



The use of perfluoroalkyl hypofluorites for an efficient synthesis of perfluorinated ethers characterized by low Ostwald coefficient

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ABSTRACT

In the reaction between perfluoroolefins and perfluoroalkylhypofluorites the existence of two different free radical reaction mechanisms is demonstrated by the presence of characteristic byproducts. These kinetic schemes can be experimentally controlled by tuning the hypofluorite concentration in the reaction media.

In particular, in the reactions between trifluoromethyl hypofluorite and highly reactive perfluoroolefins like $\text{CF}_2=\text{CFOCF}_3$ and $\text{CF}_2=\text{CF}_2$, the free radical oligomerization and dimerization products can be suppressed by utilizing the opportune experimental conditions.

The pure perfluorinated ethers obtained, having low Ostwald coefficient, can be utilized as contrast agents for diagnostic ultrasound imaging injectable microbubbles composition.

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1. Introduction

Perfluoroalkylhypofluorites are important intermediates utilized in the industrial process for the preparation of fluorinated key monomers like perfluoroalkylvinylethers [1] sulfonic-perfluoroalkylvinylethers [2] cyclic vinyl ethers monomers [3] as well as catalyst for fluoroolefins oxidations [4]. The addition reaction of hypofluorite to halogenated olefins has been studied in the previous years [5,6], kinetics studies of the free radical reaction in gas-phase [7] as well as in condensed phase have been analysed in detail [8,9]. Hypofluorites are also an important source of electrophilic fluorine and these reagents are utilized in specific and selective fluorination [10,6].

The majority of studies on perfluoroalkyl hypofluorites utilized the CF_3OF due to its kinetic stability compared to longer chain perfluoroalkyl hypofluorites perfluoro propionyl hypofluorite.

On the other hand, as pointed out in previous publications, all perfluoroalkyl hypofluorite are thermodynamically unstable [2]. In our previous studies, we have noticed that the concentration of hypofluorite in the reaction media is an important variable to control the course of the main reaction. In particular in the reaction with bis-fluoroxydifluoromethane BDM and tetrafluoroethylene

TFE, conducted in high excess of BDM, we observed the substantial absence of polymeric products deriving from TFE monomer [1]. This observation prompted us to study the addition of highly reactive fluoroolefins to perfluoromethyl hypofluorite taking into account the concentration of the hypofluorite in the reaction media. This experimental approach allowed the identification of a straight and economical methodology for the preparation of highly pure perfluoroethers having low boiling point and low Ostwald coefficient [11]. These perfluoroethers have been recently tested as fluids for the preparation of injectable microbubbles composition as contrast agents in diagnostic ultrasound imaging [12]. In many ultrasound imaging applications there is the need for contrast agents and efforts to develop suitable materials are ongoing. Gaseous micro bubbles that are effective contrast agents tend to shrink rapidly due to gas diffusion in the liquid media, therefore microbubble stability is an important issue in this application [13]. Low solubility of the gas in blood stream has been shown to be an important factor in gas microbubble stability and dimension. Industrial attention has recently focused on perfluoroethers biocompatible gases characterized by low water solubility [12].

2. Discussion

The synthetic methodologies adopted utilize the availability of highly pure perfluoromonomers $\text{CF}_3\text{OCF}=\text{CF}_2$ and $\text{CF}_2=\text{CF}_2$ as

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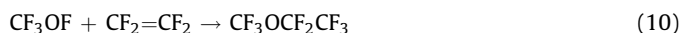
starting material. The addition of CF_3OF to fluoroolefins for the synthesis of fluoroethers has been already investigated and it has been recognized as a fast free radical chain reaction propagated by the radical CF_3O [2,9,14] and its reaction mechanism is summarized in Scheme 1 below.

We have studied the reaction between the hypofluorite CF_3OF with the olefin $\text{CF}_2=\text{CFOCF}_3$ and $\text{CF}_2=\text{CF}_2$.

