

ORGANIC AND INORGANIC HYPOFLUORITES

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I. INTRODUCTION

Considerable attention has been directed in recent years to the study of compounds, both inorganic and organic, containing the oxygen-fluorine bond. The name hypofluorite is given (13) to this class of compounds and indicates the presence of an -OF group in the same manner that hypochlorite designates the -OCl group. Interest in the hypofluorites has mainly been of a fundamental nature; however, some studies have been motivated by the desire to investigate compounds which may be suitable for advanced rocket propellants.

The review covers the compounds possessing the hypofluorite group and composed of oxygen, fluorine, and other elements. Compounds containing the oxygen-fluorine bond and composed only of these two elements, the oxygen fluorides, have been the subject (73) of a very recent review. To aid the discussion, the various hypofluorites are formally arranged according to the periodic groups. The element directly bonded to the oxygen of the hypofluorite group is selected as the group designator. This review augments and updates the somewhat abridged, authoritative review (13) of the hypofluorites and supplements certain portions of reviews (14, 35, 58) pertaining to the fluorine compounds of the group V and group VI elements. It is the hope that the present review will reliably summarize the present status of this research area and will serve as a guide to subsequent work. The bibliography covers available references up to October, 1963.

II. PERFLUOROALKYL HYPOFLUORITES

The perfluoroalkyl hypofluorites can be classified into two series, the R_fOF and the R_fCOOF series, where R_f denotes the perfluoroalkyl group. In spite

of several attempts (15, 20) to prepare higher homologs of the R_fOF series, only the initial member, trifluoromethyl hypofluorite, has been isolated. Two other known perfluoroalkyl hypofluorites, the trifluoroacetyl and the pentafluoropropionyl, are of the type R_fCOOF. The possible existence of heptafluorobutyryl hypofluorite is mentioned (48); however, since the pentafluoropropionyl compound is less stable than the trifluoroacetyl hypofluorite, it is assumed that heptafluorobutyryl hypofluorite is extremely unstable.

A. TRIFLUOROMETHYL HYPOFLUORITE, CF₃OF

Trifluoromethyl hypofluorite is formed, in high yields, by the reaction of fluorine in the presence of a silver(II) fluoride catalyst with either carbon monoxide (2, 44, 56, 75), carbon dioxide (20), carbonyl fluoride (44, 46), or methanol vapor (44). Direct fluorination (81) of solid potassium cyanate at 50 to 55° produces trifluoromethyl hypofluorite in yields up to 80%. Numerous organic compounds containing oxygen react (16) with fluorine to produce trifluoromethyl hypofluorite and other fluorinated hydrocarbons. The reaction (42) of oxygen difluoride with tetrafluoroethylene also produces small amounts of trifluoromethyl hypofluorite.

Trifluoromethyl hypofluorite, a colorless, toxic gas with an odor similar to that of fluorine, condenses to a clear, colorless liquid (56) with a boiling point (44) of -95° and an approximate liquid density (44) of 1.9 g./cc. The relationship (44) between the vapor pressure (cm.) of the liquid and the temperature (°K.) is given by the equation

$$\log P = 6.0059 - \frac{656.22}{T} - \frac{13,988}{T^2}$$

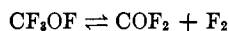
The value of 3710 cal./mole obtained for the heat of

vaporization at the normal boiling point corresponds to a Trouton constant of 20.8. Solidification of liquid trifluoromethyl hypofluorite has not been observed (44) even at the low temperature of -215° .

The molar heat of formation at 298°K . for trifluoromethyl hypofluorite from the elements, in their standard states, is estimated (57) to be -177.3 kcal., and the molar heat of formation at 298°K . from the gaseous atoms is calculated (57) to be -481.4 kcal.

