

Organic hypofluorites and their new role in industrial fluorine chemistry

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Abstract

In this work a historical background of the synthesis and chemistry of fluorinated organic hypofluorites is given and some of the known applications of this class of compounds are reviewed.

Recently, new industrial processes based on hypofluorite chemistry have been developed for the production of a variety of fluoromonomers. These processes are all based on the addition of hypofluorites having different structures to fluorinated olefins. Some mechanistic features of this key reaction are discussed, in terms of reactivity and stability of the intermediate primary radicals deriving from homolytic cleavage of the hypofluorite bond.

Various aspects of these new processes are described and, in the light of these recent achievements, it is shown how hypofluorite chemistry has acquired great importance as a powerful and versatile methodology for the production of fluoromonomers of prominent industrial interest. © 1999 Elsevier Science S.A. All rights reserved.

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1. Background

Since the discovery of the first organic hypofluorite by Cady and coworker [1], considerable attention has been dedicated to this class of compounds and many fundamental articles and excellent reviews have been written in the course of the time [2–8]. In the first years after this discovery however, the interest mainly remained in the area of fundamental chemistry.

In the 1960s, research and industrial applications in the hypofluorite chemistry were driven by their potential utility in the rocket propellant technology [9–13].

The real break-through in the synthetic methodology for the preparation of organic hypofluorites has been the fluorination of carbonyl compounds in presence of cesium fluoride as catalyst, established by Ruff and Lustig [14]. The feasibility of this method and the variety of fluorinated carbonyl and carboxyl compounds available, increased the purity and the number of organic hypofluorites isolated from that moment on, allowing the synthesis of not only monofunctional derivatives, but also of difunctional hypofluorites in essentially quantitative yields [15]. This was the case for $\text{CF}_2(\text{OF})_2$, whose synthesis has been simultaneously and independently reported by Shreeve and coworkers [16,17] using the cesium fluoride technology and by Thomp-

son [18] through direct fluorination of trifluoro-acetic salts in very low yield.

In the chemistry of organic hypofluorites, the reaction with molecules containing a carbon–carbon double bond is one of the most important from a synthetic and mechanistic point of view. In 1967 Schuman et al. [19] extended the use of this reaction for the preparation of fluorocarbon vinyl monomers having a pendent trifluoromethoxy group, with the aim to develop new fluoroelastomers.

Starting from Cady and Schuman's pioneeristic experiments this particular reaction has been extensively studied. In spite of the great number of papers and recent reviews now available in the literature, this subject is still a matter of investigation and stimulating discussion. In many cases the reaction mechanism of hypofluorites with olefins remains uncertain, since there are evidences to support both free-radical and electrophilic pathways. This is mainly due to polar and steric factors that operate together and often in opposite directions to determine the regio and stereo chemistry of the products.

In the first addition of CF_3OF to olefins Allison and Cady [20] suggested a free-radical pathway mainly due to the uncontrollable nature of the reaction. Lately Barton et al. [21] proposed an electrophilic mechanism for the fluorination of electron-rich olefins with trifluoromethyl hypofluorite, based on the regiochemistry of the addition, rearrangements and incorporation of the solvent. The electrophilic fluorination with CF_3OF and different reagents was

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reviewed by Hesse [6], and more recently, by Rozen [2], who gave an ample view of the possibility of the electrophilic fluorination reactions methodology. In general, electron-rich olefins, polar solvent, low concentration, low temperature and sometimes aerobic conditions are used to encourage electrophilic reactions and suppress fluorine radical processes [22–24].

The industrial application of these studies was dictated by the need to find a more versatile and safer substitute for perchloryl-fluoride, in order to avoid its low reactivity with nucleophiles, and contemporarily, eliminate potential hazard connected with the formation of chlorate salts. Initially, the use of hypofluorites was applied to the synthesis of fluorinated steroids and, lately, many different fluorinated organic compounds were prepared through this methodology [2].

From the industrial point of view, the battle against perchloryl-fluoride is still open, since every year new effective fluorinating agents are identified [25]. Among them, one of the most studied and probably the best candidate up to now, seems to be fluorine itself, as shown by Hesse, Burton, Rozen and lately by Chambers [26,27], in the fluorinations of aromatics in solvents as polar as pure sulfuric or formic acid.

From the mechanistic point of view, the possibility to observe different pathways in the reaction involving hypofluorites led to an interesting and vivid debate on the positively polarized fluorine in hypofluorite compounds [28] and on their reaction mechanism with olefins and aromatic compounds [2–8].

Based on the comparison of the reaction of CF_3OF and CF_3OCl with a number of alkenes, Johry and DesMarteau

[29] suggested that the results from CF_3OCl were consistent with a polar mechanism, while those with CF_3OF were more consistent with a homolytic mechanism.

Levy and Sterling [30] studied the reaction of fluoroxy-trifluoromethane with ring-substituted styrenes. They pointed out that this reagent only apparently acts as a source of fluorine cation. The authors proposed a different and more complete reaction scheme, taking into account the weakness of the oxygen–fluorine bond in CF_3OF ($44.7 \text{ Kcal mol}^{-1}$ [31]), the low polarity of CF_3OF [32], the O–F bond polarization where the fluorine atom is more negative [33], and the high difference in electronegativity between the radicals probably formed in the solvent cage [34].

The hypothesized mechanism suggests the initial formation of a spin-paired radical couple that can undergo different reactions as shown in Scheme 1.

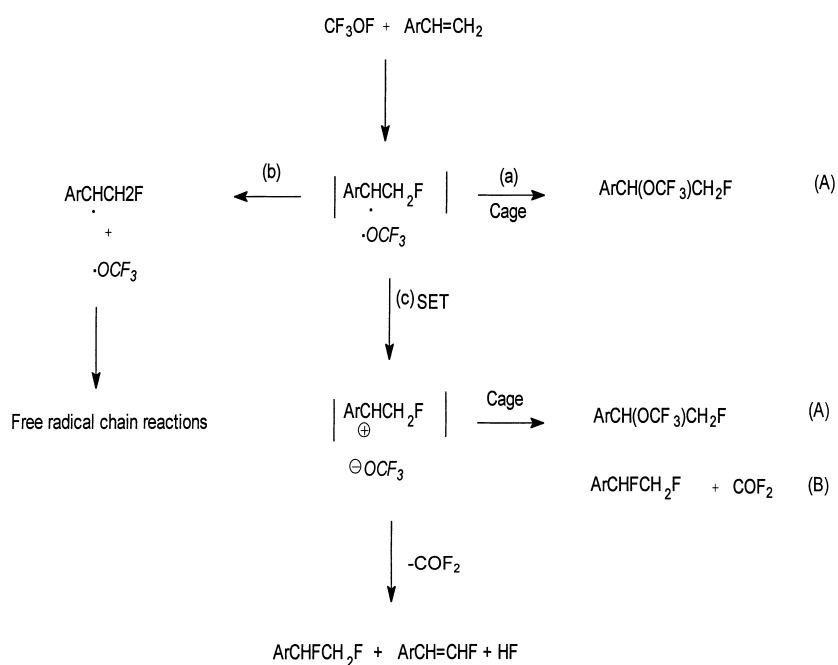
The spin-paired radicals may undergo:

