Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, ORGANIC, DIRECT FLUORINATION

Organic compounds containing fluorine are well known for their special properties, especially their inertness, very low boiling points, comparatively high melting points, and high thermal stability. Binary compounds of carbon and fluorine, ie, fluorocarbons, can be traced back to Moissan who, in 1886, discovered and isolated fluorine (1). The simplest solid fluorocarbon (2) is poly(fluoromethylidyne) $(CF)_n$, CFX (MarChem), which has a layered structure (Fig. 1). It can be synthesized by the reaction of fluorine with graphite at 300–600°C and fluorine pressures up to 101 kPa (1 atm) (3, 4). Other solids (C_4F, C_2F, etc) have also been reported from the reaction of F_2 with graphite (5, 6). This material is a grayish to white powder of variable stoichiometry and stable up to 600°C in air. Fluorinated graphite has a very low coefficient of friction, similar to Teflon, and is an excellent lubricant that can be used up to 600°C, surpassing Teflon which softens and decomposes above 350°C (see FLuorine compounds, organic–polytetrafluoroethylene). When $(CF_x)_n$ decomposes above 650°C, it yields mainly carbon black (finely divided soot) and the inert gas carbon tetrafluoride (7). Thus it can be used safely at high temperatures without risk of poisonous gases being produced on decomposition (2, 8).

Initial attempts at reactions between fluorine and hydrocarbons were described as similar to combustion and the reaction products contained mostly carbon tetrafluoride and hydrogen fluoride:

$$C_xH_y + \left(\frac{4x+y}{2}\right) F_2 \longrightarrow x\, CF_4 + y\, HF + \text{energy}$$

This reaction has often reached explosive proportions in the laboratory. Several methods were devised for controlling it between 1940 and 1965. For fluorination of hydrocarbons of low (1–6 carbon atoms) molecular weight at room temperature or below by these methods, yields as high as 80% of perfluorinated products were reported together with partially fluorinated species (9–11). However, fluorination reactions in that era involving elemental fluorine with complex hydrocarbons at elevated temperatures led to appreciable cleavage of the carbon–carbon bonds and the yields invariably were only a few percent.

Before the LaMar process was developed in 1969, the use of direct fluorination was usually considered the classical method of fluorination (12, 13) and other approaches were regarded as modern methods. Now only telomerization reactions using tetrafluorethylene and reactions in hydrogen fluoride-based electrochemical cells are more widely used than direct fluorination on a commercial scale; however, this may change in the future. Direct fluorination not only gives higher yields in most cases but preparation in this manner is applicable to a wider range of organofluorine compounds and classes of compounds inaccessible by these more established technologies. Many compounds are uniquely prepared in the laboratory by direct fluorination, and ton quantities of various fluorocarbon materials are available from 3M Co. manufactured by new direct fluorination technology.

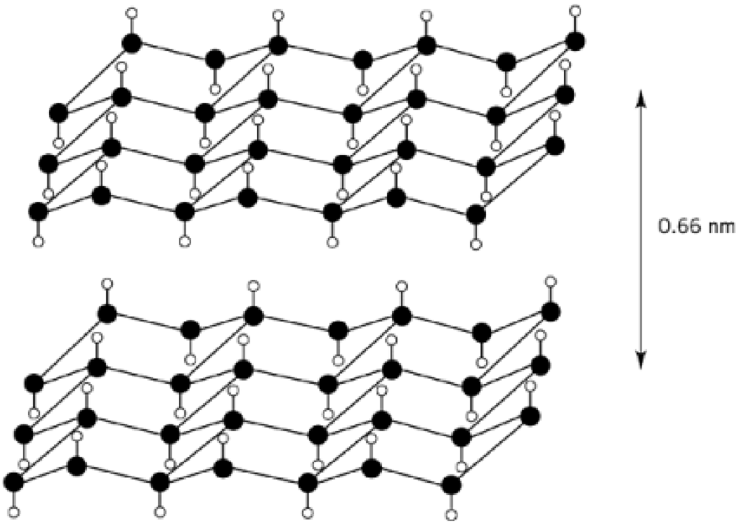


Fig. 1. Structure of poly(carbon monofluoride). ●, carbon; ○, fluorine. The interstitial space is 0.66 nm.

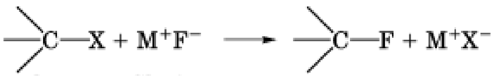
1. Metal Fluoride Method

Before the LaMar process was developed, it was generally believed that because the reaction of elemental fluorine with hydrocarbons is highly exothermic, the carbon–carbon bonds are first ruptured, creating free radicals and eventually leading to polymerization. Therefore in most instances the expected product was a complex mixture of polymers and degradation products, including pure carbon and various fragments of the original hydrocarbon material.

In the 1940s researchers developed diverse fluorination methods that avoid these problems by using certain metal fluorides, inorganic fluorides, or halogen fluorides and electrochemical or indirect methods using fluorides as reagents. Hydrogen fluoride has been successfully used as a fluorinating agent and is, in fact, still widely used industrially.