A C_s symmetry for the trifluoromethyl hypofluorite molecule with the $-\text{OF}$ group located in one of the symmetry planes of the CF_3 has been deduced from the vibrational analysis (46) of the infrared and Raman spectra. The strong infrared band at 945 cm.^{-1} for the gas (46, 56) and the strong Raman band at 939 cm.^{-1} for the liquid (46) can be attributed to the O-F stretch, which in oxygen difluoride is found (43) at 928 cm.^{-1} . The nuclear magnetic resonance spectrum (17, 52) for trifluoromethyl hypofluorite displays a large doublet for the CF_3 group and a smaller quadruplet for the $-\text{OF}$ resonance. The spin-spin coupling constant (17) between the CF_3 fluorines and the OF fluorine is 32 c.p.s. Mass spectra (56) are not very helpful in establishing purity of trifluoromethyl hypofluorite since the mass spectrum of the hypofluorite is very similar to that of carbonyl fluoride.

When trifluoromethyl hypofluorite is sparked, or is heated above 275° , decomposition occurs. The thermal decomposition reaction is reversible and the equilibrium for the change



has been studied (57) and the mechanism discussed (25). Irradiation (50) of trifluoromethyl hypofluorite with a mercury-arc lamp produces bis-(trifluoromethyl) peroxide. At room temperatures, trifluoromethyl hypofluorite is inert to Pyrex glass (44) and can be stored (56) under pressure in pretreated steel cylinders. Nickel, pretreated with fluorine, is inactive to trifluoromethyl hypofluorite at temperatures below 470° . Trifluoromethyl hypofluorite reacts (56), at room temperatures, with mercury and with lithium to form the corresponding metal fluorides and carbonyl fluoride. Hydrogen and trifluoromethyl hypofluorite do not react (9) at room temperature when sparked; however, in the presence of a hot copper catalyst, reaction (44) takes place to form carbonyl fluoride and hydrogen fluoride. Powdered sulfur rapidly reacts (56) with trifluoromethyl hypofluorite to yield unstable gaseous sulfur products.

Hydrolysis of trifluoromethyl hypofluorite occurs so slowly that it can be purified of carbonyl fluoride impurities by being kept in contact with water for days. Bromine or iodine is readily liberated (44) from solutions of their salts by the hypofluorite. Reaction of trifluoromethyl hypofluorite with sodium chloride

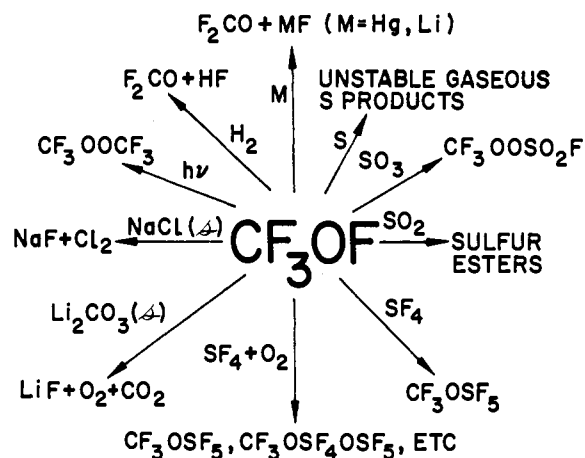


Fig. 1.—Some reactions of trifluoromethyl hypofluorite with inorganic reagents.

and potassium bromide cell windows is reported (56), and at 150° it displaces (44) chlorine from solid sodium chloride. Solid lithium carbonate reacts (56) to yield carbon dioxide, oxygen, and lithium fluoride.