The main products of the addition of CF_3OF with $\text{CF}_2=\text{CFOCF}_3$ were perfluoro-1,1-bis-(methoxy)-ethane (**L**) and perfluoro-1,2-bis-(methoxy)-ethane (**K**) in the molar ratio of 20% to 80%, respectively, as shown in reaction (9) below:



The main products of the addition of CF_3OF to $\text{CF}_2=\text{CF}_2$ was perfluoro 1-methoxy-ethane as shown in reaction (10) below and depending on the reaction condition a big amount of polymeric products were also present, see Section 4.4.2:



In the reaction mixture we have specifically looked for the presence of the termination products deriving from reaction (5) to (8) of Scheme 1. The termination products are normally found at very low concentrations in the reaction media. Therefore, it was possible to detect and analyse them only when they were substantially different from the main reaction products in terms of molecular weight, allowing separation or a substantial purification from the crude mixture by distillation. Interestingly termination products distribution and nature depends on the experimental conditions adopted in carrying out the reaction trials.

The termination product CF_3OOCF_3 deriving from reaction (6) of Scheme 1 was clearly present in the reaction where the CF_3OF concentration was maintained always above zero, on the contrary in this experimental condition the termination product $\text{C}_8\text{F}_{18}\text{O}_4$ deriving from the reactions (8) was completely absent. In this condition also the oligomerization and polymerization of the perfluoroolefins were substantially suppressed, also in the case of the very reactive TFE, see Section 4.4.3 for details.

These experimental conditions are characterized by the presence of hypofluorite during the addition reaction and can be performed by adding the olefin to the hypofluorite, these conditions herein referred as “reverse hypofluorite addition” are

different from the standard methodologies described in the literature where the hypofluorite is added to the olefin.

The standard addition methodology herein referred as “direct hypofluorite addition” where the olefin concentration was maintained always above zero, is characterized by the presence of olefin during the addition reaction and can be performed by adding the hypofluorite to the olefin. The termination product $\text{C}_8\text{F}_{18}\text{O}_4$ deriving from reaction (8) of Scheme 1 was observed only when the reactions of CF_3OF with $\text{CF}_2=\text{CFOCF}_3$ was conducted in the “direct hypofluorite addition” condition. Generally this experimental choice is mainly due to safety reasons since the perfluoroalkyl hypofluorites are thermodynamically unstable and may undergo to self-decomposed [2].

2.1. “Direct hypofluorite addition”

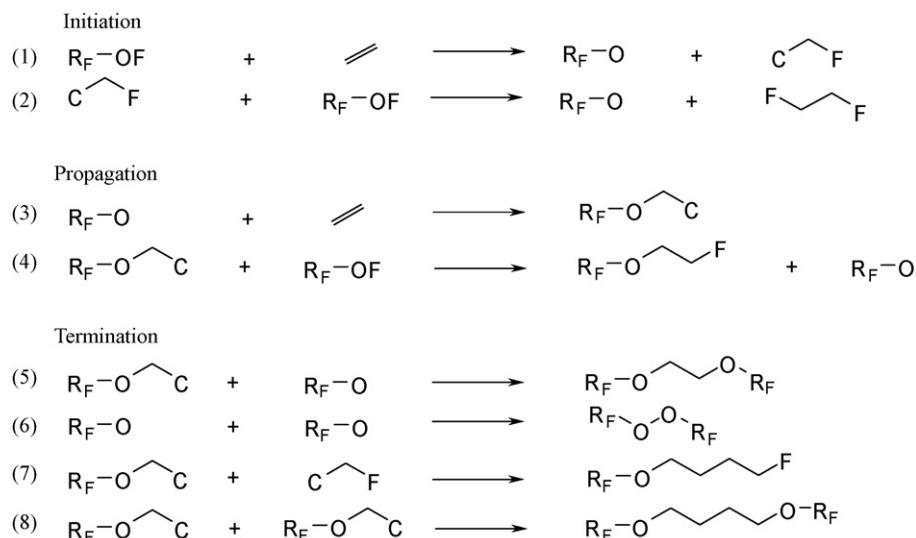
In this experimental set we have observed the presence of termination products deriving from the reaction (8) of Scheme 1. In the reaction mixture traces of CF_3OOCF_3 were also present, but this compound was also prepared from CF_3OF and carbonyl fluoride [15]. In fact traces of CF_3OOCF_3 were also observed when a stream of crude CF_3OF was bubbled through a perfluorinated solvent in absence of olefin. Therefore, we consider the occurrence of CF_3OOCF_3 as impurity already present in the reagent CF_3OF and not due to reaction (6). Moreover, in the “reverse hypofluorite addition” described in Section 2.2 below, the amount of CF_3OOCF_3 increased compare to the amount present in the “direct hypofluorite addition”. It is also important to observe that when adopting the “reverse hypofluorite addition” the termination products deriving from reaction (8) of Scheme 2 were completely absent.

