

Review

Special applications of fluorinated organic compounds

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Abstract

The applications of fluorinated organic compounds (FOCs) as finishing agent for fabrics, components of extinguishing agents, electroplating bathes, lubricating oils, oxygen carriers in blood substitutes have been discussed. Recent achievements in methods of the fluorination and general principles of the synthesis of useful perfluorinated organic compounds are given as well.

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Keywords: Electrofluorination; Fluorinated organic compounds; Oligomerization; Synthesis methods; Telomerization

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1. Introduction

The use of fluorinated organic compounds (FOCs) has increased throughout this century [1,2], and they are now ubiquitous environmental contaminants. Although generally viewed as recalcitrant because of their lack of chemical reactivity, many fluorinated organics, particularly perfluorinated compounds (PFCs), are globally distributed, environmentally persistent, bioaccumulative, and potentially harmful. Moreover,

little is known about the occurrence, transport, biodegradation, and toxicity of these compounds in the environment. In addition, several fluorinated organics are subject to at least limited biotransformation under appropriate environmental conditions. Certain volatile fluorinated compounds can be oxidized in the troposphere yielding nonvolatile compounds, such as trifluoroacetic acid. Certain nonvolatile fluorinated compounds can be transformed in the biosphere to volatile compounds.

The report about an identification of certain fluorinated surfactants in groundwater impacted by fire-fighting activity and detection of perfluorooctane sulfonate in part per-billion levels in blood samples obtained from blood banks in the United

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States, Japan, Europe, and China [3] has created an awareness of the potential environmental issues resulting from the use of fluorinated surfactants and other FOCs.

In this review, we introduce briefly the unique properties of fluorinated organic compounds. Then special applications of these organic fluoroderivatives are described. Finally, the methods of the fluorination and synthesis of useful perfluoroalkyl compounds are presented.

2. Properties of FOCs and PFCs

Extraordinary physical, chemical, and biological properties of FOCs and PFCs molecules are due to [4–6]:

- high electronegativity of fluorine atoms (4.0);
- high energy of C–F bond (approx. 466 kJ mol^{-1});
- small diameter of fluorine atoms.

The distances between atomic nuclei in C–Cl, C–C, C–F and C–H bonds are respectively 176–179, 153–155, 133–142 and 106–109 pm. On the contrary to hydrogen the fluorine atoms tightly screen a carbon chain (Fig. 1).

As a result the FOCs and particularly PFCs are extremely durable and highly resistant to hydrolysis, photolysis, microbial degradation, and metabolism by vertebrates, as well as to relatively high temperatures and X-ray and nuclear radiation [1]. For example, monofluoroacetic acid withstands boiling in 100% sulfuric acid without defluorinating. Due to small dimensions of fluorine atoms no steric hindrance is observed when hydrogen atoms or functional groups are totally substituted for fluorine atoms regardless to their dimensions and structure.

Fluorine is the most abundant halogen in the earth's crust and ranks 13th in abundance among all elements [2]. This may explain instances of natural organofluorine production. Some naturally occurring FOCs are produced by higher plants and certain microorganisms. For example, monofluoroacetic acid is produced by plants of the genus *Dichapetalum*, as well as *Palicourea marcgravii*, *Acacia georginae*, *Gastrolobium grandiflorum*, and *Oxylobium* species. The plant *Dichapetalum toxicarium* also produces fluorooleic acid, fluoropalmitic acid, and possibly fluorocaproate and fluoromyristate. Certain fungi also produce fluorinated organics. For example, *Streptomyces clavus* and *Strepto-*

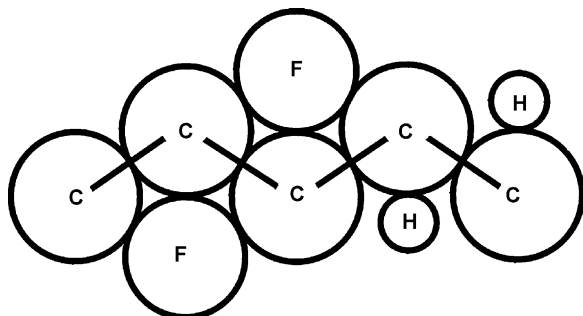


Fig. 1. Steric effects of $-\text{CH}_2-$ and $-\text{CF}_2-$ bonds. Atom radius (pm) of: F 64, H 29, C 77.