Trifluoromethyl hypofluorite reacts with gaseous sulfur trioxide (75) at 245 to 260° to form trifluoromethyl peroxyfluorosulfonate, $\text{CF}_3\text{OOSO}_2\text{F}$. The reaction of trifluoromethyl hypofluorite with sulfur dioxide, either in the gas phase (75) at 170 – 185° or in the liquid phase (53) at 90° , yields a series of esters which do not contain the O-O peroxide bond. In contrast to the rather complex reaction of trifluoromethyl hypofluorite with sulfur dioxide, its reaction with sulfur tetrafluoride (53, 54) is simple, in that trifluoromethoxysulfur pentafluoride, CF_3OSF_5 , is the only product. A similar reaction in the presence of oxygen gives (53, 54), in addition to the trifluoromethoxysulfur pentafluoride formed in the absence of oxygen, the compounds $\text{CF}_3\text{OSF}_4\text{OSF}_5$, $\text{CF}_3\text{OSF}_4\text{OOSF}_5$, and probably $\text{CF}_3\text{OSF}_4\text{OOSF}_4\text{OCF}_3$. Figure 1 summarizes the reactions of trifluoromethyl hypofluorite with inorganic materials. Simple saturated noncyclic compounds such as methane, chloroform, and carbon tetrachloride react (2) with trifluoromethyl hypofluorite to give fluorinated products. The hypofluorite reacts (2) explosively with ethylene, acetylene, and cyclopropane to give carbon, carbon monoxide, and hydrogen fluoride. However, with nitrogen dilution, trifluoromethyl hypofluorite adds quantitatively (2) across the double bond of ethylene to give trifluoromethyl 2-fluoroethyl ether. The reaction (56) of trifluoromethyl hypofluorite with tetrafluoroethylene produces, depending on the conditions, either carbon monoxide and carbon tetrafluoride or polymeric materials. Perfluorocyclopentene adds (56) to trifluoromethyl hypofluorite across the double bond to form perfluoro(methoxycyclopentane). Some of the reactions of organic materials with trifluoromethyl hypofluorite are depicted in Fig. 2.

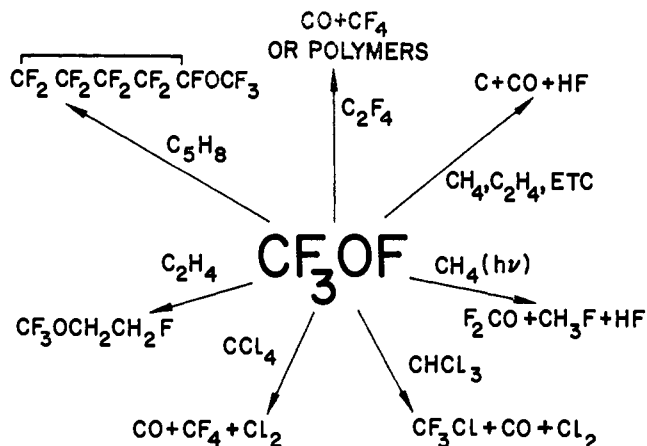


Fig. 2.—Some reactions of trifluoromethyl hypofluorite with organic compounds.

B. TRIFLUOROACETYL HYPOFLUORITE, CF_3COOF

Trifluoroacetyl hypofluorite is obtained (16, 72) by the reaction at 25° of fluorine with nitrogen-diluted trifluoroacetic acid vapor in the presence of water vapor. The reaction condensables, trapped at -183° , contain, in addition to the trifluoroacetyl hypofluorite, unreacted trifluoroacetic acid, carbonyl fluoride, carbon tetrafluoride, carbon dioxide, and silicon tetrafluoride. More volatile impurities of the condensed mixture can be swept out by slow passage of a stream of dry nitrogen through the mixture maintained at -78° since, at this temperature, the vapor pressure (72) of trifluoroacetyl hypofluorite is approximately 30 mm. Total yields of trifluoroacetyl hypofluorite prepared by this method (16) are estimated to be less than 25% of the theoretical. Attempts (72) to purify the hypofluorite by distillation have resulted in explosions.

Trifluoroacetyl hypofluorite, a colorless gas, condenses to a colorless liquid (16) having an approximate normal boiling point of $-21.5 \pm 1^\circ$. The gas slowly decomposes (72) at room temperature; complete decomposition is reached within a few hours. The thermal decomposition of trifluoroacetyl hypofluorite into carbon dioxide and carbon tetrafluoride has been studied (72) at pressures of 1.5 to 3 mm. over a temperature range of 30 to 80° . Using chlorine and bromine as free-radical traps, the rate-determining step



has apparently been isolated. If the reaction is homogeneous, and if the above step is the rupture of the O-F bond, the activation energy of 25 kcal. for the inhibited decomposition is the energy of the oxygen-fluorine bond in the compound (72).