1. cage reactions to give the adduct (A),
2. diffusion out of the cage with subsequent free-radical chain reactions, and
3. electron transfer to give an ion pair.

The ion pair is shown to react in the cage or after diffusion out of the cage.

This general mechanism has been lately considered by Mukhametshin [3] in his last review and applied to a large variety of compounds.

This apparently complex mechanism gives rise to the regio and stereo chemistry of the compounds formed in these reactions through a highly probable pathway, between electron rich olefins and strong oxidizing com-



Scheme 1.

pounds, characterized by a very weak bond like hypofluorites.

These observations introduce to the concept that diffusion out of the cage by incipient radicals and consequent chain reactions is favorable with electron deficient olefins.

This hypothesis has been experimentally proved through the EPR and ENDOR spectra of the alkylradical intermediates in the reaction of electron depleted and hindered perfluoroalkenes with hypofluorites [35,36].

In the late 1980s the availability of the ^{18}F acetyl hypofluorite for the preparation of 2-deoxy-2- ^{18}F fluoro-D-glucose, generated interest for the direct measurement of the glucose metabolism in some human pathology using the positron emission tomography (PET) [37].

Very recently, compounds with O–F bonds have earned interest in connection with the ozone depletion problem. The potential existence of F, FO, and FO₂ in the earth's atmosphere suggested the possible presence of atmospheric ozone depletion cycles based on these species. Experimental studies on this hypothesis led to the conclusion that catalytic cycles involving F, OF, and OF₂ are irrelevant with respect to the chlorine cycle [38–40].

Although this problem is not directly connected with any industrial products deriving from the hypofluorite technology, a better knowledge of this chemistry is useful to give an important answer to a worldwide anxiety. In the meanwhile a better view of the whole problem has been used to design and develop a new family of environmental-friendly fluorinated solvents [41,42].

2. Introduction to hypofluorites as industrial reagents

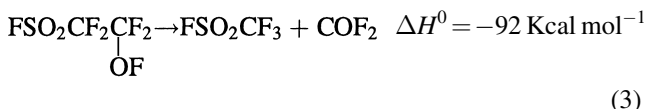
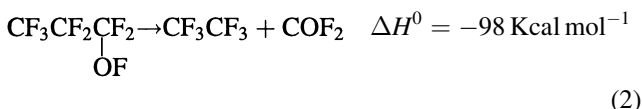
One of the major issues in the industrial development of the hypofluorite chemistry is directly connected to the high reactivity of this class of compounds, requiring strict safety precautions.

Based on the literature, as well as on the experience developed in Ausimont laboratories, the organic hypofluorites should always be regarded as potentially explosive [4,15,43–45].

This tendency to auto-decomposition is generally observed with all the hypofluorites, with the unique exception of the stable CF₃OF. However, also in this case fires and explosions can occur on contact with organic reagents. This is generally due to: low energy of the O–F bond, high oxidizing power, high-energy content and high reactivity.

These compounds are often considered as elemental fluorine analogues, but when compared to elemental fluorine, which is perfectly stable, they are intrinsically unstable and may self-decompose upon simple contact with organic impurities, metal surfaces and hot spots generated in the reaction vessels, as shown by the very exothermic decomposition reactions: reaction (1) [85], reactions (2) and (3)

[46]



To overcome this general problem precise safety precautions must be taken in handling these compounds.

The proper choices in this area has determined the Ausimont success in mastering and developing this technology up to the industrial scale, as well as contribute to the high safety standard in laboratories and plants.

Decreasing the reaction volume, either in laboratory plants or pilot plants, is one of the key rules adopted in Ausimont. In these fast reacting systems, the quantity of reactants per unit time is minimized and contemporarily it is possible to have a better control of the reaction variables such as temperature, heat evolution and reactant concentrations.

Some other important rules, suggested also in the specialized literature [4], should be taken into account. High dilution of the hypofluorite with inert fluids is normally necessary. Contact with hydrogenated materials and with unpassivated metal surfaces, as well as storage of any hypofluorite must be avoided.

In small, discontinuous scale experiments the storage is reduced to a few grams in a carefully fluorine passivated SS316 vessel at pressure below 1 atm.

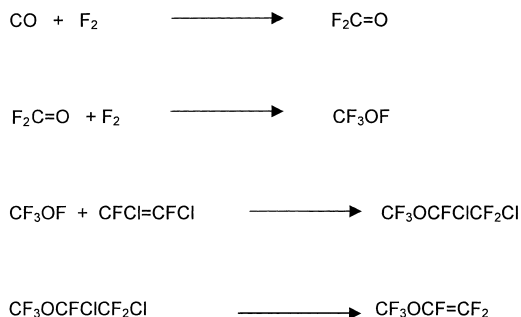
3. The Ausimont hypofluorite development

The hypofluorites: CF₃OF, CF₃CF₂CF₂OF, CF₂(OF)₂, (CF₃)₂C(OF)₂, CF₃OOCF₂OF and FSO₂CF₂CF₂OF have been largely studied in Ausimont, in terms of synthesis, stability and reactivity and are herein considered.

3.1. CF₃OF and CF₃CF₂CF₂OF

Fluoroalkyl ethers have high synthetic value as intermediates for the preparation of fluorovinylethers monomers as well as CFC's alternative solvents, fire-extinguishing and heat exchange fluids.

However, the preparation of alkyl trifluoromethyl ethers is difficult, and only a few synthetic routes are known. The standard method, i.e. the addition of alcohols to olefins, is not feasible because CF₃OH is unstable, except at low temperature, and the poor yield and variety of compounds generated by electrochemical fluorination or halogen-exchange make unpractical these methodologies [47–49]. Aldrich and Sheppard prepared alkyl trifluoromethyl ethers



Scheme 2.

by treating fluoroformates with sulfur tetrafluoride, but their method is limited only to stabilized starting material [50].

