF$_2$COF) by electrochemical fluorination of methyl-3-methoxypropionate (CH$_3$OCH$_2$CH$_2$COOCH$_3$) and using triallylamine (CH$_2$=CHCH$_2$)$_3$N for an electrolyte additive.

Perfluoro(3-methoxypropionyl fluoride) is a feedstock in the manufacture of perfluoro(3-methoxypropylvinyl ether) (M-60MP monomer) that improves frost-resistance of its co-polymers, fluororubbers, due to the depression of its glass-transition point.

The addition of (CH$_2$=CHCH$_2$)$_3$N to electrolyte provides more complete separation of CF$_3$OCF$_2$CF$_2$COF the solubility of which in anhydrous HF achieves 15 mass%. Perfluoroperfroalkylamines and perfluorocycloalklamines resulting from triallylamine electrochemical fluorination extract CF$_3$OCF$_2$CF$_2$COF from the electrolyte.

The yield by current of CF$_3$OCF$_2$CF$_2$COF (96% purity) is 51%. The yield of perfluoroamine blend (the triallylamine electrochemical fluorination products that have their own industrial applications) is 22%. Therefore, the total yield of useful products is 73%.

The proposed synthesis provides the solution for the issue of development of a method for the production of perfluoroacylfluorides $R_f$OCF$_2$CF$_2$COF with high yield. Here $R_f$ is a perfluorinated linear or branched aliphatic, mostly alkyl, radical containing 1-20 (preferably, 1-5) carbons.

\begin{itemize}
  \item \textsuperscript{1}V.V. Berenblit \textit{et al.} (Fluorine Notes Journal), 2010, 5 (72).
  \item \textsuperscript{2}Patent USA6482979, published 22.12.1999.
\end{itemize}
FLOW-CIRCULATING METHOD FOR THE PRODUCTION OF 
FLUOROCHEMICALS AND ACTIVATED HYDROGEN FLUORIDE

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The application of recirculating principle in the study and development of chemical technologies is generally known\(^1\). The principle was used in the study and development of efficient technologies for the manufacture of fluorinated products by the method of liquid-phase fluorination by hydrogen fluoride in the presence of catalysts\(^2\) thus providing 100 % conversion and 92-98 % yield of the target product.

The application of the flow-circulating principle in the synthesis of various organofluoric products made it possible to reveal the possibility of the realization of nanodispersion-dissipative state of meta-stable two-phase (vapor-liquid) liquid\(^3\). The equation for the liquid state is as follows:

\[
P_1 = P_{vap}^r - \frac{2\beta\sigma}{r} - \beta \frac{\partial\sigma}{\partial r} - r \frac{\partial P}{\partial r}
\]

To prepare the hydrogen fluoride nuclei it is necessary to know the work consumed in its formation. Taking into account the grand free energy and equation (1) the equation for the work calculation looks as follows:

\[
W = \frac{4}{3} \pi \sigma \epsilon \beta_o r_o \left[ \frac{1}{3} - \frac{28}{27} \frac{1}{k} \frac{1}{r_o} + \frac{42}{27} \left( \frac{\beta}{k} \right)^2 \frac{1}{r_o^2} \right],
\]

here \(\sigma_{\infty}\) is liquid surface tension at binodal; \(\beta_e\) and \(\beta = \nu_v/\left(\nu_v - \nu_l\right)\) – ratio of vapor \((\nu_v)\) and liquid \((\nu_l)\) volumes at binodal and between binodal and spinodal, correspondingly; \(r_o\) – equivalent radius of vapor bubble nucleus; \(1/k = -\partial\sigma/\partial P\).

<table>
<thead>
<tr>
<th>Parameters of nanodispersion-dissipative state of hydrogen fluoride</th>
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</thead>
<tbody>
<tr>
<td>Radius of critical nucleus, nm</td>
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<td>47</td>
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The results evidence that the production of hydrogen fluoride in its active nano-dissipative form requires three times less heat supply than if realized in traditional fluorination processes. The conclusion is confirmed experimentally.
DEVELOPMENT OF THE TECHNOLOGY FOR MANUFACTURE AND DEEP PURIFICATION OF PERFLUOROETHYL ISOPROPYL KETONE

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A technology for the manufacture of perfluoroethyl isopropyl ketone (brand name is “Hladon PFK-49”) is developed and implemented at RSC «Applied Chemistry», the product being an import-substituting analogue of «Novec-1230» (produced by 3M Company, USA).