Trifluoroacetyl hypofluorite diluted with nitrogen reacts rapidly with aqueous potassium iodide to liberate iodine. With insufficient nitrogen dilution, the reaction takes place with explosive violence (16).

C. PENTAFLUOROPROPIONYL HYPOFLUORITE, $\text{C}_2\text{F}_5\text{COOF}$

Pentafluoropropionyl hypofluorite is prepared (48) by the fluorination of pentafluoropropionic acid using essentially the same procedure as that employed for the synthesis (16, 72) of the lower homolog, trifluoroacetyl hypofluorite. Purification of pentafluoropropionyl hypofluorite can be accomplished, without explosion, by distillation at pressures below 100 mm. Distillations at atmospheric pressure have resulted in explosions. Based on the amount of pentafluoropropionic acid consumed, yields of the corresponding hypofluorite are approximately 10% of the theoretical.

Vapor pressures of this hypofluorite have been measured (48) at temperatures over the range of -58 to -25° . A normal boiling point of 2° is estimated (48) for the colorless liquid. At pressures of a few millimeters and at temperatures ranging from -40 to $+25^\circ$, the colorless gaseous pentafluoropropionyl hypofluorite decomposes at a moderate rate to form carbon dioxide and hexafluoroethane. Explosive decomposition has been reported (48).

Pentafluoropropionyl hypofluorite is less stable than trifluoroacetyl hypofluorite and displays the characteristic reaction of compounds containing the O-F bond by rapidly liberating iodine from aqueous potassium iodide (see Table I for physical properties of the hypofluorites).

III. GROUP V HYPOFLUORITES

Nitrogen is the only member of the group V elements that forms a bond with the oxygen of the hypofluorite group. It forms only one such compound, fluorine nitrate, the first compound containing the -OF group to be discovered and isolated. The compounds nitrosyl fluoride, ONF, and nitryl fluoride, O_2NF , do not contain the hypofluorite group; the fluorine in each of these molecules is attached to the nitrogen atom. A discussion of these two compounds is included in a recent review (41) of the nitrogen fluorides.

A. FLUORINE NITRATE, O_2NOF

Fluorine nitrate is formed by the action of fluorine on either dilute (12) or anhydrous nitric acid (66), and on dry, solid potassium nitrate (55, 71, 82) or sodium nitrate (3). Absorption of the fluorine by the anhydrous acid is incomplete at -35° , but the process proceeds nearly quantitatively at 20° . Comparable high yields of fluorine nitrate are obtained by the fluorination (3) of solid sodium nitrate. Small amounts of fluorine nitrate are obtained by the electrolysis, at 0° or below, of nitrous oxide (61, 62) or nitric oxide (31) dissolved in anhydrous hydrogen fluoride.

Fluorine nitrate is a toxic (45), colorless gas with a pungent, musty, irritating odor (12). Although in thin layers, liquid fluorine nitrate appears (66) to be colorless, in bulk it possesses a light yellow color.

TABLE I
 SOME PHYSICAL PROPERTIES OF THE HYPOFLUORITES

| Classification | Formula | Name(s) | B.p., °C. | M.p., °C. | Vapor pressure equation constants ^a | | |
|------------------------------|------------------------------------|-----------------------------------------------------------------------------|-----------|-----------|------------------------------------------------|--------------------------|--------------------------|
| | | | | | A | B | C |
| Perfluoroalkyl hypofluorites | CF ₃ OF | Trifluoromethyl hypofluorite | -95. | — | 6.0059 | 656.22 | 13988. |
| | CF ₃ COOF | Trifluoroacetyl hypofluorite | -21.5 | — | — | — | — |
| | C ₂ F ₅ COOF | Pentafluoropropionyl hypofluorite | 2. | — | b | b | b |
| Group V hypofluorite | O ₂ NOF | Fluorine nitrate, nitroxyl fluoride, nitryl oxyfluoride | -45.9 | -175. | 7.478 | 1044.9 | — |
| | F(SO ₂)OOF | Fluorosulfuryl fluoroperoxide, sulfuryl fluoride fluoroperoxide | 0. | — | 6.781 | 1063. | — |
| Group VI hypofluorites | FSO ₂ OF | Fluorine fluorosulfonate, fluorine fluorosulfate | -31.3 | -158.5 | 6.56476 | 6.2687 × 10 ³ | 6.3906 × 10 ⁴ |
| | F ₅ SOF | Pentafluorosulfur hypofluorite | -35.1 | -86.0 | 6.03633 | 4.2035 × 10 ² | 7.836 × 10 ⁴ |
| | F ₅ SeOF | Pentafluoroselenium hypofluorite | -29. | -54. | b | b | b |
| Group VII hypofluorite | O ₃ ClOF | Fluorine perchlorate, perchloryl fluoride, perchloryl oxyfluoride (755 mm.) | -15.9 | -167.3 | — | — | — |