Table 1

The critical surface energy of tightly packed hydrocarbon and halogen groups

		mN/m
Corner of aromatic ring	$=\text{CH}-$	35
Polyethylene	$-\text{CH}_2-\text{CH}_2-$	31
Methyl group	$-\text{CH}_3$	22–24
Vinyl polychloride	$-\text{CHCl}-\text{CH}_2-$	39
Vinyl polyfluoride	$-\text{CHF}-\text{CH}_2-$	28
Polytetrafluoroethylene	$-\text{CF}_2-\text{CF}_2-$	18
Difluoromethyl group	$-\text{CHF}_2-$	15
Trifluoromethyl group	$-\text{CF}_3$	6

myces cattleya produce the fluorine-containing antibiotic nucleocidin and 4-fluorothreonine, respectively. *S. cattleya* is also capable of producing monofluoroacetate. Finally, production of CFC-11, CFC-12, CFC-113, HCFC-21, HCFC-22, tetrafluoroethylene, and chlorotrifluoroethylene has been reported in volcanic gases and drill wells [2]. It is important to note that all of the known naturally produced FOCs contain only one fluorine atom, whereas synthetic FOCs often contain many fluorine substituents and some are fully fluorinated [1,2].

Fluorine essentially differs from chlorine. Only the hydrogen atoms in methane and ethane can be permanently and totally substituted for chlorine. Totally chlorinated compounds with longer chains are durable only if they contain an appropriate number of appropriately placed double bonds.

A tight packing of highly electronegative fluorine atoms in organic perfluorinated compounds causes a low surface energy and in consequence a slippery and extremely resistant to wetting surface. Examples of surface energy values are shown in Table 1.

This phenomenon is utilized in practice. Metal surfaces covered with thin layer of polytetrafluoroethylene do not wet neither with water nor oils. The surfaces of fibres, leather and plastics permanently appreted with compounds containing perfluorinated chains do not wet with any liquid applied in the everyday life preventing smudging with both, the aqueous and oily liquids. The reactive perfluoroaliphatic compounds for oleophobic finish of fabrics are of particularly importance.

The surfactants containing perfluorinated hydrophobic group show a considerable surface activity. At the appropriately chosen hydrophilic-lipophilic equilibrium it is possible to lower the water surface tension below 20 mN/m, in comparison to approx. 30 mN/m when strongly active hydrocarbon surfactants are used [7].

Given the widespread production and use of fluorinated organics, it is perhaps not surprising that organic fluorine has been detected in the blood of individuals from the general public as well as industrial workers [2]. For workers handling FOCs, organic fluorine levels of 1.0–71 ppm have been reported in their blood serum. Individuals who have not been exposed to industrial fluorochemicals had organic fluorine concentrations from 0.0 to 0.13 ppm. Some authors suggest that there is widespread contamination of human tissues with organofluorine compounds derived from commercial sources such as perfluorooctanoic acid [2].

Table 2
Typical composition of synthetic foaming agent of the AFFF type

Component	Percent of total
Surface active agent (fluorinated)	1–5
Surface active agent (hydrocarbon)	1–10
Organic solvent (e.g. DGBE: diethylene glycol monobutyl ether)	15–40
Magnesium sulfate	<5
Ethylene glycol	<20
Water	Residue

3. Perfluorinated surfactants

The phase-partitioning behaviour of perfluoroalkanes differs from that of chlorinated hydrocarbons [1]. When mixed with hydrocarbons and water, some perfluoroalkanes form three immiscible phases, indicating that perfluorinated chains are oleophobic and hydrophobic—chlorinated and brominated organics are hydrophobic and lipophilic.

When attached to a perfluorinated chain, a charged moiety, such as carboxylic acid, sulfonic acid, or a quarternary ammonium group, imparts hydrophilicity [1]. Such functionalized fluorochemicals have surfactant properties, selectively adsorbing at interfaces because of the presence of both hydrophobic and hydrophilic moieties. Fluorinated surfactants constitute an important class of fluorinated compounds that are utilized in fire-fighting applications, herbicide and insecticide formulations, cosmetics, greases and lubricants, paints, polishes, and adhesives [3].

The surfactants containing perfluorinated group are the components of the agents used for extinguishing the fires of crude oil and refinery and petrochemistry products [7–11]. In these applications they are generally termed as Aqueous Film Forming Foam (AFFF) and are also denoted as A3F. A typical composition of synthetic foaming agent of the AFFF type is shown in Table 2.

