



Review

Recent developments in the chemistry of organic perfluoro hypofluorites



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ABSTRACT

Recent findings in the synthesis of perfluoro-hypofluorites, their reactivity and their use in the preparation of important perfluoro monomers are herein summarized and analyzed. The experimental conditions to induce free radical or electrophilic reactivity as well as their use as initiation system in the oxidation and oxypolymerization of fluorinated olefins are also presented.

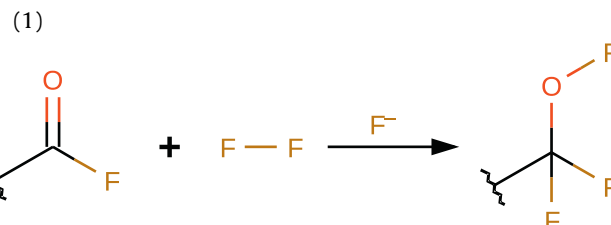
Particular emphasis is dedicated to safety issues since organic hypofluorites have the tendency to self-decompose forming gaseous compounds. The hypofluorites considered in this review are: CF_3OF , $\text{CF}_2(\text{OF})_2$, $\text{CF}_3\text{CF}_2\text{OCF}_2\text{OF}$, $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_2\text{OF}$, $\text{CF}_3\text{O}(\text{CF}_2\text{O})_n\text{CF}_2\text{OF}$, $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OF}$, $(\text{CF}_3)_2\text{CFOF}$, $(\text{CF}_3)_3\text{COF}$, $\text{FS}(\text{O})_2\text{CF}_2\text{CF}_2\text{OF}$, $\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OF}$, cyclo- $(\text{CF}_2\text{OCF}_2\text{OCF}_2)\text{-CF}_2\text{OF}$, $(\text{CF}_3)_2\text{N-CF}_2\text{OF}$.

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1. Introduction

At the beginning of the last century, the first serendipitous formation of a hypofluorite was associated with an accident during the early industrial attempts to produce fluorine through the electrochemical process. The experiments repeated on laboratory scale by Lebeau and Damiens in 1927 led to the identification of oxygen-difluoride [1,2]. It was found that oxyfluoride was produced in a side reaction starting from wet hydrogen fluoride.

The next leap in the field is ascribed to the discovery of the first organic hypofluorite by Cady and coworkers [3]. In the 1960s, research and industrial applications in the hypofluorite chemistry were driven by the rocket propellant technology [4–6]. The synthetic methodology for the preparation of organic hypofluorites was definitively improved by Ruff and Lustig [7]. The fluorination method of carbonyl compounds in presence of cesium fluoride as catalyst, shown in reaction (1), increased the number of organic hypofluorites isolated from that moment on [8].



Subsequently great attention was given to organic perfluoro hypofluorites and many articles and excellent reviews appeared in the specialized literature [9–16]. Recent developments regarding the structure of the catalyst are also present in the literature [17,18]. In particular, due to the heterogeneous nature of the reaction (1), fluorine-resistant supports with a high surface area were developed.

Due to the unique properties of the O–F bond, organic hypofluorites can act as a source of electrophilic fluorine [10,19], electrophilic alkoxylium species [20–22], as well as alkoxy radicals [23,24]. The oxygen–fluorine bond is indeed weak ($184.2 \text{ kJ mol}^{-1}$ in CF_3OF [25–27]), low polar [28], and with a slightly negative fluorine atom [29].

The use of hypofluorites was applied to the synthesis of fluorinated steroids and, lately, many different fluorinated organic compounds were prepared through this methodology [10,30–34].

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Since the availability of [¹⁸F] acetylhypofluorite, a useful fluorinating reagent for the preparation of 2-deoxy-2-[¹⁸F]fluoro-D-glucose, radio-halogenated carbohydrates have been of interest to the Nuclear Medicine Science for the direct measurement of glucose metabolism rate by positron emission tomography (PET) [35,36]. A similar procedure was used to synthesize 3-[¹⁸F]-fluoro- α -fluoromethyl-*p*-tyrosine which was recognized as a potential imaging agent for dopamine neurons [37,38]. Nowadays a full set of ¹⁸F radio-labeled substances is available for in vivo applications [39,40].

Recently, organic hypofluorites [41] as well as fluorine have been utilized as fluorinating cleaning or etching gases in the semiconductor industry. These methodologies achieve high precision etching of the silica wafers and are less harmful to the global environment.

One of the most widely studied fluorinating agents, similar to hypofluorite, is elemental fluorine, as shown by Hesse [14], Rozen [10] and Chambers [42,43]. Recently, this reagent has been utilized for the preparation of perfluoro acyl fluorides, suitable intermediates for the synthesis of fluorinated vinyl ethers [44,45].

