Prospects for the Application of New Materials Based on Fluorine-Containing Alcohols in Automobile Construction

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Abstract

A set of problems and directions of the accelerated application of fluorinated materials to solve a number of tasks in automobile industry is considered. The examples of the treatment of mechanical rubber goods with fluorinated reagents coating the surface of rubber parts with protective films that approach the characteristics of fluorinated polymers are shown. Due to these films, the used materials to not swell in petrol vapour, their wear resistance increases, friction coefficient decreases and becomes comparable with that of fluoroplastics, performance characteristics are conserved under irradiation with light. Examples of the use of acrylates modified with fluorine for corrosion-protective coatings on metal units of automobiles are given. New developments of fluorine-containing surface-active substances for use in nickel- and chromium-plating processes of metal parts, providing ecologically safe and pure conditions for the personnel of these works, are considered. The problems connected with the deposition of oil- and water-resistant coatings on glass are discussed. The efficiency of the treatment of cloth materials for car interior furnishing rendering nonflammable properties and making no flame under the action of open fire is demonstrates. New fluorine-containing lubricants for mechanisms are proposed that exceed those in use in performance characteristics. The technology of obtaining a new cleaning agent for the systems of cooling the car engine and carburetor is developed.

INTRODUCTION

Automobile transport occupies stable positions with increasing production capacities and application area. Entering the market automobiles make it an urgent question to improve their quality, decrease performance expenses, increase lifetime and improve ecology. It is impossible to achieve these goals without using new materials and new high-end technologies. At every stage of technological progress, the role and direction of fundamental investigations are to a large extent determined by the public need in new materials possessing advanced consumer characteristics and the ability to operate under much more rigid conditions. In this respect, the role of fluorinated materials that do not occur in nature is especially important. High performance characteristics of fluorinated materials obtained on the basis of organic fluorinated compounds and their advantages in comparison with hydrocarbon materials were demonstrated with many examples [1–3].

The development of new approaches to the creation of industrial technologies of the production of fluorinated materials that are in increased demand in modern industry comprises the main goal for researchers working in the area of the chemistry of fluorinated organic compounds. An important part is played by the raw material basis of key semiproducts containing fluorine and by the industrial facilities already available in Russia. This allows one to reject the processes of subsequent fluorination in many cases because direct fluorination with elemental fluorine and electrochemical fluorination in anhydrous hydrogen fluoride result in the formation of substantial amounts of side products, and expensive purification of the target products is required. On the other hand, new technologies should include a small number of stages, be highly selective and fit in the existing production.

The development of new fluorinated materials for automobile construction which can help improving the quality of automobiles, their ecological safety, performance lifetimes of many mechanisms made not only of synthetic polymers but also of metals comprises the basis of technological advance. Here one cannot do without developing high-end ecologically safe technologies based on the fundamental knowledge about the nature and properties of fluorinated organic compounds [4, 5].

These and other aspects are considered in the present paper. It is very important to supply possible consumers with the information not only about the materials modified with fluorine but also about the directions in which the properties of these unique fluorinated materials can be utilized.

RESULTS AND DISCUSSION

Fluorinated materials can be divided into two groups according to their destination:

1. Fluorinated materials for application as the main material or complete replacement of the existing materials due to higher consumer characteristics, the ability to work under extremal conditions, and improved performance characteristics.

2. Fluorinated materials for use as a minor additive (2–5 %) which modify the characteristics of the major material thus rendering new quality and new characteristics.

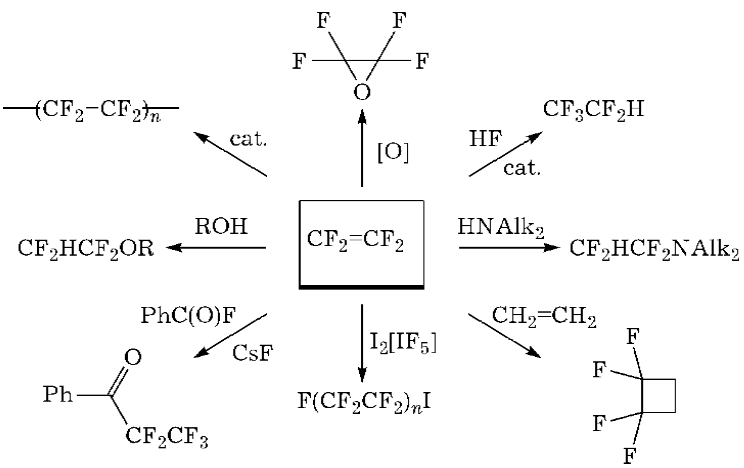
Because of this, consumers of the materials can model the properties of materials that are already in use taking into account new technological conditions. The main directions of the use of fluorinated organic compounds are rather broad and familiar to industrial staff. As far as automobile transport is concerned, several main directions can be distinguished:

1. The use of fluorinated materials and polymers in the production of parts of automobiles.

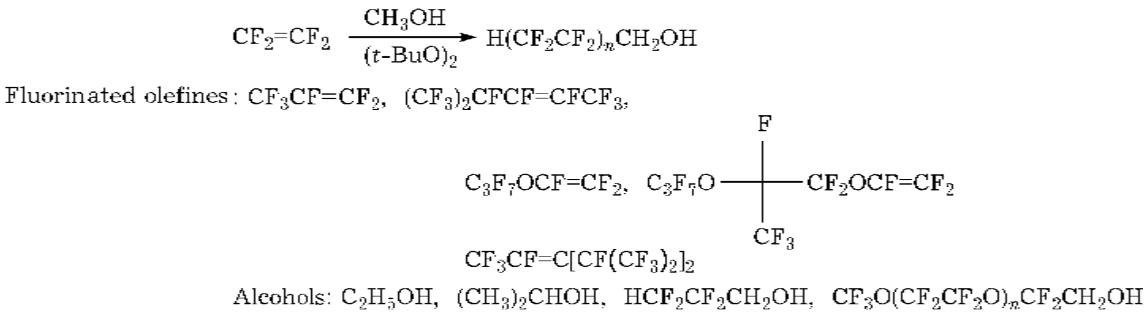
2. The use of fluorinated materials to decrease friction in mechanisms and to improve the quality of rubber parts.

3. Provision of safe performance of automobiles, including ecological aspects and economical components.

For example, the specialists of the Halogen JSC (Perm, Russia) always followed the needs of science and industry in the production of fluorine-containing semiproducts; at present, a wide range of fluorinated materials is manufactured there; some of these materials can be used in car manufacture and maintenance. An important part is played by the available modern raw material basis the grounds of which are two perfluorineolefins:



Scheme 1.



Scheme 2.

tetrafluoroethylene and hexafluoropropylene [6]. Large-scale technologies allow one to develop the production of various semiproducts which are later transformed into fluorinated materials (Scheme 1).

An important part in the development of the chemistry of fluorinated organics is given at the Halogen JSC to partially fluorinated alcohols [7–9]. It is natural since alcohols themselves and fluorinated materials based on them find application. In this situation, the technologies of obtaining not only linear telomeric alcohols but also branched fluorine-containing alcohols (Scheme 2).