Fluorination of organic compounds using high valency metallic fluorides (14) may be represented as follows:

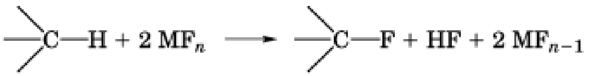
Exchange of halogen with fluorine of the metal fluorides, MF_n*:*



$$\text{C—X} + M^+F^- \longrightarrow \text{C—F} + M^+X^- \qquad (1)$$

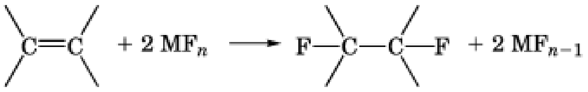
where X = Cl, Br, or I and M = K, Sb, $AgHg_2$, or Hg

Replacement of hydrogen with the fluorine of metal fluorides:



$$\text{C—H} + 2\,MF_n \longrightarrow \text{C—F} + HF + 2\,MF_{n-1} \qquad (2)$$

Addition to double bonds:



(3)

High valency metallic fluorides are very reactive compounds and most decompose in water. They include CoF_3, AgF_2, MnF_3, CeF_4, PbF_4, and possibly BiF_5 and UF_6. As shown in equations **1–3**, at elevated temperatures, usually 100–400°C, they react with organic compounds producing the fluoro derivatives and the corresponding lower fluorides such as CoF_2 and AgF. Using cobalt trifluoride [10026-18-3] at 200–400°C, all hydrogen atoms of a hydrocarbon can be replaced by fluorine if the product is thermally stable. Similar addition of fluorine to unsaturated linkages and to aromatic nuclei takes place.

The requirement that organic compounds be vaporized at temperatures averaging 280°C across the bed of cobalt trifluoride or silver difluoride causes serious limitations to the broad applicability of the synthesis of organofluorine compounds using metal fluoride technology. There are at least two companies, Imperial Smelting, Ltd. of Britain and Air Products and Chemicals of Allentown, Pennsylvania, still active in this field; the number of organic compounds that can be prepared effectively with this technique numbers approximately 100. Fused-ring aromatic compounds are the most able to survive these harsh fluorination conditions. Fluorination of polymers is almost impossible using this method because few polymers are easily volatilized. The most effective of these processes utilizing metal fluorides, the cobalt trifluoride technology, is much less flexible than the 3M electrochemical cell (Simons' cell) or the Du Pont tetrafluorethylene telomerization technology. In general, cobalt trifluoride fluorination has been more successful in the vapor phase than the liquid phase; yields tend to be low with extensive thermal degradation occurring at high temperatures.

2. Hydrogen Fluoride Electrochemical Cell Methods

Direct fluorination using hydrogen fluoride electrochemical cell methods is mechanistically similar in some regards to direct fluorination with F_2. This method uses an electrolytically activated fluoride ion produced by a Simons' designed hydrogen fluoride electrochemical cell as its primary means of fluorination. The Simons' electrochemical cell fluorination technology is practiced widely by Minnesota Mining & Manufacturing Co. (3M) of St. Paul, Minnesota. In this method, organic precursors are dissolved in liquid hydrogen fluoride and a voltage slightly under the voltage required for generation of elemental fluorine is applied across carbon electrodes. This technique, invented by J. H. Simons (15–17), has been a successful source of organofluorine compounds, functional fluids, and low molecular weight perfluorocarbon acids and diacids. There are also a number of companies in Japan and Europe that now use electrochemical fluorination for production of fluorocarbons.

The principal disadvantage to electrochemical fluorination is the requirement that the organic material be at least somewhat soluble in the polar liquid hydrogen fluoride. Therefore 3M product lines are generally based on perfluoro amines and functionalized materials such as carboxylic acids or sulfonic acids which are soluble in hydrogen fluoride (see Fluorine compounds, organic–fluorinated higher carboxylic acids; Fluoroethers and fluoramines; Perfluoroalkanesulfonic acids). Even so this technology is not capable of producing high molecular weight functional products beyond C-8 or C-10 in yields which make the process an economically viable technique. 3M uses the electrochemical cell technology to produce a well-known line of fluids known as Fluorinerts, largely based on perfluoro amines.

Other limitations of electrochemical fluorination are that compounds such as ethers and esters are decomposed by hydrogen fluoride and cannot be effectively processed. Branching and cross-linking often take place as a side reaction in the electrochemical fluorination process. The reaction is also somewhat slow because

Table 1. Thermodynamic Data[a] for Fluorination of CH_4, kJ/mol[b]

Step	Reaction	ΔH_{25}	ΔH_{325}	ΔG_{25}	ΔG_{325}
initiation					
1a	$F_2 \longrightarrow 2F^\bullet$	157.7	161.0	123.6	87.4
1b	$F_2 + RH \longrightarrow R^\bullet + HF + F^\bullet$	16.3	21.3	−24.4	−79.1
propagation					
2a	$RH + F^\bullet \longrightarrow R^\bullet + HF$	−141.4	−139.7	−151.2	−156.9
2b	$R^\bullet + F_2 \longrightarrow RF + F^\bullet$	−289.1	−290.8	−284.9	−268.4
termination					
3a	$R^\bullet + F^\bullet \longrightarrow RF$	−446.8	−451.8	−407.9	−356.0
3b	$R^\bullet + R^\bullet \longrightarrow R - R$	−350.6	−347.5	−294.1	−240.6
overall reaction	$RH + F_2 \longrightarrow RF + HF$	−430.5	−430.5	−432.6	−430.9

[a] Based on JANAF table data (25).
[b] To convert J to cal, divide by 4.184.

the organic reactant materials have to diffuse within 0.3 nm of the surface of the electrode and remain there long enough to have all hydrogen replaced with fluorine. The activated fluoride is only active within 0.3 nm of the surface of the electrode.

Fluorocarbons produced by electrochemical fluorination often have small quantities (1–5%) of up to 20 by-products produced by rearrangement. Rearrangement is not characteristic of modern direct fluorination technology using elemental fluorine. By-product formation is a particular disadvantage for applications such as production of fluorocarbon oxygen carriers, fluorocarbon blood, and other biomedical fluorocarbon products where high purity materials are required. Single compound materials are essential for advantageous consideration by the U.S. Food and Drug Administration (FDA) because each often requires individual FDA approval before the mixture receives approval.