The fire extinguishing agents of the AFFF type form an aqueous film on the surface of flammable liquid which isolates and cools the surface more efficiently than the standard protein and synthetic foams. Besides the aqueous film, a layer of foam is formed, which also isolates the fuel surface. The aqueous film is formed only at the time when the difference of the surface tensions of petroleum products and the fire extinguishing agents is larger than the interfacial tension between these liquids [7]:

$$\gamma_1 - \gamma_2 > \gamma_3$$

γ_1 is the surface tensions of petroleum products, γ_2 the surface tensions of fire extinguishing agents, γ_3 the interfacial tension at the phase boundary: petroleum products—fire extinguishing agents.

The most common medium of that type is so called “light water” [3,11,12].

Perfluorinated surface active compounds are also included in the composition of fire extinguishing agents used for fire suppression of liquids which destroy the fire extinguishing foams. These agents are most frequently denoted as AFFF-AR, where

AR denotes alcohol resistant [7]. The liquids intensively destroying the foams are the following: esters, ethers, ketones, glycols, amides, amines. Often they occur in the form of mixtures with hydrocarbons, resins used in the production of paints, varnishes, plastics, vehicle fuels.

Perfluorinated surface active compounds are also added to the galvanizing baths, especially chromium ones, in order to suppress the formation of fogs (mists) [13,14]. In dyebathes or apretting bathes the surfactants facilitate wetting the fabrics and plastics, thus increasing the rapidity and efficiency of finishing processes [15,16]. Added to lubricating oils they improve oil spread ability and in glues they increase the adhesion to cemented surfaces [17,18].

It is obvious that surfactants with perfluorinated group are not and will not be applied in mass products, e.g. in washing powders due to their costs and resistance to biological degradation. They are and will be in the future only the very specific agents for numerous and very often unique applications.

4. Biologically active compounds

The properties of fluorine and their influence on chemical and physical characteristics of organic molecules make it very attractive in the organic synthesis. The substitution of hydrogen for fluorine improves also the lipide solubility of molecules and is applied in the manufacture of various medicines. Moreover, the fluorine atom as strongly electronegative improves the chemical reactivity of molecules. The trifluoromethylene group can be considered as almost isosteric with methyl group. The presence of $-\text{CF}_3$ in place of $-\text{CH}_3$ in the biologically active compounds does not cause any essential steric consequences. Owing to that the trifluoromethylene derivatives of natural compounds are accepted by biological receptors similarly to their nonfluorinated analogues [19]. On the other hand, the chemical and physical properties of $-\text{CF}_3$ and $-\text{CH}_3$ are totally different. The compounds containing $-\text{CF}_3$ group have higher susceptibility to the action of nucleophilic agents, increased lipophilicity and resistance to the biodegradation. Due to these properties the compounds containing the $-\text{CF}_3$ group find wider and wider application in the pharmacy and agricultural chemistry [20,21].

5. Blood substitutes

Also the fluorine derivatives applied as the oxygen carriers in the blood substitutes are worthy of note. Their general characteristic is presented by Clark [22] and recently by Lowe [23,24]. From the medical point of view the fluorine derivatives as the oxygen carriers are described by many authors [25–29]. The proposed substances, examined as the oxygen carriers in hematology can be divided into the following groups:

- perfluorinated closed chain compounds: perfluorodecaline, perfluoro(methyldecaline), perfluoro(alkylcyclohexane); perfluoroadamantane and other perfluorinated oligocycloalkanes;
- perfluorinated alkanes of normal and branched chains;

- perfluorinated tertiary amines, e.g. perfluorotripropylamine and perfluorotributylamine;
- perfluorinated compounds containing oxygen in the ring, e.g. perfluorofurane;
- perfluorinated chain compounds with ether oxygen, e.g. perfluoroisopropylhexylene ether;
- highly fluorinated alkanes containing hydrogen atoms.

The essential difference in the action of perfluorinated oxygen carriers in comparison with hemoglobin is based on the oxygen combination with hemoglobin in the coordination way and the phenomenon does not follow Henry's law. The organic perfluorinated compounds dissolve oxygen (and also other gases) in a way approximate to the Henry's law. The fluorine derivatives in the blood substitutes are applied in an aqueous emulsion form with drops of the size below 0.1 μm .