The technology is based on the interaction between hexafluoropropene and hexafluoropropene oxide. The reaction is catalyzed with active carbon that contains 10-15% of CsF.

The product is intended for fire-fighting applications, and, according to the tests conducted by VNIIPO of EMERCOM of Russia, its performance properties equals or betters the import analogue.

However, for special applications the product must meet the most strict requirements, including those on toxicity. The product toxicity is known to depend on the presence of an impurity that is dimerised hexafluoropropene. Prior to deep purification its content in our product reached 0.5-1.5%. Dimeric hexafluoropropene is a mixture of three perfluoromethyl pentene isomers. Their boiling temperature (48-52°C) is close to that of the target substance, thus making it difficult to separate them by rectification. Furthermore, they are rather inert chemically, and the target substance is even more active in many reactions than the said impurity.

To remove the impurity from the product we applied their fluorination with elemental fluorine. When so doing all perfluoromethyl pentene isomers are quantitatively fluorinated to give perfluorohexanes. Perfluorohexanes are non-toxic similar to any other perfluorinated paraffins, and their boiling temperature is 56-57°C, therefore they are easily separated by rectification. The residual content of dimeric hexafluoropropene in the finish product does not exceed 1*10^-3 %.

It should be underlined that at the process conditions the target ketone virtually does not react with fluorine.

The tests conducted at «NII of Human Hygiene, Occupational Pathology, and Ecology» proved very low toxicity of “Hladon PFK-49”, similar to that of the imported analogue.

The fluorination step is included into the technology of fluoroketone manufacture.
SHIFT OF THE CHEMICAL EQUILIBRIUM BY ACTIVATED HYDROGEN FLUORIDE

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Hydrogen fluoride occupies a prominent place in the synthesis of fluorochemicals. The reactions with hydrogen fluoride participation are catalytical processes. 

In active state hydrogen fluoride can be produced without catalysts. To do this would require its transfer to a meta-stable state of two-phase (liquid-vapour) liquid revealed by us\textsuperscript{1},. The liquid state was named “nanodispersion-dissipative” in view of its main properties\textsuperscript{2}.

Of particulate interest is the determination of the influence of the size-factor on the shift of chemical equilibrium in homogenous processes of hydrogen fluoride interaction.

Using thermodynamic approach to the nanodisperse system description an equation was established that formularizes the dependence of Gibbs potential on the vapour bubble size for any liquid, including hydrogen fluoride:

$$\Delta G |^{r} = \int_{r_0}^{r} \frac{\partial G}{\partial r} dr = 2v_{\text{spin}}x\sigma_\xi \beta \left[ \frac{r-r_0}{r_0} + \frac{\beta(r^2-r_0^2)}{k_0^2 r^2} + \frac{2\beta^2(r_0^3-r^3)}{a^2 r^3} \right]$$

here $v_{\text{spin}}$ – liquid phase volume at spinodal; $x$ – share of nanodisperse phase in the system; $\beta = v_v/(v_v-v_l)$ – ratio of vapour ($v_v$) and liquid ($v_l$) volumes at binodal; $1/k = -\partial \sigma / \partial P$ ; $r_0$ and $r$ – equivalent radius of critical vaporization nucleus ($r_0$), formed at the spinodal and radius ($r$) of vapour bubble between the spinodal and the binodal.

The equation characterizes the increment (change) of hydrogen fluoride Gibbs potential during the chemical interaction in the revealed liquid state starting with the moment of the vaporization nucleus formation. From this equation it follows that the chemical equilibrium constant is determined by the size of the formed hydrogen fluoride vapour nano-bubble, thus making it possible to realize chemical interactions that do not occur at usual state of liquid.

It is confirmed by the results of studies on water oxidation of iron that occurs at 500 °C with usual state of water, and at 80 °C at its revealed state.

The liquid-phase interaction of hexafluoropropylene with hydrogen fluoride occurs only in the presence of a catalyst, e.g. tertiary amine. With hydrogen fluoride converted to the revealed state non-catalytic interaction is realized.
SYNTHESIS OF PERFLUORODIACYL PEROXIDES, KINETICS OF THERMAL DECOMPOSITION, AND THEIR USES FOR INITIATORS IN FLUOROOOLEFINE CO-POLYMERISATION

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Among numerous organic peroxides those fluorinated and perfluorinated are of special importance, because they participate in the synthesis of fluoropolymers known for excellent thermal, chemical, and weather resistance, and for their thermodynamic compatibility with other polymer materials. The said properties combination allows numerous applications of perfluorinated polymers (PFPs), first of all polytetrafluoroethylene, and co-polymers of tetrafluoroethylene, in many fields of science and technology.

