Reactions of fluoroolefins with participation of fluorine inorganic radical initiators

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Report 1. Choice of fluorine inorganic radical initiators.

Part 2. Nitrogen oxyfluorides , halogen oxyfluorides, sulfur oxyfluorides.

In nitrogen oxyfluorides (FNO,FNO_2,FNO_3,F_3NO,NF_2NO) the character of bonds dissociation differs in principal from nitrogen fluorides: most nitrogen fluorides retain the N-F bond in chemical reactions whereas reactions with dissociation of the N-F bond in the molecules of nitrogen oxyfluorides are more favorable thermodynamically and heterolytic decay of the N-F bond with formation of fluoride ion and conversion of the NO or NO_2 groups to the appropriate cation is prevailing. Such a behavior gives the grounds to consider nitrogen oxyfluorides as Lewis bases. As it should be expected, in a number of cases nitrogen oxyfluorides similarly to nitrogen fluorides react according to a mechanism of homolytic dissociation of the N-F bond that is very important for us.

Nitrosyl fluoride, FNO, and ***nitrile fluoride***, FNO_2, are strong fluorinating agents, i.e. they dissociate mainly via the N-F bond. Their interaction with unsaturated perfluorinated compounds is associated with polarization of the molecules of oxifluorides according to the scheme:

$$FNO_x \rightarrow F^{\delta -} - NO_x^{\delta +},$$

i.e. the N-O bond remains inactive.

Nitrogen fluoro oxides behave in the reaction with fluoroolefins as typical electrophilic reagents, different catalysts are used to increase nucleophility of fluoroolefins. Potassium fluoride and boron trifluoride are used for higher fluoroolefins and boron trifluoride is used for tetrafluoroethylene and perfluoroalkylvinyl ethers.

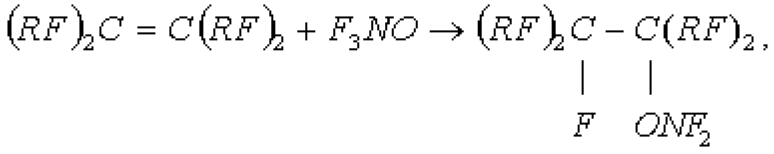
Therefore the use of FNO and FNO_2 as the sources of the radicals in the reactions of fluoroolefins is too unlikely.

Fluorine nitrate, FNO_3, is also a toxic gas. Its chemical behavior and prospects for application are in whole similar to the described above.

Nitrogen oxyfluoride, F_3NO has been up to now a compound difficult of access and chemistry of its conversions was studied rather weakly. In most of described reactions it behaves as a low-activity fluorinating agent and in interactions with Lewis acids it acts as a weak base. For the purpose of this investigation it would be of interest to study the equilibrium:

$$F_3NO \Leftrightarrow F^{\bullet} + F_2NO^{\bullet},$$

but these data are absent in the literature. Only one reaction of addition of nitrogen oxyfluoride to the substituted perfluoroolefins is known:



$$(RF)_2C = C(RF)_2 + F_3NO \rightarrow (RF)_2\underset{F}{\underset{|}{C}} - \underset{ONF_2}{\underset{|}{C}}(RF)_2,$$

It may serve in principle as a supposition to use F_3NO as the source of the radicals in the reactions of fluoroolefins, but insufficiency of the data on that specific reaction, low activity and exoticism of the methods to synthesize F_3NO do not allow at present to consider it as a real competitor to other sources of fluorine radicals though the prospects to obtain functional oxydifluoroamine groups are very alluring.

Other N-O-F compounds (F_2NONF_2, $F_2NO_2NF_5$,F_2NOF,F_2NO_2F) are exotic enough and could not be of interest in the nearest future.

Chlorine oxyfluorides are the most studied among haloid oxyfluorides. Some of them (FCl, ClO_2F_3, F_5ClO) are unstable, they are not isolated as pure compounds and are not under our consideration.

Chloryl-fluoride, $FClO_2$, is thermally stable up to approximately 250oC. At heating it is decomposed according to the scheme:

$$FClO_2 \rightarrow FClO + O \rightarrow ClF + O_2$$

The decay is strongly dependent on the reaction conditions (temperature, pressure, reactor material). It behaves towards the most of reagents as a fluorinating (and to a less degree as an oxidizing) agent.

Perchloryl fluoride, $FClO_3$ is also a moderately toxic gas with high thermal and hydrolytic stability. It is the most stable among chlorine oxyfluorides, its decay begins at a temperature above 400oC and it is possible to store it for several years. The energy of the $F\text{-}Cl\text{-}O_3$ bond rupture is 60kcal /mol and for the Cl-O bonds it is 57 kcal/mol per each. In reactions with organic compounds it acts as an oxidizer and also as an electrophilic fluorinating and perchlorylating agent.

Chlorine oxyfluoride, F_3ClO, in contrast to chloryl fluoride and perchloryl fluoride described above, possesses also oxyfluorinating ability. In dependence on the reaction conditions, it can

Chlorine oxyfluoride is much more active than the mentioned above compounds due to a more strain structure of its molecule.

Chlorine dioxytrifluoride, F_3ClO_2 is studied to a less degree in comparison with other chlorine oxyfluorides. It is a high reactive substance which is easy to reduce to chloryl fluoride. It reacts with organic compounds with an explosion and there is no practical sense to consider it as the source of radicals in the reactions of fluoroolefins.

Bromine oxyfluorides ($FBrO_22$, $FBrO_3$ and F_3BrO) were synthesized rather recently. All of them are unstable thermally and decomposed even at room temperature. They do not form stable radicals necessary in syhtheses with fluoroolefins.