In the “direct hypofluorite addition”, due to the starvation of CF_3OF in the reaction media, we have supposed the presence of a relatively high concentration of the radical (*E*) deriving from the propagation reaction (3) shown in Scheme 2.

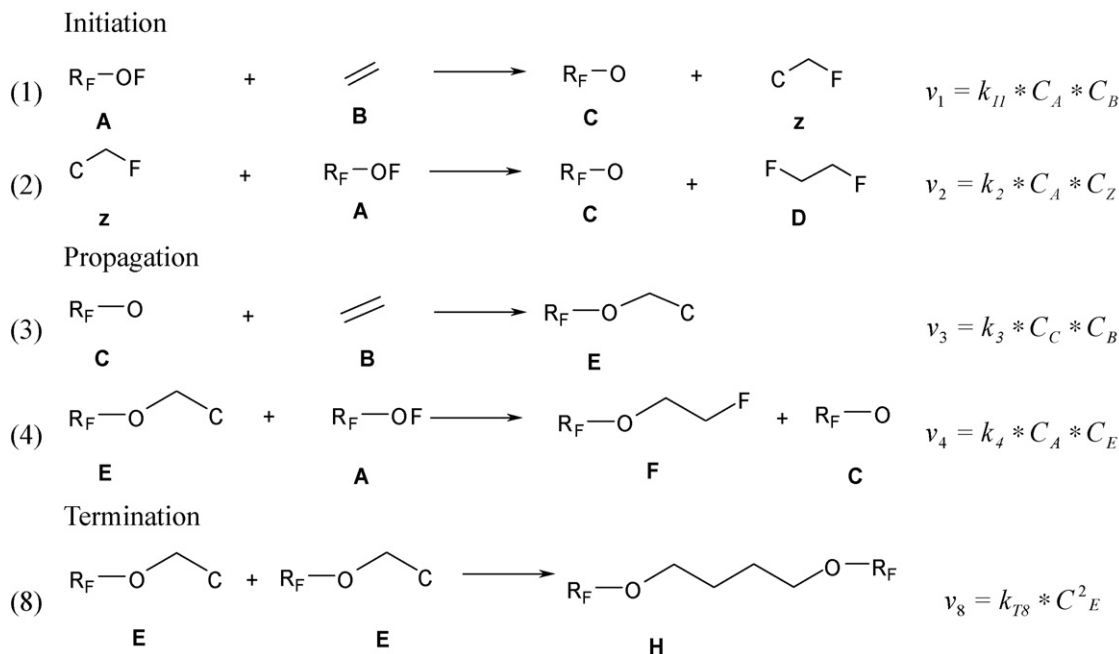
This is in agreement with the experimental finding where the termination products derive substantially from the reaction (8) when adopting the “direct hypofluorite addition” procedure.

Based on the above experimental finding, the mechanism of Scheme 1 can be simplified for the kinetic of the “direct hypofluorite addition” as shown in Scheme 2.

Since in the reaction between CF_3OF and $\text{CF}_2=\text{CFOCF}_3$ there are two possible, but not equal addition sites of the CF_3O on the olefin,



Scheme 1. Free radical pathway for the reaction of perfluoroalkyl hypofluorites $\text{R}_\text{F}\text{OF}$ with olefin $\text{C}=\text{C}$.