3. Direct Fluorination Using Elemental Fluorine

Kinetic as well as thermodynamic problems are encountered in fluorination. The rate of reaction must be decelerated so that the energy liberated may be absorbed or carried away without degrading the molecular structure. The most recent advances in direct fluorination are the LaMar process (18–20) and the Exfluor process (21–24), which is practiced commercially by 3M.

3.1. Thermochemistry

Thermodynamic considerations are of utmost importance in fluorinations. Table 1 is based on JANAF data (25) for CH_4, which indicate an average carbon–hydrogen bond strength of 410.0 kJ/mol (98 kcal/mol) based on the atomization energy of CH_4.

The limiting parameter to be considered in attempting to develop a satisfactory method for controlling reactions of elemental fluorine is the weakest bond in the reactant compound. For hydrocarbons the average carbon–carbon single-bond strength is 351.5–368.2 kJ/mol (84–88 kcal/mol). The overall reaction for the replacement of hydrogen by fluorine is exothermic enough [$\Delta G_{25} = -432.6$ kJ/mol (−103.4 kcal/mol)] for a fracture of carbon–carbon bonds if it were to occur via a concerted mechanism or on several adjacent carbon atoms simultaneously. This energy must be dissipated so as to avoid the fragmentation of the molecular skeleton. The comparison of 359.8 kJ/mol (86 kcal/mol) vs 430.9 kJ/mol (103 kcal/mol) has been cited in many previous discussions as an obvious basis to predict the failure of direct fluorination methods. For rapid reaction rates, which were employed in most previous experiments, this is a valid argument.

It can be seen from Table 1 that there are no individual steps that are exothermic enough to break carbon–carbon bonds except the termination of step 3a of −407.9 kJ/mol (−97.5 kcal/mol). Consequently, procedures or conditions that reduce the atomic fluorine concentration or decrease the mobility of hydrocarbon radical intermediates, and/or keep them in the solid state during reaction, are desirable. It is necessary to reduce the reaction rate to the extent that these hydrocarbon radical intermediates have longer lifetimes permitting the advantages of fluorination in individual steps to be achieved experimentally. It has been demonstrated by electron paramagnetic resonance (epr) methods (26) that, with high fluorine dilution, various radicals do indeed have appreciable lifetimes.

The two possible initiations for the free-radical reaction are step 1b or the combination of steps 1a and 2a from Table 1. The role of the initiation step 1b in the reaction scheme is an important consideration in minimizing the concentration of atomic fluorine (27). As indicated in Table 1, this process is spontaneous at room temperature [$\Delta G_{25} = -24.4$ kJ/mol (-5.84 kcal/mol)] although the enthalpy is slightly positive. The validity of this step has not yet been conclusively established by spectroscopic methods which makes it an unsolved problem of prime importance. Furthermore, the fact that fluorine reacts at a significant rate with some hydrocarbons in the dark at temperatures below $-78^{\circ}\mathrm{C}$ indicates that step 1b is important and may have little or no activation energy at RT. At extremely low temperatures (ca 10 K) there is no reaction between gaseous fluorine and CH_4 or C_2H_6 (28).

A simple equilibrium calculation reveals that, at 25°C and atmospheric pressure, fluorine is less than 1% dissociated, whereas at 325°C an estimated 4.6% dissociation of molecular fluorine is calculated. Obviously, less than 1% of the collisions occurring at RT would result in reaction if step 1a were the only important initiation step. At 325°C the fluorine atom initiation step should become more important. From the viewpoint of energy control, as shown in Table 1, it would be advantageous to have step 1b predominate over step 2a and promote attack by molecular rather than atomic fluorine. Ambient or lower temperatures keep the atomic fluorine concentration low.

In the addition of fluorine to double bonds, the energetic situation is less severe, ie, the addition of fluorine to double bonds is only 251.4–292.9 kJ/mol (60–70 kcal/mol) exothermic per carbon–carbon bond. This energy is not sufficient to fracture the carbon skeleton if care is taken to keep addition from occurring on several adjacent carbon atoms simultaneously. Here, as in the case of hydrogen removal, the individual steps are less exothermic than the overall reaction. It has been established experimentally that less fragmentation occurs and, correspondingly, a higher yield is obtained with most conventional fluorination processes when an unsaturated rather than a saturated hydrocarbon is the starting material. This is owing to the greater exothermicity of the reaction with hydrogen, ie, 434.7 kJ/mol (103.9 kcal/mol) per saturated carbon atom as compared with 207–289.9 kJ/mol (50–70 kcal/mol) per unsaturated carbon atom. In the case of addition of fluorine to double bonds, the initiation step (eq. 4) is probably exothermic by 20.7–190.4 kJ/mol (5–46 kcal/mol) and thus plays an important role.

$$R_2C{=}CR_2 + F_2 \longrightarrow R_2\dot{C}{-}CFR_2 + F^{\cdot} \qquad (4)$$

A second possibility is that a concerted mechanism (eq. 5) which is exothermic by 207.0–283.2 kJ/mol (50–58.4 kcal/mol) per carbon atom, is important.

$$R_2C{=}CR_2 + F_2 \longrightarrow R_2CF{-}CFR_2 \qquad (5)$$

3.2. Steric Factors

Initially, most of the collisions of fluorine molecules with saturated or aromatic hydrocarbons occur at a hydrogen site or at a π-bond (unsaturated) site. When collision occurs at the π-bond, the double bond disappears but the single bond remains because the energy released in initiation (eq. 4) is insufficient to fracture the