We are reporting the results of our study on the nature and properties of perfluorinated peroxides applicable for the initiators in the co-polymerization of tetrafluoroethylene (TFE) with perfluoro(-3,6-dioxa-4-methyl-7-octene)sulfonyl fluoride (FS-141) resulting in the formation of fluoroplast F-4SF:

\[
(m+n)\text{CF}_2=\text{CF}_2 + n\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F} \rightarrow \ [-(\text{CF}_2\text{CF}_2\text{O})_m\text{CFCF}_2\text{F})_n \]

The most of those substances are by-produced in the synthesis of FS-141 monomer, and considered as the co-polymerization initiators in the fluoroplast F-4SF non-waste manufacture process. The peroxides were synthesized following the technique that uses hydrogen peroxide and corresponding anhydride fluorides. We also studied the properties of the prepared peroxides, kinetics of their thermal decomposition, half-life periods, and their yield dependence on temperature, solvents, and rate of stirring. Most of those peroxides explode if heated, and therefore their decomposition is conducted in solvents, so that the reactions are safe and easy.

Perfluorinated peroxides participate in the first-step process of PFPs manufacture, that is initiation and generation of active polymerization centers. Those centers are free radicals formed during the hemolytic decomposition of perfluorinated peroxides under the action of temperature. We report the study of the initiator concentration impact on the kinetics of TFE and FS-141 radical co-polymerization in solvents. The growth of the initiator concentration entails:

- linear growth of the rate of co-polymerization;
- decrease in the molecular mass of the formed copolymer;
- stability of the copolymer composition (equivalent mass).
SYNTHESIS OF PERFLUOROPOLYETHERS ON THE BASIS OF PERFLUORINATED OLEFINS

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Perfluoropolyethers are non-flammable, non-toxic, non-soluble in most of organic solvents, chemically inert and resistant to concentrated acids and oxidizers, their viscous and thermal properties are excellent, solidifying points are low, and radiation stability is good, they work well in highly aggressive environment, stable up to 400°C, and thanks to their unique properties perfluoropolyethers are widely applied in various modern industrial sectors as greases, oils, hydraulic liquids, surfactants, solvents, etc.

As it had been shown in our studies, the method of fluoroolefins oxidation in the presence of chemical initiators is easier machinable as to compare with UV irradiation and does not require special equipment.

At FSUE RSC «Applied Chemistry» a technology is developed for the manufacture of perfluoropolyethers by low-temperature oxidation of hexafluoropropylene with oxygen in the presence of an initiator (elemental fluorine) and a pilot-industrial plant, of capacity 5t/year, is created.

The technological process involves the main steps as follows:
1. low-temperature co-polymerization of hexafluoropropylene with oxygen in the presence of an initiator (elemental fluorine) resulting in the formation of perfluoropolyether peroxides:
   \[ \text{CF}_3\text{O(CF(CF_3)CF_2O)_{n}(CF(CF_3)CF_2OO)_{m}(CF_2O)_{x}(CF_2OO)_{y}CF_2COF} \]
2. heat setting of perfluoropolyether peroxides resulting in the formation of perfluoropolyethers with fluoroanhydride terminal groups
   \[ \text{CF}_3\text{O(CF(CF_3)CF_2O)_{m}(CF_2O)_{x}CF_2COF} \]
3. fluorination of fluoroanhydride (ketone) terminal groups in perfluoropolyethers with elemental fluorine resulting in the formation of stable perfluoropolyethers
   \[ \text{CF}_3\text{O(CF(CF_3)CF_2O)_{m}(CF_2O)_{x}R, \text{ here R is CF}_3 \text{ or C}_2\text{F}_5} \]
4. vacuum distillation of perfluoropolyethers with separation of target fractions shown in Table below.