Scheme 2. Free radical pathway for the “direct hypofluorites addition” of perfluoroalkyl hypofluorites R_FOF to olefin $\text{C}=\text{C}$.

we assume that the two radical species **I** and **J** of Fig. 1, deriving from propagation step (3) of Scheme 2, are present in the “direct hypofluorite addition” procedure.

The radical species **I** and **J** following reaction (8) of Scheme 2 combine giving the terminating chain products **P**, **Q** and **O** deriving from the reactions (11a), (11b) and (11c) are shown:

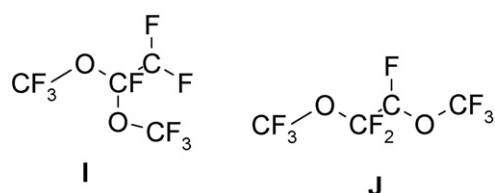
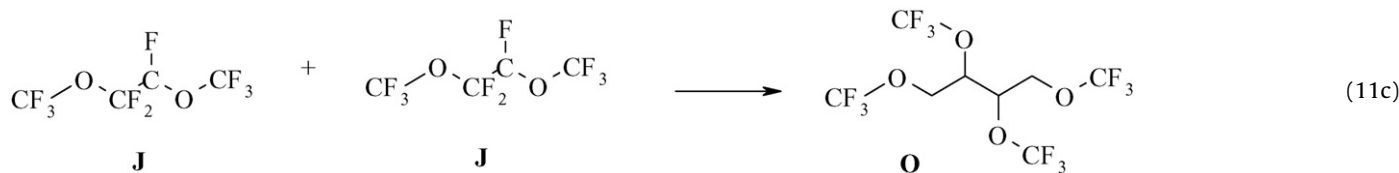
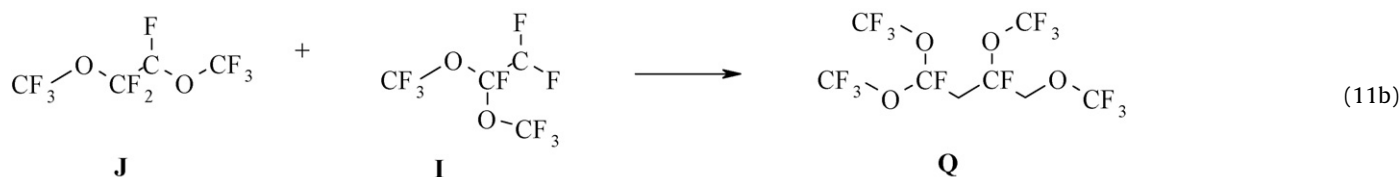
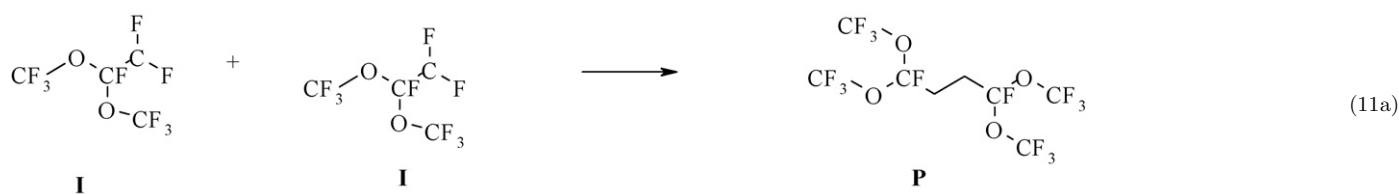


Fig. 1. Radical **I** and **J** deriving from the addition of radical CF_3O to $\text{CF}_2=\text{CFOCF}_3$.

Reactions (11a), (11b), (11c) and regiochemistry of the termination reaction (8) of Scheme 2 when the hypofluorite is CF_3OF and the olefin is $\text{CF}_3\text{OCF}=\text{CF}_2$.

Since the termination reaction (8) generates high molecular weight products, those can be concentrated by distillation of the low boiling products and then detected at higher concentration in the residue of distillation. In addition we have not observed any oligomerization of the vinyl ether, this can be predicted since perfluorovinylether do not homopolymerize especially at temperature as low as -70°C . In the reactions products the molar ratio

Eq. Set (3). Applied to the “reverse hypofluorite addition” of olefin C=C to perfluoroalkyl hypofluorites R_FOF in the steady state hypothesis.