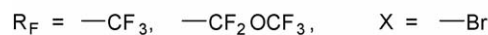
6. Methods of the fluorination and fluorinating agents

The very high exothermic effect of the substitution of hydrogen by fluorine in the organic compounds causes the necessity of the use of special technologies [30,31]. In the industry elementary fluorine is not applied for the fluorination of the organic compounds due to the violent and very often the explosive course of the reaction.

Instead, the fluorination with the elementary fluorine in the presence of an auxiliary agent of relatively high heat capacity enabling collecting the heat in the gas phase, e.g. helium, argon, nitrogen [32–34]. Of the similar importance is the fluorination in a liquid phase in the liquefied anhydrous hydrogen fluoride or 65 wt.% aqueous HF solution [35], perfluoroalkanes [36], and in low temperatures in R-11 freon [37].

Also the fluorination with metal fluorides is applied [30,31]. Metal fluorides with changeable valency are used mainly for the fluorination of hydrocarbons. The thermal effect of the reaction is much smaller if compared to the action of elementary fluorine due to the consumption of the certain amount of heat for a dissociation of fluorides. The reaction ability of the most frequently used fluorides can be arranged in the following order: $\text{AgF}_2 > \text{CoF}_3 > \text{MnF}_4 > \text{PbF}_4 > \text{BiF}_5 > \text{HgF}_2$. In practice the most often applied appears to be cobalt trifluoride and its complex salts [30,38–40].

The fluorine derivatives of hydrocarbons are also obtained from the appropriate chlorine derivatives in the reaction with hydrogen fluoride in the presence of catalysts or metal fluorides. The substitution of chlorine for hydrogen fluoride proceeds in the gas phase in the presence of the following catalysts: chromium trifluoride [41], iron(III) oxide on an activated carbon or iron trifluoride [42], thallium pentafluoride [43], chromium(III) oxide [44]. The exchange in the liquid phase is carried out in the presence of chlorine and antimony pentachloride as the catalysts [45]. Chlorine prevents the deactivation of the catalyst. The exchange of halogen with fluorine can be also performed applying complexes of hydrogen fluoride with trialkylamines $\text{R}_3\text{N}\cdot n\text{HF}$ ($n = 2-5$) [46–48]. Very convenient is the substitution of halogen for fluorine supplied in the form of fluorides of alkali metals or alkaline earths [49–51]. This refers to, e.g. the sub-



Scheme 1.

stitution of chlorine in the aromatic compounds in a suspension of anhydrous potassium fluoride in dimethylformamide under the atmospheric pressure and temperature approx. 130 °C. Also sulphur tetrafluoride is used as a selective fluorinating agent, enabling among others a conversion of aryl esters of perfluorocarboxylic acid into ethers of perfluoroalkyl chain extended by one $\text{—CF}_2\text{—}$ group [52] (Scheme 1).

The above mentioned methods are generally applied for obtaining the fluorine compounds containing several carbon atoms in a molecule or of more extended molecule. The latter contain singular fluorine atoms. Among the fluorine organic compounds the reactive perfluoroalkyl compounds $\text{C}_5\text{—C}_{10}$ are of great importance mainly in the synthesis of surfactants.

7. Synthesis of useful perfluoroalkyl compounds

The synthesis of useful compounds of perfluoroalkyl chains is based on obtaining the perfluoroalkyl chain or the introduction of functional groups into the fluorinated chain. The perfluoroalkyl chains are obtained by three methods [7,47]:

- anode electrofluorination of alkyl chains;
- telomerization of tetrafluoroethylene in the presence of adequate telogens;
- ion oligomerization of perfluoroolefines or perfluoroolefine oxides.

7.1. Electrofluorination

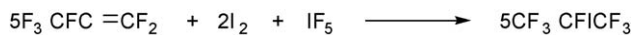
Electrofluorination is the oldest method of the synthesis of perfluoroaliphatic compounds [47,53–55]. The final product of fatty acids electrofluorination in anhydrous hydrogen fluoride or potassium hydrogen fluoride is the mixture of perfluoroacyl fluorides of various length of the carbon chain. The greatest disadvantage of the electrofluorination is its low process selectivity and considerable fragmentation of the carbon chain [56–59].