A more complete approach is the addition of trifluoromethyl hypofluorite, CF_3OF , to olefins [29].

Partly based on research that showed that CF_3OF could be added to a variety of alkenes, Ausimont has developed commercial processes utilizing perfluoroalkyl-hypofluorites R_fOF as intermediates for the preparation of fluorinated vinyl ethers $\text{R}_f\text{OCF}=\text{CF}_2$ **1** [51,52].

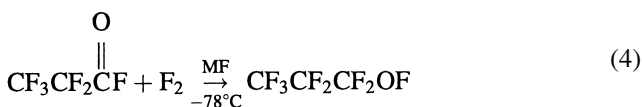
One of the most valuable compounds obtained at Ausimont with an industrial process based on CF_3OF , is perfluoromethylvinylether, $\text{CF}_3\text{OCF}=\text{CF}_2$. It is synthesized, in high yields (about 80%), following a four-step preparation as shown in Scheme 2.

In the reactions between CF_3OF and an olefin, the latter is usually present in liquid phase. Preferably, it is dissolved in solvents, such as chlorofluorocarbons, perfluorocarbons and perfluoropolyethers.

In laboratory scale experiments, the CF_3OF can be added all contemporarily into the liquid phase, already containing the olefin and the solvent. Preferably, the gaseous CF_3OF is diluted with an inert gas like N_2 , He or Ar. The reaction temperature is usually kept between -110°C and -50°C ; in these conditions the addition product is obtained in very good yield.

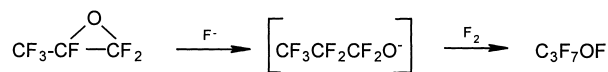
Similarly to $\text{CF}_3\text{OCF}=\text{CF}_2$ the synthesis of the perfluoropropylvinylether has been studied and developed up to industrial scale through the hypofluorite $\text{CF}_3\text{CF}_2\text{CF}_2\text{OF}$.

Prager and Thompson [53] prepared this hypofluorite for the first time in 1964 by direct fluorination of 1,1-dihydroperfluoropropanol under mild conditions. In this reaction the yield was quite low, and numerous side products were formed. In 1966 Ruff et al. [54] prepared $\text{C}_3\text{F}_7\text{OF}$ in 97% yield by the catalyzed fluorination of perfluoropropionyl fluoride in static system (reaction (4)):



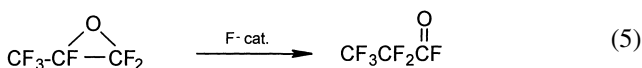
M=K, Rb, Cs.

Perfluoropropionyl fluoride can be obtained by reaction of hexafluoropropene oxide (HFPO) with catalytic amount



Scheme 3.

of fluoride ion (reaction (5)):



We have found that also the direct fluorination of HFPO in the presence of a catalytic amount of alkali metal fluorides leads to the formation of $\text{C}_3\text{F}_7\text{OF}$ in almost quantitative manner (Scheme 3):

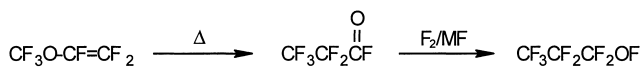
Even though $\text{CF}_3\text{CF}_2\text{CF}_2\text{OF}$ has been known for many years, no data on its boiling point have been reported in the literature. The vapor pressures were measured and the experimental points (between -110°C and -55°C) were used to determine the equation: $\ln P_{(\text{mbar})} = 16.35 - 2564/T$. The calculated boiling point is -9°C , and the Trouton's constant has a normal value of $21.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ [55].

In Ausimont, a particular two-step preparative synthesis of $\text{C}_3\text{F}_7\text{OF}$ has been adopted and developed on industrial scale. The first step consists in the preparation of perfluoropropionyl fluoride through pyrolysis of perfluoromethylvinylether [56], as shown in Scheme 4.

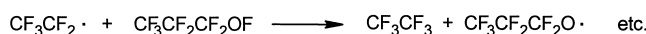
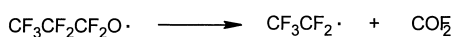
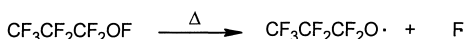
The reaction conditions for the fluorination process in the synthesis of $\text{C}_3\text{F}_7\text{OF}$ (second step in Scheme 4) must be chosen very carefully because of the possible thermal decomposition of the hypofluorite formed. In fact, higher perfluoroalkyl hypofluorites, as well as $\text{CF}_3\text{CF}_2\text{CF}_2\text{OF}$, are less thermally stable than CF_3OF .

A distinctive behavior of the thermal decomposition of higher perfluoroalkyl hypofluorites, is the free radical chain pathway of this reaction.

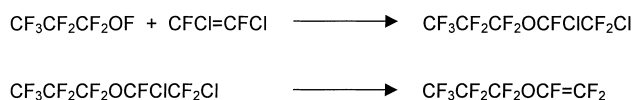
It depends on the tendency of the intermediate alkoxy radical to homolitically cleave the C–C bond, forming a fluorocarbon radical which abstract fluorine from the starting perfluoroalkyl hypofluorite, thus propagating the decomposition reaction as shown in Scheme 5.



Scheme 4.



Scheme 5.



Scheme 6.

Because of this tendency, inadequate control of the reaction conditions frequently leads to extensive decomposition of the starting hypofluorite¹.

A commercial process based on $\text{C}_3\text{F}_7\text{OF}$ is the production of perfluoropropyl vinyl ether as shown in Scheme 6.

In the first step of the synthesis, represented by the addition reaction of $\text{C}_3\text{F}_7\text{OF}$ to the olefin, the yield is largely influenced by the reaction conditions. The yields in this step are very acceptable, while the analysis of the by-products supports the decomposition pathway shown in Scheme 5. In fact, the major by-products of the reaction are COF_2 (40–50% based on the starting hypofluorite), $\text{CF}_2\text{ClCF}_2\text{Cl}$, CF_3CF_3 and $\text{CF}_3\text{OCFCICF}_2\text{Cl}$.