In particular, equation (Eq. (II)) below describes the consumption rate of the perfluoroolefins in the “reverse hypofluorite addition” methodology:

$$\frac{d}{dt} [=] \approx -k_3 \sqrt{\frac{k_{11}}{k_{76}}} \sqrt{[R_FOF]} \sqrt{[=]}^3 \quad (\text{II})$$

3. Conclusions

Analysis of the products present in the reaction between CF_3OF and $CF_2=CFOCF_3$, including the termination products, confirmed the mechanisms proposed for two different experimental addition methodologies. In the “direct hypofluorite addition”, where the CF_3OF concentration was close to zero, dimeric like products or oligomers were present in the crude reaction mixture. In the “reverse hypofluorite addition”, where the fluoroolefin concentration was close to zero, dimeric like products or oligomers of the fluoroolefins were absent and the peroxide CF_3OOCF_3 was the unique termination product. This experimental approach allowed the identification of a straight and economical methodology for the preparation of highly pure perfluoroethers having low boiling point and low Ostwald coefficient.

4. Experimental

4.1. Safety

Based on the literature data [18] organic hypofluorites should be always regarded as potential explosives. For safety reasons CF_3OF was diluted with helium in a molar ratio of 1/1. Any contact between hypofluorites and the operator must be avoided; the reactors and the hypofluorite plant must be perfectly sealed and located in a dedicated area. More information regarding the toxicity and handle information of these chemical categories are available in the literature [2,19]. In particular information on the toxicity of the volatile termination product CF_3OOCF_3 have been recently reported [20]. The aggressive volatiles CF_3OF and CF_3OOCF_3 , due to their low boiling point, can be directly eliminated through the vent of the reaction mixture at the end of the reaction.

4.2. Methods

- The synthesis of CF_3OF was carried following a modified procedure described in the literature [16] using an under-stoichiometric amount of fluorine in order to avoid the presence of byproducts induced by the presence of fluorine. Depending on the relative amounts of reagents it can take about 30 min for reaching the steady state. The preparation and reactions of CF_3OF were realized in a continuous S.S. laboratory scale apparatus equipped with on line GC/TCD, 8 m PTFE + Kel-F oil packed column and on line Thermo Nicolet 380 FT-IR, PTFE gas-phase cell with CaF_2 windows, volume 8 cm³, length 10 cm.
- Reagents $CF_3OCF=CF_2$, $CF_2=CF_2$, $CFCl=CFCl$ and solvent $CF_2Cl-CFCl-CFCl-CF_2Cl$ were purchased from Solvay Solexis and utilized without any further purification.
- Off-line volatile compounds were handled assuming ideal gas behaviour in a glass and/or stainless-steel system equipped with glass/PTFE or stainless-steel valves. Pressures were measured with an Endress + Hauser transducer PMP 131-A3B01A2N coupled with an Endress + Hauser RIA 250 digital display.

- Off-line IR spectra of the purified mixture of isomers has been obtained on a Thermo Nicolet 380 FT-IR with a glass made gas-phase cell, volume 56 cm³, length 10 cm, equipped with KBr windows and filled with less than 5 mbar of product.
- ¹⁹F NMR spectra were recorded on a Bruker AV 500 MHz spectrometer; chemical shifts are expressed as δ values with neat $CFCl_3$ as an internal reference (ppm = 0).
- Mass spectra were performed on a Varian Mat CH-A spectrometer in the electron impact mode at ionization energy of 70 eV.

4.3. Direct hypofluorite addition

4.3.1. General procedure

The “direct hypofluorite addition” procedure consists of bubbling a stream of hypofluorite into a solution of the olefin maintained at the desired temperature in a semi-batch method in order to operate in excess of olefin. The addition reactor is standard dimensions designed 250 ml AISI 316 cooled by an external vessel. The reactor is realized with a discharge bottom valve and two feeding tubes. The reactor's head is equipped with: an outgoing tube for collecting the off-gas stream and a mechanical/magnetic transmission stirring system. The feed of the addition reactor and the off-gases are analysed on-line via IR, GC-TCD and GC-IR. At the end of the addition the reactor has been stripped with 4 nL/h of helium for about 30 min, the vessel is unloaded and the resulting mixture has been analysed via GC, GC-MS e NMR ¹⁹F. The raw reaction mixture has been distilled in vacuum or at atmospheric pressure.