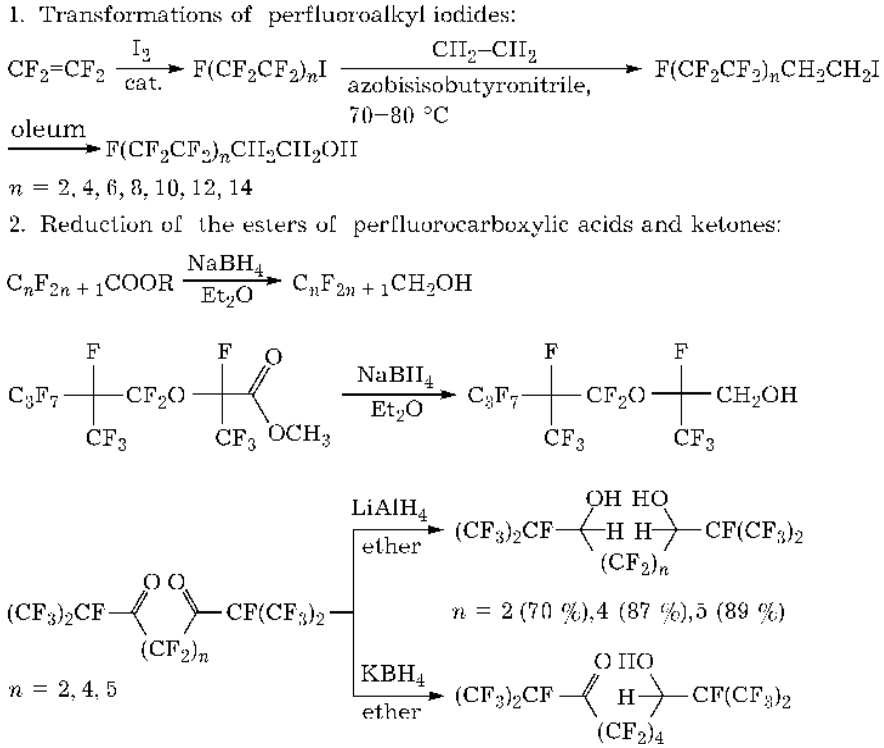
The method is based on the interaction of tetrafluoroethylene with methyl alcohol under elevated temperature and pressure in the presence of a peroxide initiator with decomposition temperature above 100 °C (*tert*-butyl diperoxide, *tert*-butylperoxy-2-ethylhexanoate, peroxides of carboxylic acids and esters, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane, *etc*.) [10–14]. Fluorinated primary alcohols like $H(CF_2CF_2)_nCH_2OH$ ($n = 1-6$) are obtained. The process conditions are: heating of the peroxide initiator (3.5-15.4 %) in alcohol at 110–120 °C and a pressure 3.4–6.5 kg/cm^2 with controlled introduction of fluorinated olefin and pressure increase to 9–15 kg/cm^2 at a temperature of 150 °C. The process is conducted with the ratio of fluorinated olefin to initiator equal to 7.2–28.1 : 1, and with the addition of 0.2–1.2 % polyfluorinated alcohol [14]. Both the decomposition of the radical initiator to give the radical and its reaction with the alcohol are initiated under these conditions. For instance, $CHF_2CF_2CH_2OH$ is obtained with the yield of 99.8 % in the reaction of methyl alcohol with tetrafluoroethylene in the presence of di(*tert*-butyl)peroxide [14].

In the pilot version, a safe and almost waste-free production of partially fluorinated alcohols was realized with the yield close to the theoretical one on the basis of the reactions of tetrafluoroethylene and hexafluoropropylene with aliphatic alcohols in the presence of a peroxide initiator. It was established that the chain length in partially fluorinated alcohols is essentially dependent on the ratio of tetrafluoroethylene to the initiator, which allows one to obtain the required telomeric alcohol. On the basis of these results, an industrial installation for obtaining telomeric alcohols was made, which broadened the possibilities of obtaining semiproducts for the synthesis of fluorinated organics. The method was introduced into industry.

The developed technology of the production of these alcohols allows one to obtain target products with essentially lower costs than the known methods of obtaining fluorinated alcohols can afford (for example, according to the methods presented in Scheme 3), which opened the area of application of these materials [2, 15–17].

High-molecular compounds possessing good lubricant properties were obtained using fluorinated alcohols. These compounds are inert liquids differing from each other in viscosity, colourless and odourless, nonflammable, fire-safe, with high thermal and corrosion stability to metals and non-metal materials, ecologically safe, possessing high thermal physical and dielectric characteristics. Some chemical reactions of fluorinated alcohols are shown in Scheme 4 [18].

For example, lubricant based on telomeric alcohols and polyfluorinated aromatics [18] or the derivatives of dicarboxylic acid [19] exhibit the following advantages:



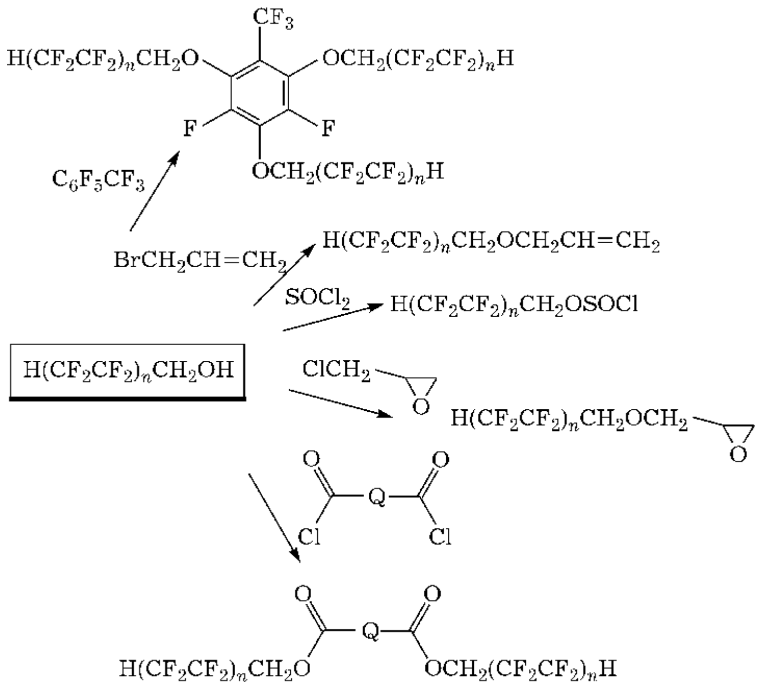
Scheme 3.

– increased thermal stability (working tempeature: 450–550 °C),

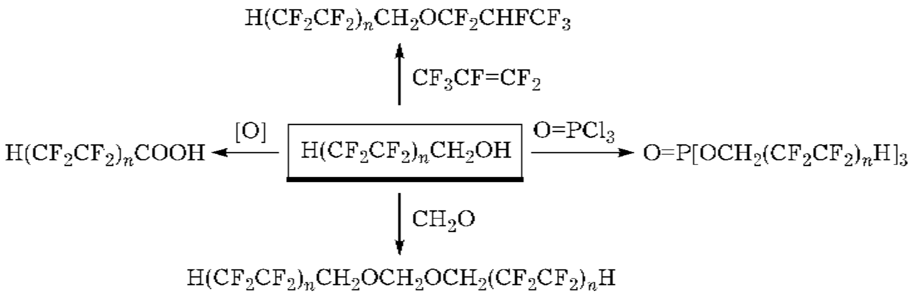
– high antiadhesion and lubricant characteristics within a broad temperature range, wear resistance, which allows using them to lubricate bearings and other moving parts,

– small friction coefficient and low viscosity, the possibility to increase the latter by adding tetrafluoroethylene or other fillers,

– safety of performance (LD_{50} 5000–8000/kg, the third class of danger),



Scheme 4.



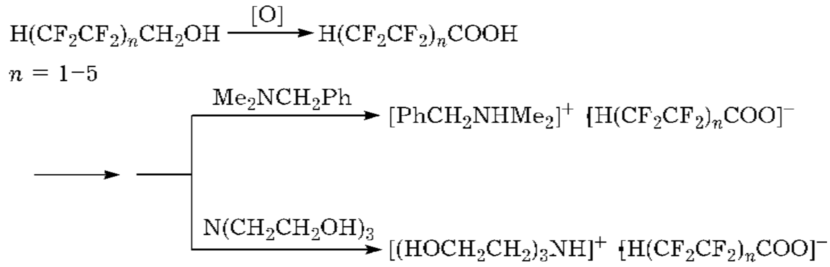
Scheme 5.

– produce only slight contamination of the mould and the surface of molded parts, which simplifies their extraction, improves the conditions for rolling the parts of different profiles from metals.

Fluorine-containing alcohols turned out to be very efficient O-nucleophilic reagents, which allows one to manufacture various semi-products for practical application on this bases (Scheme 5). For example, the derivatives of alkyl(polyfluoroalkyl)phosphate are used as an additive to lubricant oil and provide anti-corrosion, antiwear, antiscuff and demulsifying properties of the parts made of inorganic materials [20].

Oxidation of fluorinated alcohols allows one to develop the technology of perfluorocarboxylic acids [21–23] which win wide application as semiproducts for obtaining various salts possessing surface-active properties (surfactants), which provides a broad range of their practical application (Scheme 6). First, their high stability to chemical agents – acids, alkalis, *etc.* should be stressed, as well as thermal stability. Second, fluorinated surfactants possess higher surface activity than usual hydrocarbon ones. They are extremely efficient in decreasing surface tension (they form films on the surface of water and acids; these films prevent the release of heavy metal aerosols and vapour of various compounds from electrolytes). When adsorbed on water surface, fluorinated compounds can decrease the surface tension of water to 15 10^{-3} N/cm. Third, since the surfactants of this type are efficient in very low concentrations, one should expect that the amount of the compound used will decrease, which provides not only economic profits but also essential advantages form the viewpoint of environmental protection.