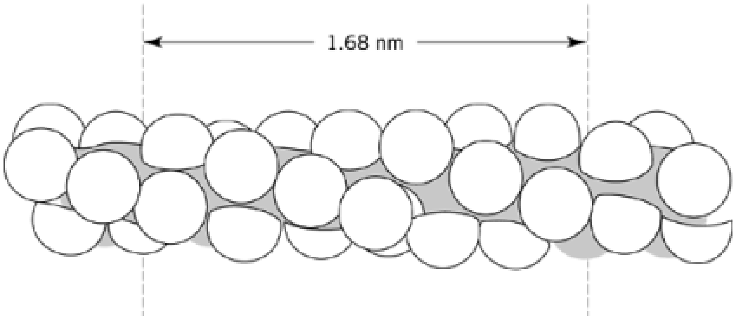


Fig. 2. The steric protection of the carbon backbone by fluorine of a polytetrafluoroethylene chain. The helical configuration with a repeat distance of 1.68 nm results from the steric crowding of adjacent fluorine.

carbon–carbon single bond. Once carbon–fluorine bonds have begun to form on the carbon skeleton of either an unsaturated or alkane system, the carbon skeleton is somewhat sterically protected by the sheath of fluorine atoms. Figure 2, which shows the crowded helical arrangement of fluorine around the carbon backbone of polytetrafluoroethylene (PTFE), is an example of an extreme case of steric protection of carbon–carbon bonds (29).

The nonbonding electron clouds of the attached fluorine atoms tend to repel the oncoming fluorine molecules as they approach the carbon skeleton. This reduces the number of effective collisions, making it possible to increase the total number of collisions and still not accelerate the reaction rate as the reaction proceeds toward completion. This protective sheath of fluorine atoms provides the inertness of Teflon and other fluorocarbons. It also explains the fact that greater success in direct fluorination processes has been reported when the hydrocarbon to be fluorinated had already been partially fluorinated by some other process or was prechlorinated, ie, the protective sheath of halogens reduced the number of reactive collisions and allowed reactions to occur without excessive cleavage of carbon–carbon bonds or runaway exothermic processes.

3.3. Kinetic Control

In direct fluorination processes, concentration, time, and temperature can be controlled. In most previous work, the fluorine was diluted with an inert gas such as nitrogen, helium, or even carbon dioxide. However, the concentration of fluorine in the reactor was kept at a constant level, usually 10% or greater, by premixing the inert gas with fluorine in the desired proportion and then introducing this mixture into the reactor. The rate of reaction between a hydrocarbon compound and a 10% fluorine mixture is relatively high, and this very exothermic process can lead to fragmentation and, in some cases, to combustion. The initial stages of reaction are most critical; nearly all the fragmentation occurs at this time. An initial concentration of 10% fluorine or more is, for most compounds, much too high for nondestructive fluorination.

Molecular relaxation processes such as vibrational or rotational relaxations or thermal conduction make it possible to dissipate the energy released during fluorination. Such relaxation processes can minimize the chances that the energy required to break the weakest bond is appropriately localized if the reaction sites are widely distributed over the system. Therefore, in the initial stages of fluorination, it is necessary to reduce the probability of adjacent reaction sites simultaneously occurring in the same molecule, or in adjacent molecules in a crystal, by diluting the reactants and relying on relaxation processes to distribute the energy over the entire system and thus avoid fragmentation.

Reactant molecules are able to withstand more fluorine collisions, as they become more highly fluorinated, without decomposition because some sites are sterically protected, ie, collisions at carbon–fluorine sites are obviously nonreactive. The fluorine concentration may therefore be increased as the reaction proceeds to obtain

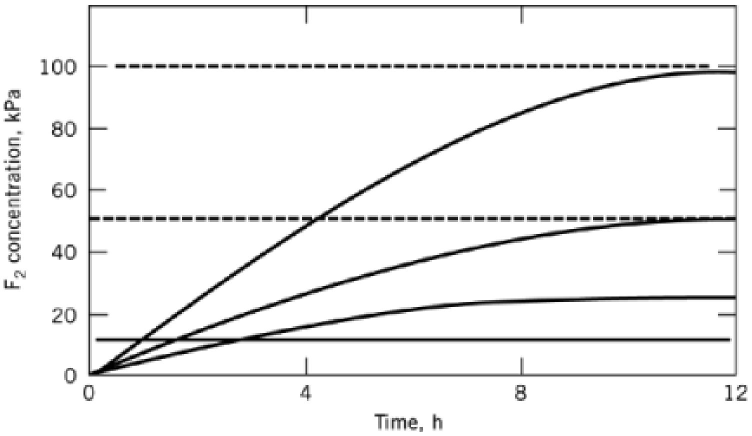


Fig. 3. Fluorine dilution scheme direct fluorination. 1 atm=101.3 kPa.

a practical reaction rate. Actual dilution schemes to achieve successful fluorination must be individually tailored for specific reaction systems and may, in some cases, include a stepwise procedure. In Figure 3, the horizontal line at about 10 kPa (10%) represents the 1940s approach to direct fluorination. High initial concentrations result in extensive fragmentation. The curved lines that asymptotically approach 101.3 kPa (1 atm) of fluorine pressure or 50.6 kPa (0.5 atm) of fluorine pressure, etc, represent the controlled approach of the LaMar process (18–20)

To achieve the very low initial fluorine concentration in the LaMar fluorination process initially a helium or nitrogen atmosphere is used in the reactor and fluorine is bled slowly into the system. If pure fluorine is used as the incoming gas, a concentration of fluorine may be approached asymptotically over any time period (Fig. 3). It is possible to approach asymptotically any fluorine partial pressure in this manner. The very low initial concentrations of fluorine in the system greatly decreases the probability of simultaneous fluorine collisions on the same molecules or on adjacent reaction sites.

Thus, for a successful fluorination process involving elemental fluorine, the number of collisions must be drastically reduced in the initial stages; the rate of fluorination must be slow enough to allow relaxation processes to occur and a heat sink must be provided to remove the reaction heat. Most direct fluorination reactions with organic compounds are performed at or near room temperature unless reaction rates are so fast that excessive fragmentation, charring, or decomposition occurs and a much lower temperature is desirable.