<table>
<thead>
<tr>
<th>Boiling range °C</th>
<th>Vapour pressure, mm Hg</th>
<th>Viscosity, sst</th>
<th>Mol. mass, a.u.</th>
<th>Solidifying temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>80-130</td>
<td>10⁻³</td>
<td>5-15</td>
<td>1200</td>
<td>&lt; -80</td>
</tr>
<tr>
<td>130-180</td>
<td>10⁻⁵</td>
<td>50-90</td>
<td>1500</td>
<td>~ -70</td>
</tr>
<tr>
<td>180-240</td>
<td>10⁻⁷ - 10⁻⁸</td>
<td>100-150</td>
<td>2500</td>
<td>~ -50</td>
</tr>
<tr>
<td>&gt;240</td>
<td>10⁻¹⁰</td>
<td>400-700</td>
<td>5000</td>
<td>~ -40</td>
</tr>
<tr>
<td>&gt;320</td>
<td>10⁻¹⁴</td>
<td>1000-1800</td>
<td>10 000</td>
<td>~ -30</td>
</tr>
</tbody>
</table>

Perfluoropolyethers on the basis of tetrafluoroethylene are distinguished by even lower solidifying temperatures (-110 °C - -130°C). The method for their manufacture is developed at FSUE RSC «Applied Chemistry», and the product manufacture at a typed experimental plant is planned.
PERSPECTIVES OF THE MONTREAL PROTOCOL AND THE MANUFACTURE OF THE THIRD GENERATION OF NON-OZONE-DEPLETING SUBSTITUENTS

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The most important industrial sectors, first of all the manufacturers of refrigeration equipment, air-conditioners, foams, aerosols (including medical preparations), etc. are the chief consumers of chemicals regulated by the Montreal protocol (MP) on substances that deplete the ozone layer (ODS).

The Montreal protocol is being permanently updated. The main steps of the process are as follows:
- regulation down to the total phaseout in production/consumption of the controlled substances of Annex A, B: chlorofluorocarbons (CFCs), and bromofluorocarbons (halons) – 1987-1996.
- regulation down to the total phaseout in production/consumption of the controlled substances of Annex C: hydrochlorofluorocarbons (HCFCs) – 1996-2020 г.

Currently the Meetings of the MP Parties consider the inclusion of new Amendments to the MP, so that to start the regulation and phaseout in production/consumption of non-ozone-depleting hydrofluorocarbons (HFCs) with high global warming potentials (GWP): HFC 134а, HFC 125, HFC 227ea, etc. Some Parties, first of all EU members, started already HFC and other greenhouse gases phaseout in their economies.

In the Russian Federation the CFC and halons phaseout process entailed changeover of national industrial sector, first of all, to the “1st generation substituents” that were domestically produced HCFCs (HCFC 22, 21, etc.), and, partially, to the “2nd generation substituents” that were imported HFCs. It should be mentioned that HFC manufacture (HFC 125, HFC 152a, HFC 227ea, etc.) had been started in our country on the basis of domestically developed technologies, but then was stopped.

HFC phaseout in industrial sector requires the introduction of the “3rd generation substituents”, those being fluorinated ethers, ketones, and olefins with zero ODPs and very low GWPs.

FSUE RSC “Applied Chemistry” had developed the technologies for the production of all generations of ODS substituents: HCFCs, HFCs, PFCs. Currently we are in the close proximity to the completion of development of the technologies for the manufacture of the “3rd generation substituents”, including fluoropropenes, fluoro ketons, fluorinated ethers, etc.

The absence of domestically made ODS substituents threatens the most important sectors of the national economy with total dependence on imports, and that is why the creation of industrial facilities for the production of the above named chemicals is among the top-priority tasks for the Russian chemical industry.
SYNTHESIS OF FLUOROPOLYMERS WITH FUNCTIONAL GROUPS
FOR PROTON-CONDUCTIVE MEMBRANES

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Proton-conductive polymers find expanding industrial and scientific research applications. The use of proton-conductive membranes improves not only environment safety of the production facility but also its efficiency (power installations, water electrolysis, chlorine and caustic production).

The manufacture of fluorinated co-polymers is a step in the membrane manufacture, and it is a complicated process that requires detailed studies.

There is a number of methods for tetrafluoroethylene co-polymerization with functional fluoromonomers in solvents, in supercritical liquids, and in water-emulsion systems. The latter has the advantage of higher monomer conversion with less complicated apparatus.

We investigated the main regularities of the water-emulsion co-polymerization process:

- the dependence of the co-polymer composition on the process conditions;
- the dependence of the co-polymer composition on the monomer conversion;
- the main kinetic parameters of the co-polymerization process;
- the dependence of the polymer properties on the impurities content in relevant monomers.

Reasoning from the above regularities we assumed the peculiarities of the co-polymerization mechanism.

A mathematical model is offered that describes the above regularities.