We will present only some examples of the use of surfactants. First, since fluorine-containing surfactants are foam-forming substances, they can be used as compositions for fire fighting by producing an air-mechanical foam [24]. In spite of the high cost, the efficiency of surfactants based on fluorinated compounds is beyond doubt. These compounds are used to extinguish fire in reservoirs with petrol and other highly inflammable organic solvents, especially in public places. Foam of fluorinated organics act efficiently because the solution released from the foam forms a film on the surface of an inflammable liquid which prevents foam from destroying. In addition, fluorine-containing surfactants possess chemical and thermal stability, biological and surface stability. The high extinguishing ability of film-forming foam based on fluorinated compounds allows one to supply the foam under a layer of



Scheme 6.

an inflammable compound, as well as from above in mounted jets, which simplifies extinguishing. The film on the surface of an inflammable liquid prevents inflammable vapour from getting into the combustion zone and protects foam from destruction, thus ensuring rather high fire-extinguishing effect. Foam-formers based on fluorinated organics are hardly inflammable liquids; their working solutions are fire- and explosion-safe. Foam-formers PO-6FP, Foretol, POF-9M, Universalny and others have been developed in Russia [25].

For instance, PO-6FP is intended for extinguishing burning hydrocarbons with an air-mechanical foam with fresh water, Foretol is for polar liquids (alcohols, organic acids, *etc*.). The experimental production of layer foam-forming agent PO-6FP (TU 241279-130-05807960−97) was established at Halogen JSC in Russia [25]. An analogue of PO-6FP is the Light Water foam-forming agent manufactured by 3M company (USA). The PO-6FP foam-forming agent is a biologically degradable product with the degree of decomposition >80 %. There is a limitation of applicability: it is not suitable for extinguishing the fire of class B_2, C, D. The fluorinated synthetic film-forming Penofor foam-former (the newest development of Polyfen-Trade Company, St. Petersburg) is the most efficient one; it is manufactured on the basis of home raw material [26].

Freons 125 (Halogen JSC, Perm) and 227ca are used as fire-extinguishing means, but the former is preferable. The action of these freons involves an aerosol cloud that covers the object in fire and hinders (or completely stops) the access of atmospheric oxygen to the combustion zone, thus ceasing combustion.

The second example refers to the ability of fluorine-containing surfactants to inhibit corrosion of metals under the action of acids. They are efficient both when introduced into a corrosive acidic medium or when deposited as a thin protective film on metal surface in contact with acids. Since chromate baths containing sulphuric acid and exhibiting a strong oxidation action are used in electrochemical chromium-plating, the process is carried out at high current density; usual organic surfactants do not survive under these conditions and get decomposed [27]. The foam-forming ability of fluorine-containing surfactants is almost unaffected by electrolytes. They are not decomposed under the conditions of electrochemical chromium-plating and decrease the surface tension of the liquid in the plating bath causing the formation of a uniform foam layer on its surface thus preventing the evolution of poisonous mist. Surfactants possess the aerosol-suppressing ability during the electrolysis of various metals and do not have any negative effect on the quality of the cathode material and on the current efficiency. They are also able to decrease the rate of chromium-plating and diminish corrosion of the part to be plated [28]. These properties of fluorinated surfactants are used in electrolytic copper- and nickel-plating which are widely used in automobile production.

The third example refers to the cleaning of car body metal surfaces. Since fluorine-containing surfactants are characterized by the high stability to strong acids and concentrated alkalis and also decrease surface tension (the surface tension of aqueous solutions of usual surfactants can be decreased to $(25-27) \cdot 10^{-3}$ N/cm, while that for fluorinated ones can be decreased to $(15-20) \cdot 10^{-3}$ N/cm), their addition into the alkaline cleaning compositions allows one to increase their efficiency substantially [28]. The compositions of this type are efficient in removing the coatings and adsorbed substances from the surface of steel plates. In addition, it is possible to use these surfactants to wash an apparatus from various organic deposits, *etc*.