4.3.2. Reaction of CF_3OF with $CF_2=CFOCF_3$

The addition reaction is operated in a semi-batch technique, 120 g of a solution containing 50% of $CF_3OCF=CF_2$ (MVE) in $CF_2Cl-CFCl-CFCl-CF_2Cl$ are introduced in the reactor as described in Section 4.3.1 above. The mixture into the addition reaction is cooled at the temperature of -80 °C. The charged reactor has been fed with a stream containing CF_3OF 2.3 nL/h, He 2.5 nL/h and COF_2 0.4 nL/h. for about 3 h.

During the reaction time it has been observed the presence of $CF_3O-CF_2-CF_3$ in the off-gases by on line GC-IR analysis, this product derive from the initiation reaction (1) and (2) of Scheme 2, this product has been also recognized by NMR ¹⁹F as traces in the volatile fraction after distillation [21].

The raw mixture contains the solvent $CF_2Cl-CFCl-CFCl-CF_2Cl$, the main products **L** and **K** in the ratio $L/K=4$, the unreacted $CF_3OCF=CF_2$ and dimeric like products ($C_8F_{18}O_4$) deriving from reaction (8) of Scheme 2, these products are also described in literature [16]. Selectivity of the reaction defined as moles of the addition products **L** + **K** over moles of reacted alkene is 94%.

Characterization of $CF_3OCF_2CF_2OCF_3$ and $(CF_3O)_2CF_2CF_3$: The linear product **L** and the ramified **K** have very similar S.B.P. Therefore, they have been characterized as one pseudo compound. Standard boiling point 19.9 ± 0.5 °C.

Antoine equation parameters:

$$\begin{aligned} A &= -4754.5159 \\ B &= +1227925345.2414 \\ C &= -258557.7393 \end{aligned}$$

$$P^s = 10^{(A - (B/(T + C)))} [\text{bar}] T [K].$$

Enthalpy of vaporization evaluated at the boiling point 30.2 ± 0.1 kJ/mole.

Entropy of vaporization evaluated at the boiling point = 103.2 J/mole ± 0.6 J/(mole K).

The entropy of vaporization has been calculated following the Trouton's rule. ($\Delta S_{ev} = R \ln(P_{vap}/P_{ref}) + \Delta H_{ev}/T_{ev} = \Delta H_{ev}/T_{ev}$).

^{19}F NMR (**L**): δ -57.8 (s, 6F, $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_3$), -92.7 (m, 4F, $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_3$).

^{19}F NMR (**K**): δ -57.1 (s, 6F, $(\text{CF}_3\text{O})_2\text{CFCF}_3$), -88.3 (d, 3F, $(\text{CF}_3\text{O})_2\text{CFCF}_3$), -102.6 (m, 1F, $(\text{CF}_3\text{O})_2\text{CFCF}_3$).

MS m/z (rel. int.): 135(6), 119(30), 97(4), 69(100), 50(6), 47(5).

IR (cm^{-1}) of the mixture **L** 80%, **B** 20%: 1291 (s), 1251 (s), 1199 (m), 1167 (s), 1153 (s), 1128 (m), 1102 (w).

4.3.3. Reaction of CF_3OF with $\text{CF}_2=\text{CF}_2$

The reactor is charged with about 176 g of PFPE Galden[®] LS155 (b.p. 155°C) and cooled to -100°C . A gaseous stream constituted of $\text{CF}_2=\text{CF}_2$ (TFE) 3 nL/h and He 3 nL/h, has been fed until 18.0 g of TFE are condensed in the reactor, the gaseous stream of TFE is then stopped. Subsequently a stream constituted by CF_3OF 1.8 nL/h, He 4.0 nL/h, has been fed in the addition reactor for 1 h.