Low temperature fluorination techniques (-78°C) are promising for the preparation of complex fluorinated molecules, especially where functional groups are present (30), eg, fluorination of hexamethylethane to perfluorohexamethylethane [39902-62-0], of norbornane to perfluoro- (C_7F_{12}) and 1-hydro undecafluoronorbornane [4934-61-6], C_7HF_{11}, and of adamantane to 1-hydropentadecafluoroadamantane [54767-15-6].

4. Experimental Techniques

In early reaction systems (9, 10, 31, 32) the vaporized hydrocarbon was combined with nitrogen in a reactor and mixed with a nitrogen–fluorine mixture from a preheated source. The jet reactor (11) for low molecular weight fluorocarbons was an important improvement. The process takes place at around 200–300°C, and fluorination is carried out in the vapor state.

At 200–300°C many compounds, both organic and inorganic, are marginally stable, and certainly not in their lowest vibrational states. They may even undergo some pyrolytic decomposition. Thus the addition of

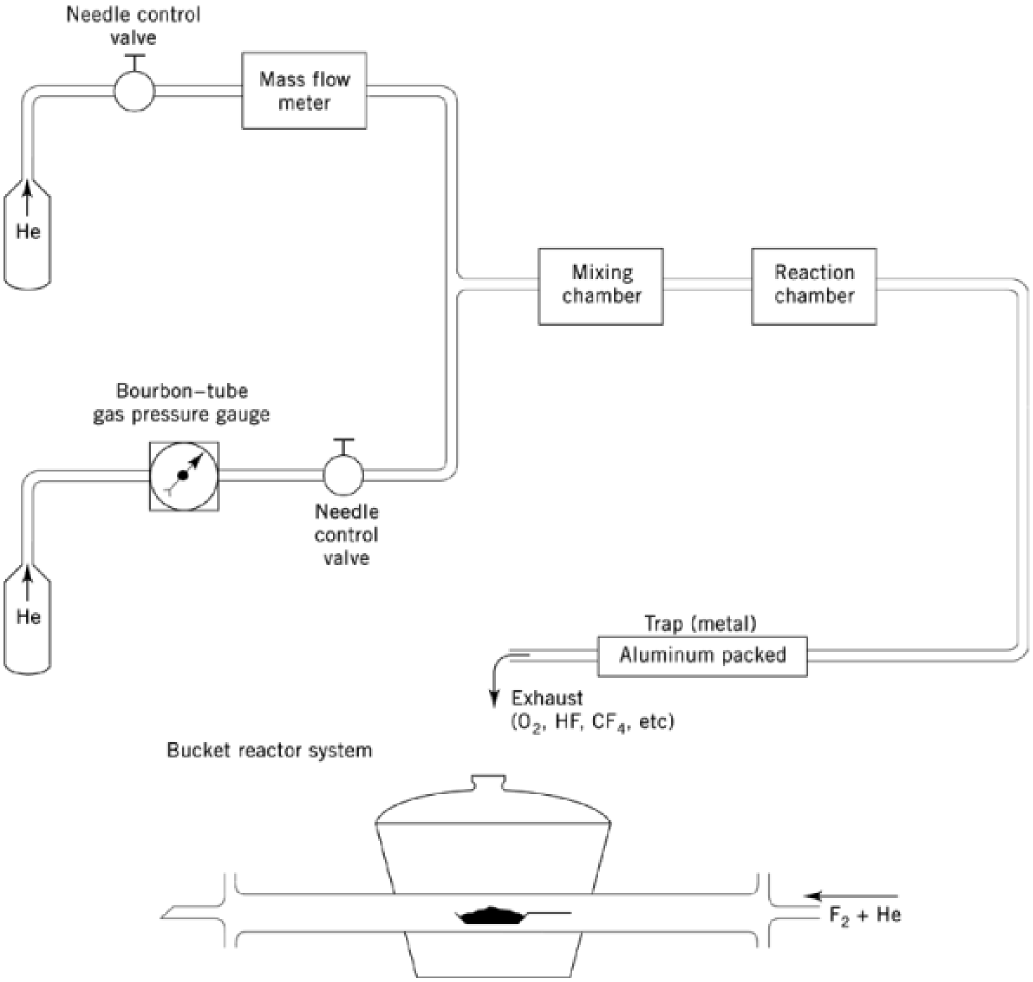


Fig. 4. Diagram of typical fluorination apparatus.

extra energy produced by the interaction of fluorine with these compounds is likely to produce substantial fragmentation. Vaporization of high molecular weight hydrocarbons is rather difficult, and their fluorination was not successful in the early jet fluorination studies.

The typical fluorination apparatus used in the LaMar process for these reactions is simple in design (Fig. 4) (33). It is essential that the materials of construction are resistant to fluorine (34). The presence of even traces of oxygen or moisture can have a deleterious effect and, therefore, extreme precautions must be taken to eliminate these contaminants.

The connections are conveniently made of 0.635 cm OD copper tubing. When the fluorocarbon produced in the reaction is volatile, a cold finger-type trap can be placed between the reaction chamber and the trap to catch volatile products. The temperature of the trap must be high enough to pass unreacted or excess fluorine and nitrogen but cold enough to condense the reaction products. Before the reaction is started ,the whole system is purged with helium or nitrogen for ca 30 minutes and then 0.5–2 mL of fluorine and 50–100 mL of nitrogen per minute are passed through the system. Solid material has to be ground to a very fine powder (37 mm ($\sim$100 mesh)) to achieve complete fluorination.