Iodine has the largest number of oxyfluorides (FIO_2, FIO_3, F_3IO, F_3IO_2,F_5IO,$FOIOF_4$). They are more stable than bromine oxyfluorides, particularly F_3IO_2. In a number of papers one can find their interactions with Lewis acids and bases, with inorganic compounds but they do not form the necessary radicals as in the case with bromine oxyfluorides.

Sulfur oxyfluorides and their derivatives represent the largest number of compounds (F_2SO, $FClSO$, F_2SO_2, $FClSO_2$, $FBrSO_2$, F_4SO, F_5SOF,FSO_2OHal, $F_2S_2O_5$, $FClS_2O_5$, $F_2S_2O_6$, $F_2S_3O_8$, $F_4S_2O_5$, $F_{10}S_2O_2$). A study of their properties began in 1896 when thionyl fluoride was synthesized for the first time. The S-F bond ,as it was mentioned above, is strong enough and seldom participates in chemical conversions. The oxyfluorides containing the SO-X fragment (F_5SOF, FSO_2OHal, $F_2S_2O_5$, $F_2S_2O_6$, $F_2S_3O_8$, $F_4S_2O_5$ and $F_{10}S_2O_2$) are of the most interest in this group of compounds because the SO-X bond is labile enough and able to homolytic dissociation. Nevertheless pyrosulfuryldifluoride, FSO_2OSO_2F, pyrosulfurylfluoride chloride , FSO_2OSO_2FCl , trisulfuryldifluoride $FSO_2SO_2SO_2F$ and monoperoxytetrafluorooxyfluoride do not form the radicals and, hence are not further considered.

Pentafluorosulfurylhypofluorite ,F_5SOF, is a highly reactive gas , readily able to homolytic decomposition via the O-F bond with formation of the F_5SO and F□ radicals.

Fluorine fluorosulfate,FSO_2OF, behaves similarly. It is a highly reactive explosive gas dissociating to the F' and FO2SO' radicals. When fluorine is replaced with other haloids, in the mentioned hypofluorites ionicity of the bond in Cl-Br-I series is increased significantly and the energy of the Hal-O bond dissociation is increase together with it. Thus, in the molecule of FO_2SO-F it is 33 kcal/mol, and in the molecule of FO_2SO-Cl it is already 45 kcal /mol. Hypobromites and hypoiodites actually are not of interest as radical reagents. Difluoroaminosulfate, FO_2SONF_2, relates to the same class, here the difluoroamino group behaves as a pseudohaloid.

Compounds containing in their structure the S-O-O- fragments (F_5SOOSF_5, FO_2SOOSO_2F, FO_2SOOF) are extremely liable to homolytic dissociation because the O-O bond in them is considerably weakened owing to electronegative substituents. So, for kcal/mol whereas in peroxydisulfuryl difluoride, $FO_2SO-OSO_2F$ it is only 22 kcal/mol. Among the mentioned peroxide compounds of sulfur, symmetrical structures are most liable to homolytic decay of the O-O bond. They are bis(pentafluorosulfuryl)peroxide, F_5SOOSF_5, and peroxydisulfuryl difluoride, FO_5SOOSO_2F. From the two latter compounds, peroxydisulfuryl difluoride is of the greatest interest, it is easily dissociated according to the scheme:

It is thermally stable, toxic, volatile liquid with a boiling temperature of 67oC. Its vapor pressure at room temperature is about 200 Torr. $S_2O_6F_2$ equilibrium has been described in many papers and the most common value is the value of dissociation energy equal to 22.4kcal/mol. Similarly to the reactions of tetrafluorohydrazine, the rate of peroxydisulfuryl difluoride dissociation exceeds the main reaction rate and therefore the main reaction is interaction of fluorosulfonate radical with a different reagent.

Conclusion.

Among the mentioned above compounds, the following ones possess the greatest ability to generate radicals: dioxydifluoride, oxygen difluoride, chlorine monoxide, tetrafluorohydrazine, chlorodifluoroamine, bis(pentafluorosulfuryl)peroxide, peroxydisulfuryl difluoride, peroxysulfuryl difluoride, fluorosulfates of fluorine, chlorine and difluoroaminofluorosulfate. Their dissociation energy to radicals is in the range from 18 kcal/mol (In the FO-OF molecule) to 45 kcal/mol(in the $Cl-OSO_2F$ molecule). These compounds are the most perspective as radical reagents in the reactions of fluoroolefins but dioxydifluoride and fluorine fluorosulfate are extremely explosive compounds and it is very dangerous to work with them. In the molecules of difluoroaminofluorosulfate and chlorine fluorosulfate the NF_2 and Cl groups have positive polarization, therefore they are not merely radical reagents. Peroxysulfuryldifluoride is rather a fluorinating agent, its reactions with homolytic dissociation to the FO_2SO' and OF radicals has not been mentioned.

From the rest compounds, tetrafluorohydrazine (the dissociation energy of 20.5 kcal/mol) and peroxydisulfuryldifluoride(22.4 kcal/mol) are the most attractive. They are heat stable, moderately toxic and relatively available compounds which may be synthesized independently.

Peroxydisulfuryl difluoride was chosen for our studies because it had a number of advantages in comparison with tetrafluorohydrazine. It is a liquid under standard conditions, less dangerous and above all fluorosulfonate groups obtained in its reactions may be readily conversed to the appropriate fluoroanhydrides which in their turn are convenient starting materials to synthesize compounds with different functional groups.

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