The presence of $\text{CF}_3\text{OCFCICF}_2\text{Cl}$ is due to the reaction between CF_3OF and the olefin. CF_3OF is generated during the synthesis of the hypofluorite by the fluorination reaction of COF_2 , which in turn is generated by the decomposition of $\text{CF}_3\text{CF}_2\text{CF}_2\text{OF}$ (see Scheme 5).

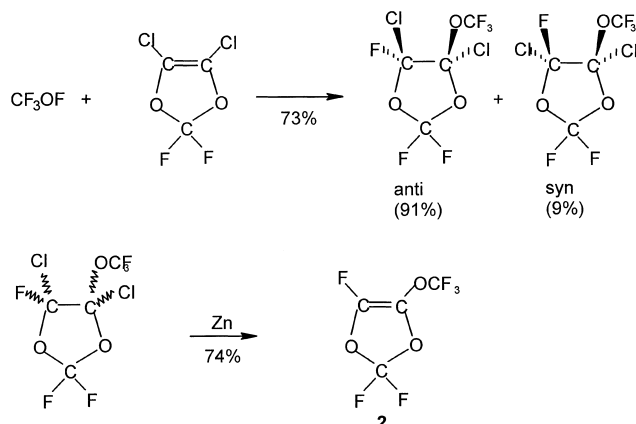
The quantity of this by-product can be maintained within 4% of the reaction products through an accurate tuning of the experimental variables in the synthesis of the hypofluorite.

Therefore, by simply monitoring COF_2 and $\text{CF}_3\text{OCFCICF}_2\text{Cl}$ by-products at the end of the production scheme, it has been possible to optimize both the synthesis of the hypofluorite and its reaction with the olefin.

Perfluorovinylethers ($\text{R}_f\text{OCF}=\text{CF}_2$), such as (**1**), are an important class of monomers [60–62] that are used in thermoplastic fluoropolymers as well as in fluoroelastomers [61].

Recent advances in this area include development of amorphous perfluoroplastics [63–68], some of these materials can be obtained by random copolymerization of perfluoro-1,3-dioxoles with TFE [62].

Recently, Ausimont has developed a commercial process, based on the hypofluorites technology for the production of a wide variety of 2,2-difluoro-1,3-dioxolanes [85] and per-



Scheme 7.

fluorodioxoles [69,70,94–96]. Among these compounds, the 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (**2**) is of particular importance also because of its reactivity properties and convenient preparation [69,70]. One of its possible preparation method is based on the addition of CF_3OF to 4,5-dichloro-2,2-difluoro-1,3-dioxole as shown in Scheme 7.

In this synthesis the stereoselectivity for the addition reaction of CF_3OF to 4,5-dichloro-2,2-difluoro-1,3-dioxole leads to the formation of the anti-isomer as the major product (see Scheme 7). This high stereoselectivity is quite unusual for the addition reaction of CF_3OF to alkenes, especially to electron poor ones, because of the operating free radical reaction mechanism [29].

It is important to note that in the addition of CF_3OF to dichlorodioxole the fluorination products of the starting dioxole are always present among the reaction products in a molar amount between 5% and 15%. Also this fluorination reaction has a certain degree of stereoselectivity, leading to 4,5-dichloro-2,2,4,5-tetrafluoro-1,3-dioxolane with an isomeric syn/anti ratio of 68/32.

These results can be hardly accounted for simply considering a free radical mechanism, but they can be better explained by the coexistence of both free radical and polar mechanism, based on a SET pathway (Scheme 8).

The free radical mechanism gives rise to the anti-addition of the CF_3OF to dichlorodioxole and the SET mechanism gives an excellent explanation for the fluorination of dioxole. Otherwise it would be necessary to accept the highly improbable homolytic cleavage of a carbon fluorine bond in the alkoxy radical $\text{CF}_3\text{O}^\bullet$.

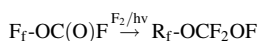
The anti-addition of CF_3OF , is more probably due to an *out-cage* reaction and the *syn* fluorination to an *in-cage* reaction [Scheme 8 pathways (b) and (c)].

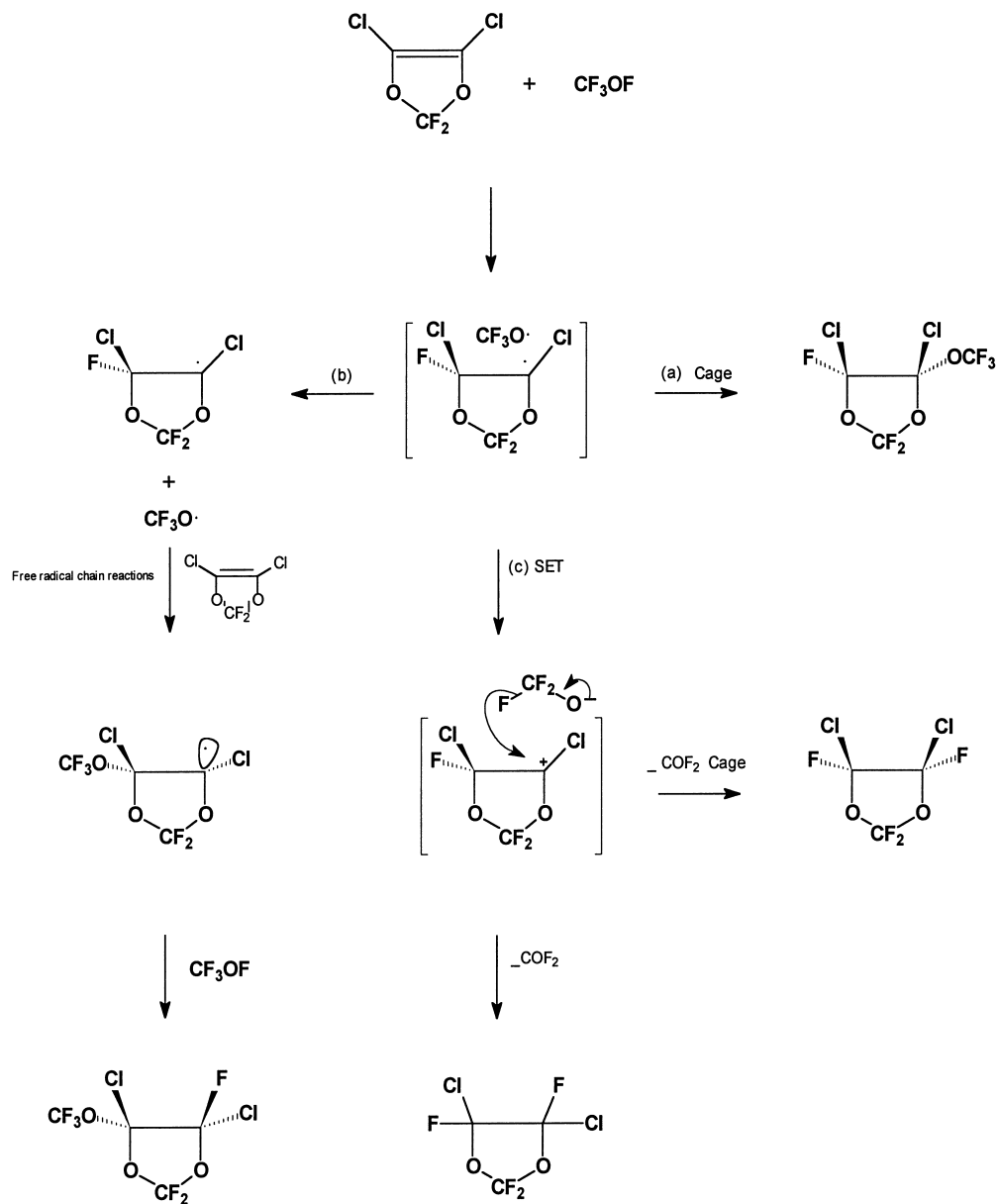
The radical addition mechanism of hypofluorite to electron poor haloolefins has been supported by kinetic studies of the gas-phase thermal reaction (from +20°C to +75°C) between CF_3OF with hexafluoropropene [71–74] and trichloroethene [75].