A method is developed for the preparation of fluoromonomer water emulsion distinguished for its high stability, and the optimal parameters of the water-emulsion co-polymerization process are determined.
FLUORINATED SURFACTANTS ON THE BASIS OF PERFLUOROPOLYOXACARBONYC AND SULFONIC ACIDS

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Fluorinated surfactants (F- surfactants) exceed significantly hydrocarbon surfactants (usually applied in industry) by their chemical and thermal resistance, and by their surface activity ($\sigma = 15\div20$ mN/m) that expands the technological aspects of their applications, while decreasing their rate of consumption when used.

The methods for the production of carbonic and sulfonic acid fluorides are developed, and those for the production of F- surfactants based on them, and applicable as foaming agents in fire-fighting compositions, additives to electrolytes, oils, varnishes, etc. At the same time efficient non-ionic F- surfactants became available those being promising and rapidly developing class of surfactants, taking into account their high bio-degradability, that is the main criterium of environmental safety.

F- surfactants on the basis of perfluoropolyoxacarbonic acid fluorides $\text{CF}_3\text{O-}\left[\text{CF(CF}_3\text{)}\text{CF}_2\text{O}\right]_m\text{CF(CF}_3\text{)}\text{COF}$ and corresponding sulfonic acid fluorides $\text{C}_2\text{F}_5\text{OCF(CF}_3\text{)}\text{O-CF}_2\text{CF}_2\text{SO}_2\text{F}$ are prepared via the addition of dimethylpropane diamine $\text{NH}_2\text{-}(\text{CH}_2\text{)}_3\text{N(CH}_3\text{)}_2$ followed with the formation of quaternary ammonium bases (cation-active F- surfactants)

$$\text{RFCONH(CH}_2\text{)}_4\text{-N(CH}_3\text{)}_2\text{C}_2\text{H}_4\text{OH}^+\text{Cl}^- \quad \text{here } \text{RF}=\text{CF}_3\text{O[CF(CF}_3\text{)-CF}_2\text{O]}_n\text{-CF(CF}_3\text{)-}$$

and $\text{RFSO}_2\text{NH(CH}_2\text{)}_3\text{N(CH}_3\text{)}_2\text{C}_2\text{H}_4\text{OH}^+\text{Cl}^- \quad \text{here } \text{RF}=\text{C}_2\text{F}_5\text{OCF(CF}_3\text{)O-CF}_2\text{CF}_2\text{-}$

the yield of F- surfactants is 93-95%

The F- surfactants, thus obtained, are vaseline-like substances, $d=1.5-1.56$ g/cm$^3$, $\sigma =16-20$ mN/m, efficient in fire-fighting compositions, in additives to accumulator batteries, etc.

The resistance of sulphamide groups (-SO$_2$N-) to both alkaline and acid hydrolysis exceeds considerably that of carbamide groups (-CON-), making it possible to use F- surfactants derivatives with sulphamide groups in very aggressive environment.

Widely known are epilam compositions based on the derivatives of perfluoropolyoxacarbonic acids applied for oil additives, and for surface modifiers (for anti-friction treatment of surfaces).

The methods for the synthesis of non-ionogenic F- surfactants are investigated, those being oxyethylated fluoroacids, fluorinated alcohols that contain active hydrogen $\text{RFCOO(CH}_2\text{CH}_2\text{O})_n\text{H}$, $\text{RF CH}_2\text{O(CH}_2\text{CH}_2\text{O})_n\text{H}$

Here $\text{RF}=\text{CF}_3\text{O[CF(CF}_3\text{)-CF}_2\text{O]}_n\text{-}$, $m=1-3$, $n=3-10$

and perform as efficient and biodegradable oil additives, and washing reagents.
REACTIONS OF TRIFLUOROACETIC ACID WITH DINITROGEN PENTOXIDE

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It is of common knowledge that, in solutions of strong mineral acids $H^+X^-$ (e.g., $HNO_3$, $H_2SO_4$), $N_2O_5$ transforms to $NO_2^+X^-$ and $HNO_3$ and the latter in turn undergoes further ionization. Therefore the nitronium cation $NO_2^+$ concentration in high excess of acid ($n \geq 8$) is in a linear relationship with the $N_2O_5$ proportion. If $n \approx 2$, molecular $HNO_3$ is still present e.g. in $H_2SO_4$ solution.

$$N_2O_5 + n H^+X^- \rightarrow NO_2^+X^- + HNO_3 \rightarrow 2 NO_2X^- + H_3O^+X^-$$

The interaction of $N_2O_5$ with weaker organic acids has not been actually elucidated. We studied reactions of $N_2O_5$ with AcOH and $CF_3COOH$ (TFA) by Raman spectroscopy. It was shown that $N_2O_5$ in excess AcOH transformed to a stoichiometric mixture of $AcONO_2$ and $HNO_3$. No analytical line of $NO_2^+$ (~1400 cm$^{-1}$) was fixed spectrally, which testifies to its absence, although intensive lines both of individual $AcONO_2$ (~338 cm$^{-1}$) and of its mixture with $HNO_3$ (~1304 cm$^{-1}$) were recorded.