Oxyfluoride compounds have also been studied in relation to the ozone depletion problem, leading to the conclusion that catalytic cycles involving F, OF, and OF₂ are irrelevant with respect to the chlorine cycle efficiency [46–48]. This research also allowed the development of a new family of refrigerants, hydrofluoroethers, characterized by low ozone depletion potential (ODP) and low global warming potential (GWP) [49,50].

The industrial use of hypofluorites takes advantage from the great synthetic flexibility of the hypofluorite chemistry allowing the preparation of diversified perfluorovinylether monomers [9,51–53]. In particular, the use of organic hypofluorites has been successfully applied in the development of new fluoroelastomers [54].

Perfluorovinylether monomers represent the key building blocks for the preparation of different and innovative polymers, like amorphous fluoropolymers with *T_g* ranging from +300 °C [51,55,56] to –70 °C [57–59] as well as sulphonic [60] and carboxylic functionalized perfluoropolymers [52]. These fluoropolymers find their emerging applications in many industrial strategic areas including electronics, automotive, optics, aeronautical applications, membranes and coatings.

Since the commercial introduction of TFE–PFA (tetrafluoroethylene-perfluoroalkylvinylethers, R_FOCF=CF₂) copolymers in 1972 [61] the research on the preparation and characterization of new fluoropolymers based on different PFA monomers has grown in the area of fluoroplastics and fluororubbers [62,63]. In this respect, this research has been a success factor for the identification and commercialization of innovative amorphous as well as crystalline fluoropolymers.

Important advances in this area include the development of amorphous perfluoroplastics [62]. Some of these materials can be obtained by random copolymerization of perfluoro-1,3-dioxoles with TFE [55,64–68].

In the chemistry of organic hypofluorites, the reaction with molecules containing a carbon–carbon double bond plays an important role, both from a synthetic and mechanistic point of view.

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 supporting both the free-radical and the electrophilic pathway [10,11,14,30,31,52,69]. In general, electron-rich olefins, polar solvent, low concentration, low temperature and sometimes aerobic conditions are preferred to promote electrophilic reactions

and at the same time these conditions suppress or inhibit fluorine radical processes [32–34,70].

The observation of different reaction mechanisms involving hypofluorites led to a debate on the positively polarized fluorine in hypofluorite compounds [71] and on their reaction pathway with olefins and aromatic compounds [10,72].

Radical chain reactions are favorable with electron deficient olefins [9]. However, in presence of a radical activator, the chain reaction can be favored even with electron rich olefins [73].

The free radical pathway was experimentally proved through the EPR and ENDOR spectra of the alkyl radical intermediates in the reaction of electron depleted and hindered perfluoroalkenes with hypofluorites [24,74,75]. Extensive kinetic studies of the free radical mechanism of thermal gas-phase addition of trifluoromethyl hypofluorite CF₃OF to electron deficient olefins have been done by Shumacher and Czarnowski [76–78].

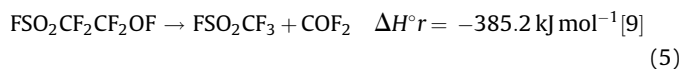
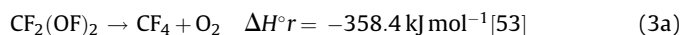
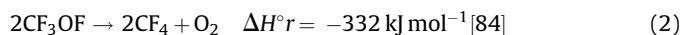
The free radical chain initiation capability of CF₃OF was also industrially developed in the production of perfluoropolyethers via free oxypolymerization of fluoro-olefins. In this reaction oxygen is inserted as a monomer in the polymeric back-bone. The insertion of oxygen gives a further evidence of the free radical pathway in the addition of hypofluorites to highly fluorinated olefins [79–81].

2. Safety precaution in the use of hypofluorites

The major concerns in the development of the hypofluorite chemistry is due to the high reactivity of this class of compounds as well as to their instability requiring strict safety precautions. Based on the literature, as well as on the experience developed in our laboratory, organic hypofluorites should be considered toxic substances and latent explosives [8,12,82,83].

This tendency to auto-decomposition is observed with some differences amongst the hypofluorites, CF₃OF (FTM) being the more stable. However, with any hypofluorite fires and explosions can occur on contact with organic reagents. This behavior is due to the low energy of the O–F bond, the high oxidizing power, the high-energy content and the high reactivity.

From this point of view perfluoro-hypofluorites cannot be considered as elemental fluorine analogs, since fluorine is perfectly stable, on the contrary hypofluorites are intrinsically unstable and may self-decompose upon simple contact with organic impurities and metal surfaces thus generating hot spots in the reaction vessels, as shown by the very exothermic decomposition reactions (2)–(5).



Although many hydrogen-containing hypofluorites have been synthesized and characterized, in particular CH₃OF [21], CH₃C(O)OF [10], (CH₃)COF [20], normally these are prepared and immediately used as diluted solutions at low temperature to avoid any undesired decomposition.

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