¹Note 1: Generally, the stability of the perfluoroalkyl hypofluorites decreases by increasing the length of the alkyl chain [4], one interesting exception to this rule is represented by the hypofluorites of general formula $\text{R}_f\text{OCF}_2\text{OF}$ where R_f can also be a perfluoropolyether segment.

This class of hypofluorites is more stable than the respective perfluoroalkyl hypofluorites due to the low tendency of the alkoxy radical $\text{R}_f\text{OCF}_2\text{O}^\bullet$ to give homolytic β -scission to R_f and COF_2 , due to the higher energy of the C–O bond compared to the C–C bond.

Actually, this particular class of hypofluorites is prepared from fluoroformates under photolytic conditions in presence of elemental fluorine, as shown as follows [57–59]





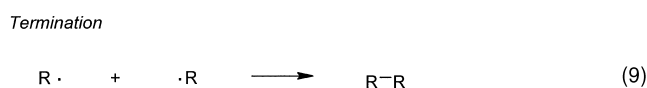
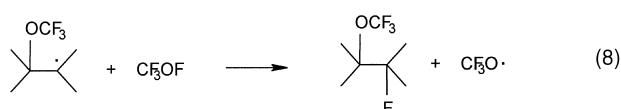
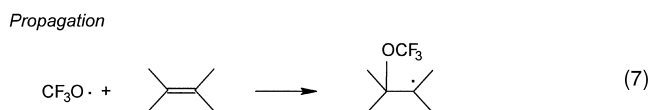
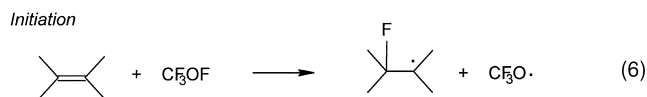
Scheme 8.

Very recently, the hypothesis of a free-radical mechanism has been strongly reinforced. The addition reactions of CF_3OF to chloro fluoro olefins have been studied in solution at low temperatures (-78°C and -105°C), and their relative rate constants have been determined using the kinetic approach of competition reactions [76]. The reactivity, the regio, and stereoselectivity were consistent with a free radical chain-propagating mechanism (Scheme 9).

According to this pathway, the addition of CF_3OF is initiated by the bimolecular reaction between CF_3OF and alkene (reaction (6)), and the chain-terminating step is a recombination of two radicals (reaction (9)). The radical chain seems to be quite long since the analysis of the reaction products showed in all runs only traces of the possible termination products. The electrophilic character

of the $\text{CF}_3\text{O}^\bullet$ radical was evident considering both the regiochemistry and the relative rate constants for the addition to some alkenes, for example $\text{CH}_2=\text{CHF}$, $\text{CH}_2=\text{CF}_2$ and $\text{CHF}=\text{CF}_2$. The trend is in agreement with the data previously reported by Tedder and co-workers [77] for the strongly electrophilic CF_3^\bullet radical. In fact, for both radicals $\text{CF}_3\text{O}^\bullet$ and CF_3^\bullet , the overall addition rate decreases by decreasing the electron density of the olefin through the progressive increase of the number of fluorine atoms on the double bond.

A further proof for the existence of such mechanism relies upon the recently reported observation and structural characterization of intermediate radicals by EPR and ENDOR techniques in the addition of CF_3OF to hexafluoropropene dimers and other perfluoroalkenes [35,36]. In these works



Scheme 9.

was shown that only radicals deriving from reaction (7) of the Scheme 9 are detectable at steady-state concentration during the reaction of CF_3OF and $\text{R}_f\text{OCF}_2\text{OF}$ with alkenes.

It is also important to note that the reactions between hypofluorites and many olefins are self-initiated even at very low temperature and that the hypofluorite acts as initiator and transfer agent simultaneously.

This is particularly useful with highly reactive fluoro-olefins like tetrafluoroethylene [78,79] and chlorotrifluoro-

ethylene [80–83], which can be easily polymerized and oligomerized with hypofluorites even at temperature as low as -80°C . The polymer so obtained is end capped by the stable $\text{CF}_3\text{O}-$ and F groups as pointed out by Cady and coworker [84] in his early works (Scheme 10).