All $N_2O_5$ solutions in TFA ($n = 2–4$), opposite to AcOH, contained $NO_2^+$ whose concentration relative to the anhydride’s covalent form remained actually unchanged, i.e. did not depend on the TFA excess. The solution also included $CF_3COONO_2$ (TFAN) detected from the available lines at ~213, ~890, and ~1280 cm$^{-1}$ that were different from covalent $N_2O_5$ frequencies (~860, ~1240 cm$^{-1}$). This was indicative of the formation of an equilibrium mixture of nitric anhydrides $N_2O_5$—TFAN with $N_2O_5$ predominating.

$14^N$ NMR analyses of $N_2O_5$ in TFA showed that the signal from freshly prepared solution (~62 ppm) at 0.5 h shifted (~66 ppm) to region where $\delta_T$ TFAN (~80 ppm) and $NO_2^+$ (~130 ppm) usually were detected. At that, line broadening from 25 to 40 Hz was observed, which pointed to $N_2O_5$ intermolecular interactions with the reaction products. Hence, the reaction of $N_2O_5$ with TFA is equilibrium, which has been confirmed by quantum chemical calculations performed with Gaussian 09 Revision D.01 DFT B3LYP/6-311++g(d,p). The Gibbs free energy for transforming $N_2O_5$ to TFAN and $HNO_3$ was $-81$ cal/mol and the equilibrium constant $\approx 1.1$.

The reaction of 1 mol trifluoroacetic anhydride (TFAA) with 2 mol $HNO_3$ gave a mixture of $N_2O_5$ with TFA. It means that TFAA-sourced TFAN reacted mostly with $HNO_3$ to yield $N_2O_5$ wherefrom the ionic form was generated in the presence of $HNO_3$.
RADIATION-CHEMICAL SYNTHESIS OF TETRAFLUOROETHYLENE TELOMERES IN ALCOHOLS.

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Radical polymerization of tetrafluoroethylene (TFE) in alcohols initiated by UV radiation, material initiators leads to the formation of fluorinated alcohols with the general formula H(CF₂CF₂)nCR₁R₂OH, where R₁, R₂ - alcohol molecule fragments, n (~ 1-5) - the average length of a chain. Such low molecular weight compounds used for the synthesis of fluorinated surfactants, thermally conductive fluids, and other medicinal substances, etc., but not useful for protective coatings and hydrophobic composites. Radiation-chemical method of initiation (γ-rays) allows to carry out the process of telomerization of TFE in solutions of various telogens and to receive telomeres with a chain length from several units and tens to hundreds of links of TFE. Length of a chain depends not only on synthesis conditions, but considerably, is defined by solvent.

In work as telogen ethanol, trifluoroethanol and their mixes of various structure are used. Radiation telomerization process may be carried out at room temperature and at low temperatures (in the post-effect mode). The method of kinetic calorimetry studied the kinetics of the process. In ethanol there is a formation of telomeres to chain length ~ 1-5 links of TFE. When using trifluoroethanol form viscous colloidal solutions of long telomeres. It is shown that in trifluoroethanol process proceeds in order to more effectively than in ethanol, required dose of several kGy to complete monomer conversion. Molecular structure and properties of the telomeres were studied by IR spectroscopy and TGA analyzes.

Properties and applicability telomers depend not only on the functional end groups, but also on chain length. The low molecular weight telomers of TFE in ethanol can be used for further synthesis, and in trifluoroethanol - for obtaining the fluoropolymer composites. To create the hydrophobic coating materials are needed telomeres with an intermediate length of a chain, which, on the one hand, possess good thermal stability, and on the other side form a continuous coating. For the purpose of receiving such telomeres TFE telomerization in ethanol mixes with trifluoroethanol of various compositions is carried out. It is shown that selection of the composition of telogen (trifluoroethanol + ethanol) can be controlled not only telomerization process parameters (speed, radiation dose, area, etc. of the reaction.), but also properties of the received telomers (chain length, solubility, thermal stability). By reacting a mixture of alcohols of different composition, it was possible to obtain telomeres with a chain length of from several to tens of TFE units, keeping at the same time the spirit terminal OH- groups. This is important from the viewpoint of further practical use of the obtained telomer is as intermediates for synthesis of new substances and to create hydrophobic protective antifriction coatings on various materials and composites.