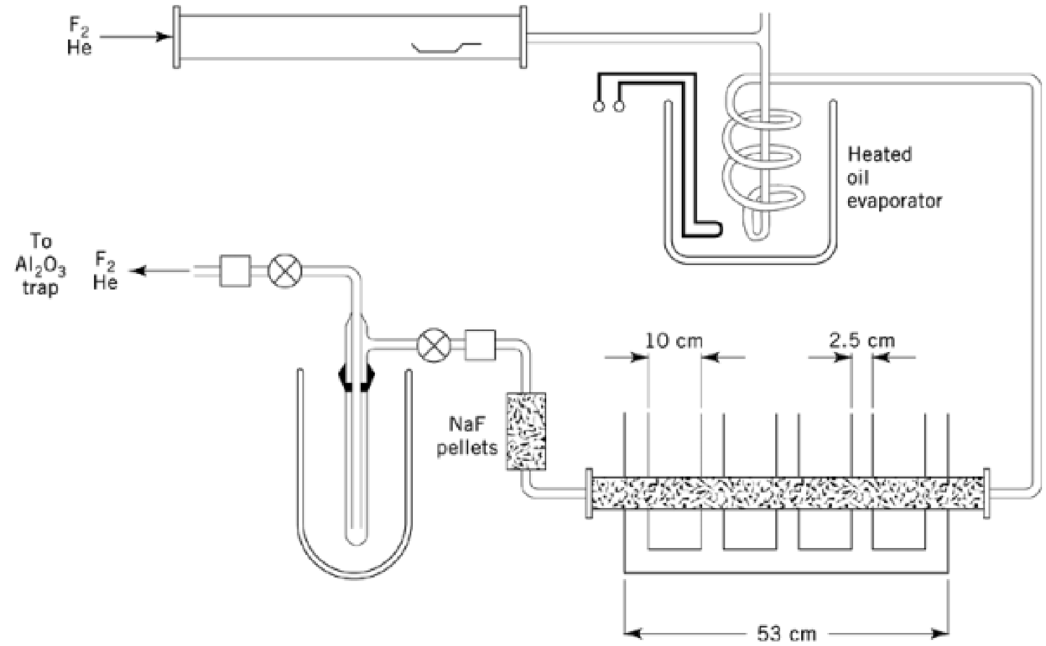


Fig. 5. Cryogenic reactor system.

A special cryogenic reactor (35) in which the reactions of fluorine with liquid and gaseous samples can be controlled at very low temperatures is shown in Figure 5. Reactants are volatilized into the reaction zone of the cryogenic reactor from the heated oil evaporator prior to initiation of the reaction. The main reaction chamber is a nickel tube, 2.54 cm in diameter, packed with copper turnings. The compartments $(10.1 \times 10.1 \times 20.2\ \text{cm})$ are constructed of stainless steel and insulated with urethane foam and act as heat sinks. All connections are made of 0.635 cm copper or aluminum tubing. A sodium fluoride trap is used to remove the hydrogen fluoride from the reaction products. By cooling or warming the compartments, they can be used to create a temperature gradient along the reaction tube. Because the products are highly fluorinated, they are usually volatile and tend to move through the reactor tube rapidly, depending on the temperature gradient. This provides a continually renewed surface of reactant at the optimum temperature for fluorination. Fluorinated copper turnings effectively increase the surface area of the compound exposed to fluorine. The individual zones of the reactor may be cooled with various solvent–solid carbon dioxide or with solvent–liquid nitrogen slushes. Preferably, the temperature is precisely regulated with an automatic liquid nitrogen temperature controller. In addition to the four-zone reactor shown in Figure 5, a multizone reactor can also be used; an eight-zone reactor has been found to be particularly efficient (36). Internal Freon cooling is effective for controlling the temperatures of the various compartments (37).

Oxygen or moisture has to be excluded because the presence of oxygen leads to cross-linking, presumably with epoxy bridges, to carbonyl groups, which give acid fluorides, and to peroxides (38). Cross-linking obviously decreases the yield of pure perfluorocarbon. It can be detected by infrared absorption in the $1600 - 2000\ \text{cm}^{-1}$ region and by noting the polymeric nature of the products, ie, high melting points, low vapor pressures, etc. On the other hand, oxyfluorination is a technique offering unique possibilities for the functionalization of fluorocarbons and for the preparation of functional fluorocarbon membranes (39).

4.1. Aerosol-Based Direct Fluorination

A technology that works on liter and half-liter quantities has been introduced (40–42). This new aerosol technique, which functions on principles similar to LaMar direct fluorination (Fig. 5), uses fine aerosol particle surfaces rather than copper filings to maintain a high surface area for direct fluorination. The aerosol direct fluorination technique has been shown to be effective for the synthesis of bicyclic perfluorocarbon such as perfluoroadamantane, perfluoroketones, perfluoroethers, and highly branched perfluorocarbons.

4.2. Modern Direct Fluorination

Direct fluorination technology has been scaled up at Exfluor Research Corp. of Austin, Texas (21–24). The synthesis of perfluoroethers by this method is licensed to 3M Co. where it is practiced on a commercial (multiton) scale. Using direct fluorination it is possible to produce almost any desired fluorocarbon structure for which there is a hydrocarbon or organic structural precursor (22–24, 43). There are two basic approaches to controlling direct fluorination: the LaMar method where the rate of fluorine addition is the limiting factor, and the Lagow-Exfluor method in which the rate of addition of the hydrocarbon is the limiting factor. A highly effective solvent fluorination technology with rapid heat transfer has been developed on this principle by Exfluor Research Corp. Multikilogram quantities of new fluorocarbons are produced in yields ranging from 95 to 99% with this technology (21). This technique is capable of producing very high molecular weight perfluoro acids and diacids that are precursors for new fluorocarbon copolymers. This is accomplished rapidly and on a commercial scale with essentially no branching or rearrangement.