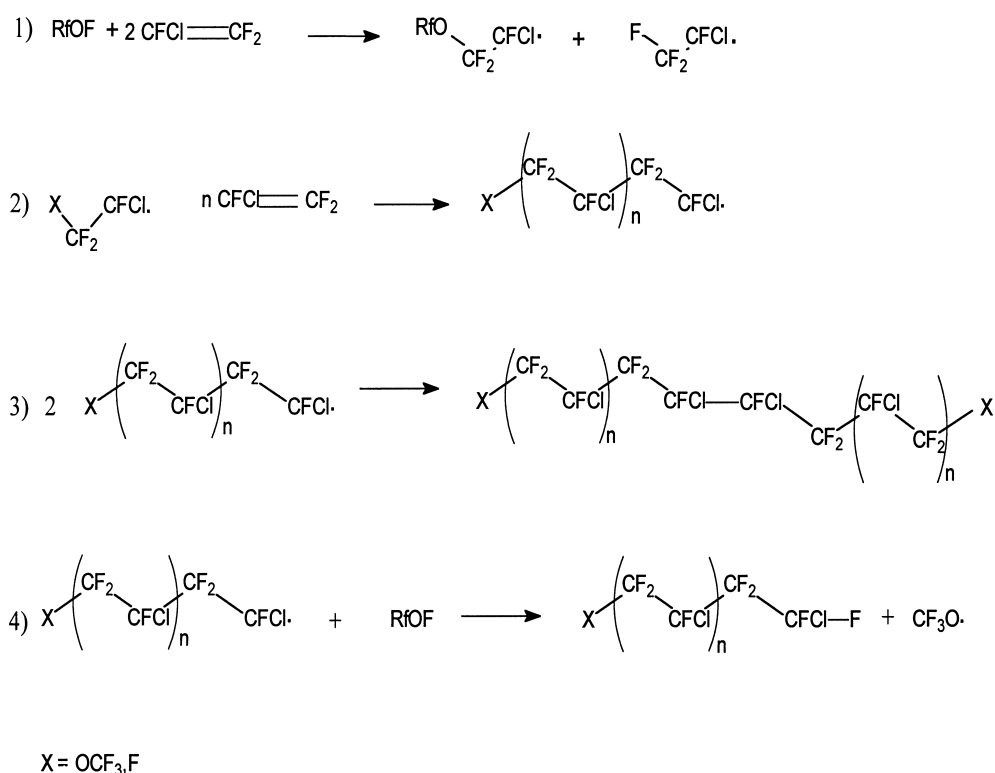
Accordingly, this method could be regarded as a useful tool for the preparation of highly stable fluoro-polymers. However, since the hypofluorites have a great tendency to transfer a fluorine atom to the growing radical, this initiation system has been mainly exploited for the preparation of oligomers and telomers.

The radical nature of the intermediates involved in these reactions is also supported by evidence of reaction inhibition when oxygen is present in the system. A few per cent of oxygen is very effective to stop the polymerization and to inhibit the addition of hypofluorites to fluoro-olefins [85].

By increasing the oxygen content in the reacting mixture the oxygen itself can act as comonomer in the polymerization of fluoro olefins: at low temperature and with perfluoro-olefins like $\text{CF}_2=\text{CF}_2$ and $\text{CF}_2=\text{CFCF}_3$, the reaction proceeds to form a more complex oligomeric and random peroxidic polyether structure [86–90].

These peroxidic polyether materials are industrially transformed into stable, low boiling perfluoropolyethers (PFPEs) through the removal of their peroxidic links [59].

PFPEs inert fluids obtained through the hypofluorite technology have lower molecular weight as compared to those obtained from the well-known perfluoroolefins photo-



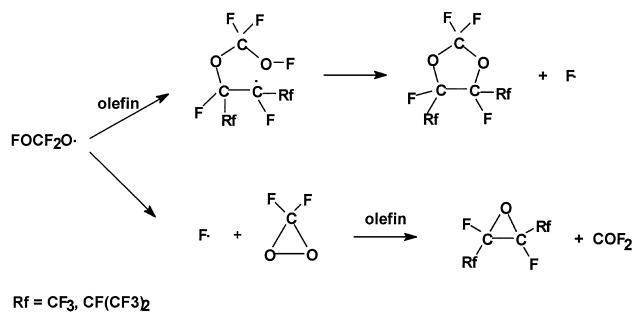
Scheme 10.

Some experimental evidences support the radical nature of this reaction. The reaction is inhibited by oxygen. In the final mixture small amounts of by-products deriving from the β -scission of carbon–chlorine bond of the radical intermediates (in the case of chlorinated olefins), are always present. Moreover traces of coupling products, coming from the termination step, have been detected by GLC/mass spectroscopy.

The reaction is common to different carbon–carbon double bonds and is quite versatile: the substituents on the double bond of the olefin will be the substituents in 4,5 positions of the dioxolane. Olefins like tetrachloro, trichloro, dichloro ethylenes, 1,2 dichlorodifluoroethylene, chlorotrifluoroethylene, hexafluoropropene, perfluoroalkyl vinyl ethers give the related dioxolanes in good yields (50–90% based on BDM moles). The stereochemistry of the addition is not dependent on the geometry of the starting olefin: this further supports the radical step by step mechanism, where the rotation of the C–C bond in the intermediate (**a**) accounts for the observed diastereoisomeric end-product ratio.

Internal and cyclic perfluoroalkenes are less reactive or unreactive at all, to give dioxolanes. Octafluoro 2-butene and perfluoro 4-methyl-2-pentene (the kinetic dimer of hexafluoropropene) require higher temperatures (close to room temperature) to react with BDM [85], both the conversion and the dioxolane yield are low (28% yield for 61% conversion and 5% yield for 81% conversion, respectively). However, in the presence of fluorine or UV light as radical initiator, the reaction proceeds at lower temperature and with better yield (34% and 43%, respectively). It is interesting to note that with these internal olefins, without UV initiation, the related oxirane becomes the main product of reaction [99]. BDM is not an epoxidating agent in condensed phase with reactive alkenes. On the other hand, difluorodioxirane has been demonstrated to be a good epoxidating agent both in gas and condensed phase [100]. We have made the hypothesis that the propagating $\text{FOCF}_2\text{O}^\bullet$ oxyradical, with these poorly reactive olefins (or even in the gas-phase with reactive olefins) by intramolecular elimination of fluorine gives difluorodioxirane, which then oxydizes the olefin to epoxide [85,99] (Scheme 13).

Cyclic perfluoro alkenes do not give dioxolanes with BDM either at room temperature or under UV irradiation. This behavior is in sharp contrast with the easy addition of CF_3OF to perfluorocyclobutene and pentene, and suggests



Scheme 13.

that the steric requirements for BDM addition play an important role with these particular alkenes.

Similarly to $\text{CF}_2(\text{OF})_2$, the addition of fluoroxydifluoromethyl trifluoromethyl peroxide $\text{CF}_3\text{OOCF}_2\text{OF}$ to fluoro-olefins, under controlled conditions, leads to 1-3 dioxolanes as well as to the simple addition products of the O–F function across the double bond [101], as shown in Scheme 14.