This work was supported by the Russian Foundation for Basic Research (№ 16-03-00296)
MECHANISM OF CHANGE OF PTFE SURFACE ENERGY BY GAMMA-IRRADIATION

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Low surface energy of PTFE restricts its compatibility with other materials, including development of composite materials. Improvement of adhesive and contact properties of PTFE surface is urgent in the connection with its applications in microelectronics and demands for adhesive joints.

It is known that the action of ionizing radiation increases adhesion of PTFE. Conventional explanation of this increase is based on the formation of polar groups — carbonyl, hydroxyl, peroxide, etc. This approach does not explain the observed experimentally rather weak dependence of water contact angle on the dose above 200 kGy\(^1\). In addition, the absence of quantitative model precludes estimation of possible contribution of polar products to the change in the surface energy of irradiated PTFE.

The aim of this work is to study PTFE adhesion at various conditions of \(\gamma\)-irradiation and to estimate quantitatively contributions of various mechanisms to the change in surface energy. For this purpose we measured contact angles for water and tetradecane, isothermal polarization and depolarization currents for irradiated samples of sintered PTFE (F4), disks molded from irradiated PTFE powder (F4P), PTFE samples preliminary modified above the melting point with 200 kGy dose (F4RM). The samples were irradiated at room temperature in the presence of atmospheric oxygen with doses of 10; 50; 100 kGy.

The work of adhesion increases significantly with irradiation dose. Effect of irradiation on the work of water adhesion is stronger for F4RM as compared with F4 and F4P. For tetradecane the changes in work of adhesion for F4 is close to that for F4RM. Effect of pH of water on the work of adhesion is strong for irradiated F4 and weak for F4RM. Contributions of various components to the work of adhesion were determined. For F4RM contribution of dispersive component to the work of adhesion is much lower (by 5 times) than that of polar component. For F4 these contributions differ by 1.5 times. Dispersive contribution to the work of adhesion is in agreement with values calculated by the Lifshitz theory. To explain the increase in the polar component we consider a mechanism\(^2\) connected to the accumulation of long-lived electron-hole pairs in the irradiated PTFE. Dissociation of ion pairs and charge transfer through phase interface form double electric layer at phase interface, leading to significant decrease in the contact angle.

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WATERPROOFING OF POROUS CERAMIC MATERIALS BY THE METHOD OF SUPERCritical CARBON DIOXIDE

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Porous materials created from the fibers, used for the active and other insulating purposes. The starting materials for them may be different polymers and ceramics, especially oxide. Unlike polymers, their oxides have a high melting temperature - it is equal to 1728\textdegree C SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} - 2050\textdegree C, however porous inorganic materials are useful at temperatures above 1000 \textdegree C, they can also be used for fire-resistant products. The presence of water in the space interfibrillar changes for the worse and thermal performance properties of the material, so the actual task of hydrophobic fibers to protect products against water penetration.

The report describes the use of the method of hydrophobic silica ceramic porous material of silicon oxide brand TZMK-10 using as a repelling agent solution fluorparafina brand PPU-90 in Supercritical CO\textsubscript{2}.

Hydrophobization TZMK sample plates through fluorparaffin powder was performed in an autoclave at a pressure of 20 MPa CO\textsubscript{2} at 70 \textdegree C, provided that the supercritical state of carbon dioxide. Exposure was performed for 3 hours, during which, dissolution occurred fluorparafina molecules in the SC-CO2 and its penetration into the sample. Next, the decompression of the autoclave was made.

The measured values of the contact angle after modification reach 155\textdegree, which corresponds to the superhydrophobic state. It was found that for 5 hours of contact under saturated water vapor at a decreased angle of nine degrees.