The raw reaction mixture contains the solvent, the product $\text{CF}_3\text{OCF}_2\text{CF}_3$ and a complex mixture of polymeric and oligomeric byproducts. The characterization data of the ether $\text{CF}_3\text{OCF}_2\text{CF}_3$ match with the data available in the literature [21]. Selectivity defined as moles of the addition products over moles of reacted alkene is 48%.

4.4. Reverse hypofluorite addition

4.4.1. General procedure

The “reverse hypofluorite addition” procedure consists of bubbling a stream of olefin into a solution of the hypofluorite in order to operate in excess of hypofluorite at the desired temperature.

The reaction is carried in the CSTR described in Section 4.3.1 with a continuous feed of both the reagents.

The reactor is charged with the solvent, cooled at the desired temperature and a gaseous stream consisting of CF_3OF (2.35 nL/h), He (2.5 nL/h), COF_2 (0.3 nL/h) is fed in the reactor for about 12 min before starting to add the olefin. After adding the olefin, for safety reasons it is compulsory to eliminate the residual hypofluorite before opening the reactor. In order to remove the majority of the overloaded hypofluorite from the bulk, the liquid phase has been stripped with an stream of 4 nL/h of helium for about 30 min at the temperature between -80 and -90°C , after that maintaining the temperature in the range -80 to -90°C about 2 ml of $\text{CFCl}=\text{CFCl}$ have been added in the reactor to eliminate the remaining traces of hypofluorite. The traces of CF_3OF react completely with $\text{CFCl}=\text{CFCl}$ producing $\text{CF}_3\text{O}-\text{CFCl}-\text{CF}_2\text{Cl}$ [22].

4.4.2. Reaction of $\text{CF}_2=\text{CFOCF}_3$ with CF_3OF

In the reactor are introduced 60 g of $\text{CF}_2\text{Cl}-\text{CFCl}-\text{CF}_2\text{Cl}$ as solvent and cooled at -80°C . After the CF_3OF saturation period of 12 min a pure stream of gaseous of $\text{CF}_3\text{OCF}=\text{CF}_2$ (2.21 nL/h) is also feed in the reactor, the molar ratio between the reagents $\text{CF}_3\text{OCF}=\text{CF}_2$ and CF_3OF is 0.94/1. The reaction is carried on for 4 h. During the reaction time it has been observed in the off-gas the presence of the lightweight termination and initiation byproducts.

Those products **G** and **D** have been also found in the reaction raw mixture and have been recognized respectively as $\text{CF}_3\text{OOFCF}_3$ [23–25] and $\text{CF}_3\text{O}-\text{CF}_2-\text{CF}_3$ [21] from data available in the literature. It is important to note that products **P**, **Q**, **O** described in Section 4.3.2, are completely absent in the reaction mixture.

Selectivity defined as moles of the addition products **L** + **K** over moles of reacted alkene is 98%.

4.4.3. Reaction of $\text{CF}_2=\text{CF}_2$ with CF_3OF

The reactor is initially filled with about 176 g of PFPE Galden[®] LS155 (b.p. 155°C) and cooled to -100°C . After a saturation period of 12 min with CF_3OF (2.0 nL/h), He (4.0 nL/h) a gaseous stream constituted by $\text{CF}_2=\text{CF}_2$ (1.8 nL/h) and He (2 nL/h) is also introduced in the addition reactor, both gaseous stream are maintained for 3 h, the molar ratio between TFE and CF_3OF is 0.90/1. After interrupting the reagent flow, the liquid phase, maintained at a temperature of -90°C , has been stripped for 30 minutes with 4.2 nL/h of helium. During the reaction time it has been observed evidences for the formation of the products **G** ($\text{CF}_3\text{OOFCF}_3$) deriving from termination step 6) of Scheme 3.

The raw reaction mixture contains the solvent, the product $\text{CF}_3\text{OCF}_2\text{CF}_3$ and only traces of $\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_3$.

Selectivity defined as moles of the addition products over moles of reacted alkene is 99%.

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