The fourth example is connected with the development of low-energy sorption layers of surfactants on the surface of solids as a result of chemisorption, which allows one to decrease (several times) the friction coefficient and wear of contacting surfaces, to increase the reliability and operation resource [28]. They are also used to deposit protective coatings on metal surfaces. Fluorine-containing surfactants are strongly held on the surface under treatment. These films are stable toward the action of water and oil. Thus treated copper and brass conserve luster and do not undergo corrosion even in the atmosphere containing hydrogen sulphide or sulphur dioxide.

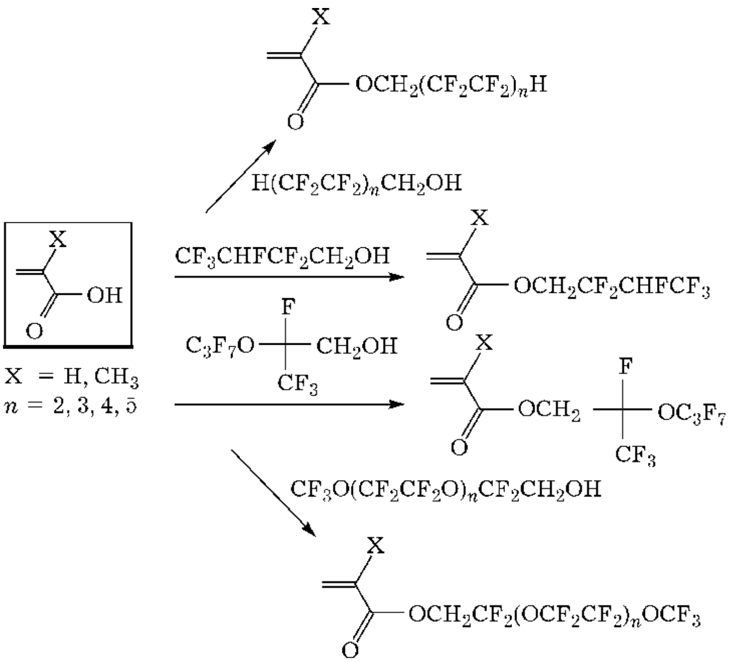
Modification with fluorine at the ester fragment of acrylates and methacrylates allows obtaining monomers from which then polymers with different molecular mass can be obtained (Scheme 7). The latter polymers can be used in cloth treatment, in obtaining coatings and films on inorganic materials, membranes for air and petrol purification that do not swell in organic solvents. These fluorinated alcohols are an alternative to more expensive and less available fluorinated alcohols like $F(CF_2CF_2)_nCH_2CH_2OH$ and $F(CF_2CF_2)_nCH_2OH$ [15–17].

Polymerization of fluorine-containing acrylates leads to polymer products which do not swell in organic solvents and petrol. Therefore, they can be used to manufacture automobile glass. Low-molecular polyacrylates may be dissolved in special solvents, which allows one to obtain films on the front glass of a car ensuring low weeping and good transparence of the glass. On this basis, it is possible to make a cushioning flexible shockproof coating on the car body with high adhesion to the inorganic coating.

CONCLUSIONS

The data reported above allow one to state an increasing attention of researchers to the development of new approaches to the introduction of polyfluorinated fragments into organic molecules and to the transformation of simple substituents into complicated functional groups. In this respect, the use of partially fluorinated alcohols obtained on the basis of polyfluoroolefins opens wide possibilities for the synthesis of new fluorine-containing materials. Substantial success achieved during the recent years in the development of a method to synthesize partially fluorinated alcohols which help in introducing fluorine-containing fragments into organic molecules shows that in a number of cases these methods can compete with conventional well known methods. A number of processes have clear advantages and real possibilities to be used in industrial technologies.

In the present work, mainly with telomeric alcohols as examples, we made an attempt to demonstrate novel approaches and synthetic possibilities of the new semiproducts, to show the trends and the main directions of investigations into the synthesis of polyfluorinated organics containing various molecular frameworks and functional groups. Thus, the technology of obtaining telomeric alcohols introduced into industry made an impetus to their extensive and multiaspect investigation and synthesis of the new fluorinated materials because these processes are rather simple and can be realized on the



Scheme 7.

industrial scale. It is natural that the described examples do not embrace the whole range of possibilities and specific examples of the use of fluorinated materials in the production of automobiles. One can expect that other reactions leading to the formation of fluorinated organics can be revealed in the future.

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