The authors thank the Russian Federal Property Fund (grant №16-29-05334) for financial support.
THERMODYNAMIC FEATURES OF THE THERMAL POLYMERIZATION PERFLUOROPROPYLVINYL ETHER AT HIGH PRESSURES

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Perfluoropropyl vinyl ether (PPFPVE) does not form homopolymers by radical polymerization at ordinary pressures, but is able to polymerize at high pressures. PPFPVE the polymerization was conducted at pressures 3-12 kbar (300-1200 MPa) and temperatures of 50-240°C. It was found that the rate of polymerization under pressure increases with increase of temperature up to a certain limit, beyond which the rate of polymerization and yield of polymer tends to fall to zero, i.e. the limiting temperature of polymerization is observed. It was found that the limiting polymerization temperature depends on the pressure. The logarithmic dependence of the limiting temperature of the thermal polymerization on pressure is presented in Fig.1.

![Graph showing the logarithmic dependence of the limiting temperature of the thermal polymerization on pressure.]

\[ \ln T_c = 0.00002 \times P + 5.9837 \]

Extrapolation of the curve of Fig.1 at P=1 bar allows you to estimate limiting the temperature at ordinary pressure: at P=1 bar \( T_c = 124^\circ C \). Data on the limiting temperatures of the polymerization reaction, PPFPVE and measured values of \( \Delta V \) (reaction volume) were used to estimate the enthalpy of the polymerization \( \Delta H \) using equation Clausius-Clapeyron:

\[ \frac{d \ln T_c}{dP} = \frac{\Delta V}{\Delta H} \]

The values of \( \Delta V \) and the calculated values of \( \Delta H \) at different pressures are given in the Table.

<table>
<thead>
<tr>
<th>( T_c ), K</th>
<th>( P ), MPa</th>
<th>( \Delta V ), cm(^3)/mol</th>
<th>( \Delta H ), kcal/mol</th>
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<tbody>
<tr>
<td>452</td>
<td>528,0</td>
<td>-(8,4±1)</td>
<td>-(10,1±1)</td>
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<tr>
<td>473</td>
<td>704,0</td>
<td>-(10,3±1)</td>
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<td>494</td>
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<td>-(14,2±1)</td>
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<tr>
<td>515</td>
<td>1056,0</td>
<td>-(13,3±1)</td>
<td>-(16±1)</td>
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</tbody>
</table>
SYNTHESIS OF 2,2,2-TRICHLORO-1,1-BIS(TRIFLUOROMETHYL)ETHYL ACRYLATE AND RELATIVE POLYMER

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Synthesis of halogenated (fluorine- and chlorine-containing) monomers is one of intensively investigated fields of organic and macromolecular chemistry. Among these compounds, the preparation of fluorinated acrylates is of great value\textsuperscript{1}. As a rule fluoroaliphatic acrylate polyesters have glass transition temperature < 100°C, and therefore these polymers are not considered as materials for manufacture of optical waveguides\textsuperscript{2}. To prepare perspective fluoropolymers for integrated optical devices, a new acrylic monomer derived from perfluoro-2-trichloromethylisopropanol was synthesized\textsuperscript{3}.

\[
\begin{align*}
\text{CF}_3 & \quad \text{CF}_3 \\
\text{O} & \quad \text{CCl}_3\text{CO}_2\text{Na} \\
\text{DMF} & \quad \text{HO} \\
\text{HO} & \quad \text{CCl}_3 \\
\text{CF}_3 & \quad \text{CH}_3=\text{CHC(O)}\text{Cl} \\
\text{N}(\text{C}_2\text{H}_5)_3 & \quad \text{CH}_3\text{CN} \\
\Rightarrow & \quad \text{CF}_3 \\
\Rightarrow & \quad \text{CF}_3 \\
\Rightarrow & \quad \text{CCl}_3
\end{align*}
\]

Poly(perfluoro-2-trichloromethylisopropyl acrylate) \textbf{P2} was prepared by free-radical bulk polymerization of monomer 2, and its physicochemical properties were studied. A number of close analogues of 2 – fluoroaliphatic esters of acrylic, \(\alpha\)-chloroacrylic, and \(\alpha\)-fluoroacrylic acids and their polymers were synthesized. It was shown that \textbf{P2} is superior to its closest analogues in terms of a combination of thermal and optical properties and can be used for manufacturing optical waveguides.

This work was supported by the Russian Foundation for Basic Research (project no.13-03-12265 ofi_m) and the Russian Science Foundation (project no.14-19-01659).

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11th All-Russia Conference “FLUORINE CHEMISTRY» marking the 110th anniversary of Professor Ivan L. Knunyants June 26-30, 2016 r. Moscow Russia

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