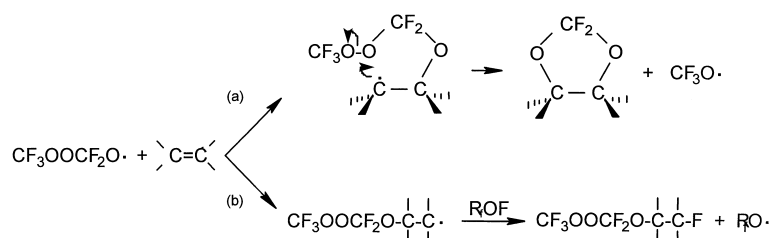
The reaction proceeds to linear addition external-transfer product at lower temperature (b), and to dioxolane internal-transfer product at higher temperature (a). This is probably due to the higher energy of the oxygen–oxygen bond as compared to the O–F bond, and to a different concentration of the hypofluorite in the solution.

Dioxolanes are important intermediates for the synthesis of 1,3-dioxoles [59,102,103], which are key monomers for the access to the last generation of perfluorinated material.

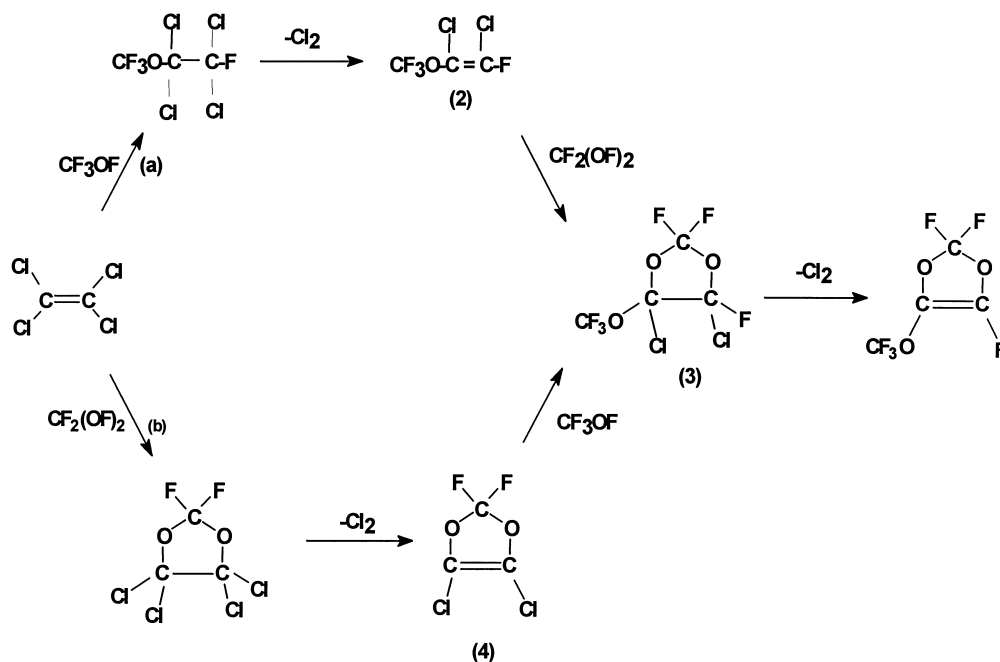
Ausimont has studied and commercially developed the production of some monomers of this class [102,103], in particular of 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD) [69,70,99,104]. This monomer is obtained by a multi-step, versatile process which starts from easily available chloroethylenes, and utilizes alternating addition steps of CF_3OF and BDM interspersed with elimination reactions.

In particular the four-step synthesis of TTD from tetrachloroethylene is reported in Scheme 15.

Two routes are available, depending on the first addition of CF_3OF (a) or $\text{CF}_2(\text{OF})_2$ (b) to the starting olefin. Route (a) leads to the intermediate 2-trifluoromethyl-1-fluoro-1,2-dichloro vinyl ether (**2**), after the standard addition of CF_3OF to tetrachloroethylene and dechlorination of the product (81% and 83% yield, respectively). As we have previously pointed out [14] the addition of BDM to olefins is



Scheme 14.



Scheme 15.

non-stereospecific: this has been further confirmed during the addition to (2) (1/1 *cis/trans* mixture) which leads to a 67/33 ratio of *erithro* and *threo* stereoisomeric dioxolanes (3) (yield: 66%).

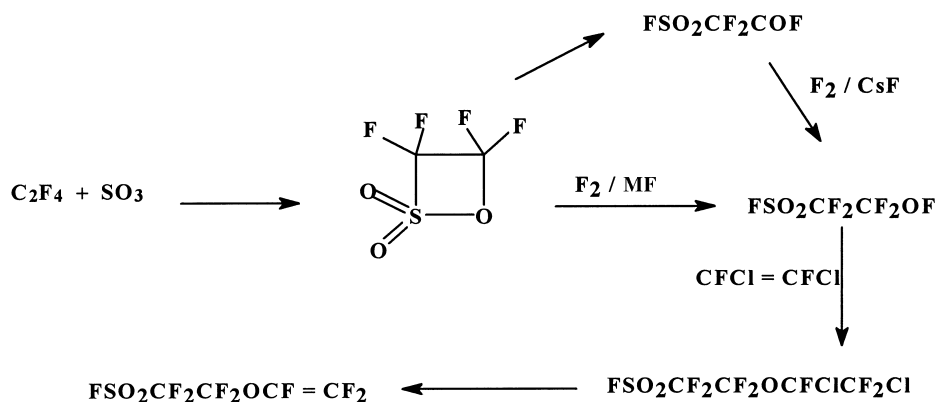
In route (b) the intermediate 2,2-difluoro-4,5-dichloro-1,3 dioxolane (4) is obtained by addition of BDM to tetrachloroethylene and dechlorination of the tetrachlorodioxolane (75% and 81% yield, respectively). The addition of CF_3OF to (4) gives the same dioxolane (3) as in route (a) but in a 9/91 *erithro/threo* ratio (66% yield). The next dechlorination step is not dependent on the stereochemistry of dioxolanes. In fact, the reaction proceeds as well in spite of the mutual position of the chlorine substituents. The stringent requirement of antiperiplanarity of chlorines to obtain dioxoles in good yield, as in the case of the 2,2,4,5-tetrafluoro-4,5-dichloro-1,3-dioxolanes is not necessary

[55,69,70,102,103], probably because of the stabilization of the intermediate carbanion by electron-inductive effect of the trifluoromethoxy substituent [104].