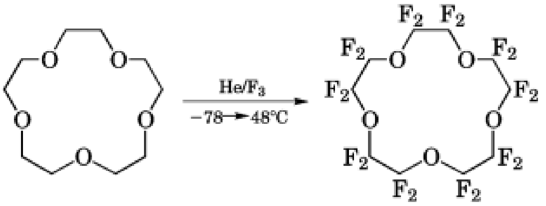
5. Applications

In 1954 the surface fluorination of polyethylene sheets by using a solid CO_2 cooled heat sink was patented (44). Later patents covered the fluorination of PVC (45) and polyethylene bottles (46). Studies of surface fluorination of polymer films have been reported (47). The fluorination of polyethylene powder was described (48) as a fiery intense reaction, which was finally controlled by dilution with an inert gas at reduced pressures. Direct fluorination of polymers was achieved in 1970 (8, 49). More recently, surface fluorinations of poly(vinyl fluoride), polycarbonates, polystyrene, and poly(methyl methacrylate), and the surface fluorination of containers have been described (50, 51). Partially fluorinated poly(ethylene terephthalate) and polyamides such as nylon have excellent soil release properties as well as high wettability (52, 53). The most advanced direct fluorination technology in the area of single-compound synthesis and synthesis of high performance fluids is currently practiced by 3M Co. of St. Paul, Minnesota, and by Exfluor Research Corp. of Austin, Texas.

The following companies manufacture organic fluorine compounds by direct fluorination techniques: 3M; Exfluor; Air Products and Chemicals, Inc., Allentown, Pennsylvania; MarChem, Inc., Houston, Texas; Ozark-Mahoning, Inc., Tulsa, Oklahoma; and PCR, Inc., Gainesville, Florida.

5.1. Simple and Complex Organic Molecules

Using modern direct fluorination technology, the synthesis of even the most complex perfluorocarbon structures from hydrocarbon precursors is now possible. For example, syntheses of the first perfluoro crown ethers, perfluoro 18-crown-6, perfluoro 15-crown-5, and perfluoro 12-crown-4 (54) have been reported. Perfluoro crown ethers (54, 55) are becoming important as the molecules of choice for many ^{19}F-nmr imaging applications (56) in humans and are particularly effective in brain and spinal diagnostics when

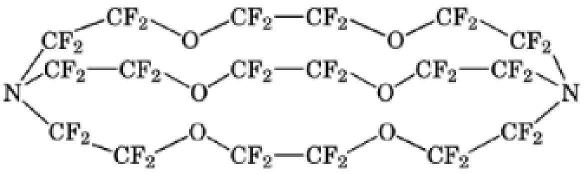


15-crown-5

perfluoro 15-crown-5

administered to the cerebrospinal fluid compartment. Synthesis scale-up of perfluoro 15-crown-5 (54, 55) and plans for commercialization are underway while research is being conducted on other biological applications of these new compounds (57). In collaboration with Air Products, excellent brain imaging scans have been obtained by infusing the perfluoro 15-crown-5 in spinal fluids. Toxicology reports on these are very favorable with essentially no toxic effects physiologically in several different animals.

Perfluoro crown ethers from the hydrocarbon dibenzo crown ethers have also been synthesized (58) and the first perfluorocryptand molecule [2.2.2] has been reported (59). The perfluorocryptand is a stable, inert, high boiling clear oil.



Hydrocarbon crown ethers coordinate cations; however, both the perfluoro crown ethers and the perfluorocryptands coordinate anions. For example, perfluoro crown ethers and perfluorocryptands tenaciously encapsulate O^{-}_2 and F^{-} (60, 61).

The first several perfluoro spiro compounds have also been synthesized (62). An example of this technology is the synthesis and crystal structure of perfluoro-1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane.

Many novel small molecule perfluoropolyethers have been made using direct fluorination technology. For example, even branched ethers such as perfluoro(pentaerythritol tetramethyl ether) can be prepared:

$$C(CH_2{-}O{-}CH_3)_4 \xrightarrow{F_2} C(CF_2{-}O{-}CF_3)_4$$

Very good low temperature fluids are obtained by direct fluorination of trialkylorthoformates (63):

$$HC(OCH_2CH_3)_3 \xrightarrow{F_2/He} FC(OCF_2CF_3)_3$$

Perfluoropolyethers emerged on the market in the early 1970s; however, for the next 15 years there were only two basic structures known. The first perfluoropolyether was the homopolymer of hexafluoropropylene oxide produced by Du Pont having the structure

$$\left(CF_2{-}\underset{\displaystyle CF_3}{\underset{|}{CF}}{-}O \right)_n$$

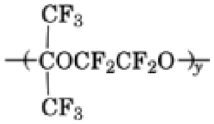
Du Pont called this new lubricant material Krytox (64, 65) and initially it had such extraordinary properties that it sold for \$200/kg (\$187kg ca 1993). Krytox was and is used in most of the vacuum pumps and diffusion oil pumps for the microelectronics industry in this country and in Japan because it produces no hydrocarbon (or fluorocarbon) vapor contamination. It has also found important applications in the lubrication of computer tapes and in other data processing applications as well as military and space applications.

Materials similar in high temperature properties to the Du Pont material with better low temperature properties have been synthesized using direct fluorination. The first was produced by reaction of fluorine with inexpensive hydrocarbon polyethers such as poly(ethylene oxide). In the simplest case, poly(ethylene oxide) is converted to the perfluoroethylene oxide polymer:

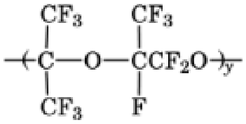
$$HO{\left(CH_2CH_2O \right)}_nH \xrightarrow{F_2/He} R_f(OCF_2CF_2)_nOR_f$$

This simple reaction chemistry was first reported in 1978 (66).