7.2. Telomerization

The advantageous method of perfluoroalkyl chains synthesis is the telomerization [7,60–64]. In the method proposed by Haszeldine [65], it is based on the polyaddition of tetrafluoroethylene to trifluoromethane iodide and is initiated thermally or by UV radiation (Scheme 2).



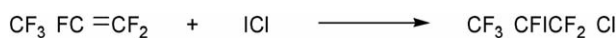
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

The development of the telomerization is founded on syntheses of new telogens. In the beginning of the sixties of previous century the synthesis of telogen was elaborated basing on the addition of iodine and pentafluoride iodine to tetrafluoroethylene or hexafluoropropylene [7,66–68] (Scheme 3).

The similar effects of fluoroiodination of perfluoroolefins were obtained by Krespan [69], while carrying out the reaction of perfluoroolefin and potassium fluoride and iodine in the aprotic solvent. The method is cheaper as it eliminates expensive pentafluoride iodine (Scheme 4).

Good and cheap telogen was obtained in the reaction of iodine chloride with hexafluoropropylene [70] (Scheme 5).

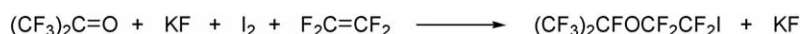
The other telogen (so called ether telogen) was obtained in the reaction of alkali metals fluorides and perfluoroacetone, iodine and tetrafluoroethylene in the anhydrous aprotic solvent [71] (Scheme 6).

During the telomerization, depending on the telogen type, the telomers of straight or branched chains are formed (Scheme 7).

The progress in telomerization of tetrafluoroethylene technology was based on passing from a periodical to continuous method and choosing the catalyst enabling lowering the process temperature. Thus, the side reactions of tetrafluoroethylene were restricted, mainly the dimerization to perfluorocyclobutane [72,73].

7.3. Oligomerization of perfluoroolefines

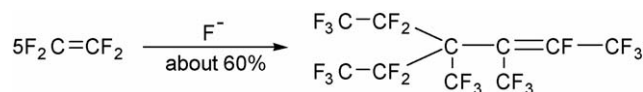
Another method of perfluoroalkyl chain synthesis is the oligomerization of perfluoroolefines. It can proceed according to free radical or ion mechanism. The free radical oligomerization most frequently is initiated thermally (200–300 °C) and gives cyclic dimers. In the case of tetrafluoroethylene or hexafluoropropylene, respectively perfluorocyclobutane and perfluorodimethylcyclobutane are formed [74]. The anion oligomerization proceeds only in the presence of fluoride ion in the aprotic solvent and in the temperature range 50–150 °C [75,76].



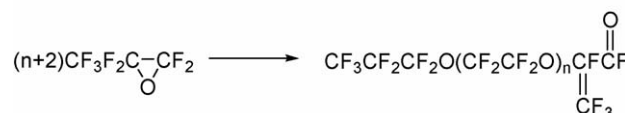
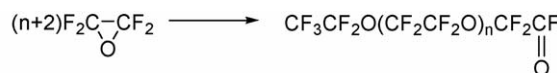
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

According to ICI method during the oligomerization of tetrafluoroethylene mainly branched dimers are formed [77] (Scheme 8).

7.4. Oligomerization of perfluoroalkyl oxides

Of similar importance is the oligomerization of perfluoroalkyl oxides. The Du Pont Company first patented the oligomerization of tetrafluoroethylene oxide initiated by the ionizing radiation [78], and perfluoropropylene oxide in the presence of carbonyl or cesium fluoride [79], or other alkali metals fluorides [80], or perfluoroacyl fluorides [81]. The process proceeds at low temperatures and leads to the formation of oligomers having the structure of linear polyethers, ended with fluorocarbonyl group [82–84] (Scheme 9).

The solvents most frequently used in these processes are: glymes, tetrahydrofuran, nitriles, methyl trifluoroacetate, hydrocarbons and liquefied perfluoropropylene. The detailed description of the mechanism and kinetics of the oligomerization of perfluoropropylene oxide is given by Hill [85].

8. Conclusions

The number of synthetic fluorinated organic compounds because of their useful properties has significantly increased over the past few years. Fluorinated organic compounds particularly perfluorinated compounds have been used in engineering and chemical industries, electronics industries and even medicine. Their synthesis is based on classical fluorination process as well as electrofluorination, telomerization, and oligomerization process. Although fluorinated organic compounds are generally viewed as recalcitrant because of their high stability, several questions surrounds about their potential environmental issues.

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