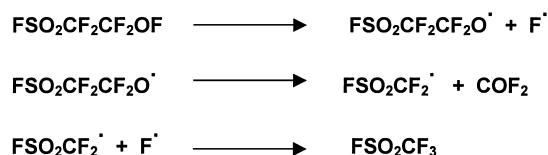
3.3. $\text{FO}_2\text{SCF}_2\text{CF}_2\text{OF}$

Fluorinated β -sulfones are readily formed by addition of sulfur trioxide to fluorinated olefins [105]. The isomerization of β -sulfones to α -fluorosulfonyl-fluoroalkyl acyl fluorides provides the starting intermediates to fluorosulfonic monomers, which are one of the best entry to functionalized polymeric materials [106–109], whose utility depends on their acidity, inertness to corrosive environments and permselectivity to ions.

The up-to-date Ausimont application of the chemistry of fluorinated hypofluorites is the synthesis of perfluoro-3-oxa-



Scheme 16.



Scheme 17.

5-fluorosulfonyl-pent-1-ene, a known monomer, but previously synthesized in a somewhat complex way [110–113] (Scheme 16).

The fluorosulfonyl hypofluorite can be synthesized by catalytic fluorination of either tetrafluoroethane- β -sultone or α -fluorosulfonyl difluoroacetyl fluoride [114–116].

The relationship between the vapor pressure (mbar) of this hypofluorite and the temperature (K) is given by the following equation [55]:

$$\ln P = 12.31 - 1810/T$$

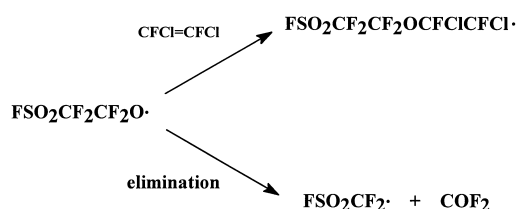
Its estimated boiling point is therefore $+63^\circ\text{C}$.

As any fluoroalkyl hypofluorite other than CF_3OF , it shows intrinsic thermal instability: pure samples decompose quantitatively in 10 min, at 10 Torr and 40°C , in the dark [116] (Scheme 17).

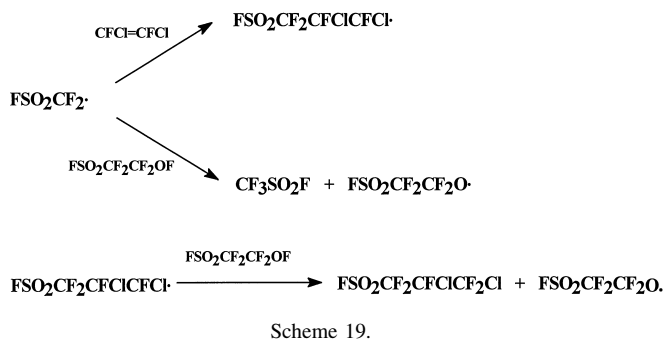
It is important to underline that the decomposition tendency of this hypofluorite over activated CsF or KF (also reported in the only scientific paper dealing with this compound [116]), can be overcome during its synthesis through the use of a carefully dimensioned flow system.

The addition of diluted fluorosulfonyl hypofluorite to fluoroolefins and particularly to 1,2-dichloro-difluoro ethylene, in the presence of solvents like chlorofluorocarbons, hydrofluorocarbons, perfluorinated alkanes or ethers, proceeds through a typical radical chain mechanism, similar to that outlined before for CF_3OF addition. However, in this case the propagating alkoxy radical can undergo an elimination of COF_2 instead of the expected addition to the olefin (Scheme 18).

The yield of the desired addition product $\text{FSO}_2\text{CF}_2\text{C-F}_2\text{OCFCICF}_2\text{Cl}$ is more than acceptable and depends on the experimental conditions. The distribution of products is very informative about the selectivity of the competing reactions. There are some by-products (about 5–8%) containing the $\text{FSO}_2\text{CF}_2\text{CF}_2\text{O-}$ group derived from usual side reactions of radical species, like adducts containing one chlorine atom less or more than expected ($\text{FSO}_2\text{CF}_2\text{C-}$



Scheme 18.



Scheme 19.

$\text{F}_2\text{OC}_2\text{F}_4\text{Cl}$ and $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OC}_2\text{F}_2\text{Cl}_3$) and telomers of the olefin ($\text{FSO}_2\text{CF}_2\text{CF}_2\text{O}(\text{CFCICFCl})_n\text{F}$, $n=2,3$).

Another set of compounds contains the FSO_2CF_2- moiety, the prevalent being $\text{FSO}_2\text{CF}_2\text{CFClCF}_2\text{Cl}$ (about 5%). This compound was not expected on the basis of previous experimental data concerning the addition of heptafluoropropyl hypofluorite to the same olefin. During the addition reaction, both hypofluorites give substantial β -scission associated with the formation of low boiling material, like $\text{CF}_3\text{SO}_2\text{F}$ and C_2F_6 , but, in the latter case, the radical $\text{CF}_3\text{CF}_2^\cdot$ does not add to the olefin as observed in the case of the $\text{FSO}_2\text{CF}_2^\cdot$ radical (Scheme 19).

The β -scission reaction during addition actually accounts for the majority of the decomposed hypofluorite. Further work to minimize side reactions and to improve the yield of the desired fluorosulfonic adduct is in progress.

4. Conclusions

During the last two decades fluorine chemistry has continuously grown in terms of scientific contributions, as well as in the variety of innovative technologies and applications.

Contrary to this general trend, the fascinating and promising hypofluorite chemistry, after a first rapid growth in the 1960s and 1970s, mostly due to military and pharmaceutical applications, practically ceased, probably because of the difficulties encountered with hypofluorites manipulation.

Only recently, also thanks to the work done in Ausimont and in other laboratories where this chemistry never declined, organic hypofluorites are being considered a family of versatile and important industrial intermediates for the preparation of a large variety of products.

In many cases the use of hypofluorite chemistry allows to establish a straightforward technology for the synthesis of highly innovative fluoromonomers suitable for the preparation of sophisticated fluoropolymers.

The latest find their emerging applications in many industrial strategic areas which include electronics, automotive, optics, aeronautical, membranes and coatings.

To day achievements are indeed a solid base for further developments of this chemistry and its applications.

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