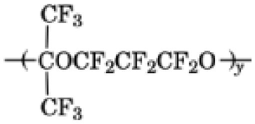
Other interesting perfluoro ether structures can be obtained by copolymerization of hexafluoroacetone with ethylene oxide, propylene oxide, and trimethylene oxide with subsequent fluorination to yield the following structures (67):



$$-\!\left(\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{C}}OCF_2CF_2O \right)_{\!y}\!-$$



$$-\!\left(\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{C}}-O-\overset{\displaystyle CF_3}{\underset{\displaystyle F}{C}}CF_2O \right)_{\!y}\!-$$



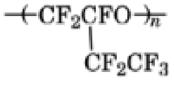
$$-\!\left(\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{C}}OCF_2CF_2CF_2O \right)_{\!y}\!-$$

Two of the perfluoropolyether fluid structures yet to be commercialized are interesting. The first structure is a strictly alternating copolymer of ethylene oxide and methylene oxide, which has the longest liquid range of any molecule containing carbon (40). The second structure is the perfluoromethylene oxide polyether which has low temperature liquid properties down to $-120^\circ C$:

$$-\!\left(CF_2O-CF_2CF_2O \right)_{\!n}\!-$$

$$-\!\left(CF_2O-CF_2-O \right)_{\!n}\!-$$

Other perfluoropolyether structures that have been synthesized are (24, 43)



$$-\!\left(CF_2\underset{\displaystyle CF_2CF_3}{C}FO \right)_{\!n}\!-$$

$$-(\mathrm{CF_2}\underset{\underset{\mathrm{CF_2Cl}}{|}}{\mathrm{C}}\mathrm{FO})_n-$$

5.2. Hydrocarbon Polymers

It is difficult to produce perfluorocarbon polymers by the usual methods. Many monomers, such as hexafluoropropylene, polymerize only slowly because of the steric hindrance of fluorine. Furthermore, some monomers are not very stable and are difficult to synthesize. Direct fluorination can be used for the direct synthesis of fluorocarbon polymers (68–70) and for producing fluorocarbon coatings on the surfaces of hydrocarbon polymers (8, 29, 44–47, 49, 68–71).

Thus fluorocarbon polymers can be produced with chemical compositions similar to polytetrafluoroethylene by the direct reaction of fluorine with polyethylene and the perfluoro analogues of polypropylene and polystyrene can be prepared. These fluorocarbon polymers differ from the more familiar linear structures because carbon–carbon cross-linking occurs to a significant extent during fluorination. Most of these fluoropolymers are white solids with high thermal stability; some are stable in air as much as 200°C above the ignition temperatures of their corresponding hydrocarbon precursors. Hydrocarbon polymers such as polyethylene and the new surfaces formed by direct fluorination have been studied by esca which shows that the surface is truly converted to a fluorocarbon polymer (72). Most of these fluorocarbon surfaces are inert and many of them have good lubricant properties. The fluorination of PVC has been followed with esca and $(\mathrm{CF}_x)_n$ polymer was also identified (73).

5.3. Surface Fluorination of Polymers

Fluorocarbon-coated objects have many practical applications because the chemically adherent surface provides increased thermal stability, resistance to oxidation and corrosive chemicals and solvents, decreased coefficient of friction and thus decreased wear, and decreased permeability to gas flow. Unusual surface effects can be obtained by fluorinating the polymer surfaces only partially (74).

5.4. Natural and Synthetic Rubber

Fluorination of natural or synthetic rubber creates a fluorocarbon coating (29, 75, 76) which is very smooth and water repellent (see Water, waterproofing and water/oil repellency). Rubber articles such as surgical gloves, O-rings, gaskets, and windshield wiper blades can be fluorinated on the surface while the interior retains the elastic, flexible properties of the natural rubber. Fluorinated O-rings can be used without extra lubricant in corrosive atmospheres since the fluorocarbon is unreactive. In food-processing equipment, grease or lubricants are eliminated and do not contaminate the food products. Fluorinated O-rings have smooth surfaces, very low frictional coefficients, and enhanced thermal stabilities. Fluorinated windshield wiper blades have a very low coefficient of friction, run smoother with less squeak, their surface is more resistant to the sun's uv radiation and attack by ozone, and they require less electrical energy for operation.

Many applications of this technique are apparent in medicine, such as surgical rubber gloves, rubber sheets, drain tubes, catheters, etc. Since talcum or other lubricating powder often used with surgical gloves can cause allergic reactions, thin powderless gloves are desirable. Teflon or silicone films have proved unsuccessful for surgical gloves. However, an excellent direct fluorination process has been developed (76) whereby the inside surface is fluorinated under expanded conditions at elevated temperatures. A very smooth surface is obtained and powder is not required. At the same time, the outside surface remains rough so that surgical instruments can be held firmly without slippage. The tactile sensitivity of the tips of the fingers seems to be increased, and the problem of powder forming lumps or a mud-like slush inside the glove is eliminated.

5.5. Blow-Molded Containers

A surface-fluorination process (Airopak) has been developed by Air Products & Chemicals for the blow-molding industry to produce solvent-resistant polyolefin containers. In this application, the air that is normally used to blow-mold containers is replaced by a low concentration of fluorine in nitrogen. Airopak containers produced by this process show outstanding resistance to nonpolar solvents (50, 51, 77, 78) and such blow-molding fluorination procedures have been widely used for the last 10 years by Ford Motor Co. and many European auto manufacturers to produce low cost–high performance gas tanks for cars and trucks. A similar technology is now practiced by Fluoroseal, Inc. (Houston, Texas). This group has generated a successful product line based on post-treating containers and other objects with elemental fluorine.

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