^a $\log P = A - B/T - C/T^2$, where T is in °K. and P is in mm. (except for CF₃OF where P is in cm.). ^b Vapor pressure measurements reported, but no equation; refer to text.

Boiling points (12, 66) for the liquid, ~ -42 and -45.9° , and a critical temperature (66) of 67.2° have been reported. The vapor pressure (mm.) of liquid fluorine nitrate measured (66) over the temperature range -128 to -68° increases in accordance with the equation

$$\log P = 7.478 - \frac{1044.9}{T}$$

A heat of evaporation equal to 4726 cal./mole and a Trouton constant of 20.8 can be computed using the vapor pressure equation. The density (66) of liquid fluorine nitrate is 1.507 g./cc. at the boiling point; the density (g./cc.) at other temperatures can be calculated using the equation

$$d_{\text{liq}} = 2.2148 - 0.003114T$$

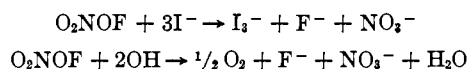
The surface tension (40) of liquid fluorine nitrate is 21.5 and 23.4 dynes/cm. at -64.1 and -80.4° , respectively. Fluorine nitrate solidifies at -175° to a white solid with a density (66) of 1.951 g./cc. at -193.2° .

Calorimetric studies of the fluorine nitrate synthesis by the direct fluorination of sodium nitrate (3) and of the reaction of fluorine nitrate with concentrated potassium hydroxide solutions (74) have yielded the respective values of $+2.5 \pm 0.6$ and -4.2 ± 0.9 kcal./mole for the heat of formation of gaseous fluorine nitrate.

A configuration consisting of three oxygen atoms coplanar with the nitrogen atom and the fluorine atom bonded to one of the oxygen atoms is regarded as the most probable on the basis of electron diffraction (55) and infrared absorption (6, 71) studies.

Although reported (66) to be stable in dry glass, quartz, and several metals, fluorine nitrate is extremely explosive in both the gaseous and solid state. Violent explosions often occur in the condensed material with no apparent cause. Kinetic studies (70, 71, 76, 78)

have been made of the thermal decomposition of fluorine nitrate under various conditions of temperature and pressure and in the presence of added foreign gases. Similar studies (77) of the kinetics of the thermal reaction between nitrogen dioxide and fluorine nitrate are reported. Fluorine nitrate is moderately soluble in water with which it slowly reacts liberating oxygen, is decomposed (12) by aqueous solutions of potassium iodide and potassium hydroxide



and reacts (82) with aqueous silver nitrate to precipitate black silver oxide. In the gas phase, fluorine nitrate reacts (10) hypergolically with ammonia, nitrous oxide, and hydrogen sulfide, and to varying extents, after spark initiation, with hydrogen, hydrogen chloride, carbon monoxide, and boron trifluoride. Mixed (66) with alcohol, ether, or aniline, fluorine nitrate explodes. However, it does not react with glacial acetic acid or acetone, in which it is soluble. Antimony(V) chloride and titanium(IV) chloride form (66) rather unstable, yellow, solid complexes with fluorine nitrate.

IV. GROUP VI HYPOFLUORITES

In contrast to the behavior of the group V elements, most of the group VI elements combine with the oxygen of the -OF group to form hypofluorites. Combined with oxygen, the -OF group is present in the oxygen fluorides and in a fluoroperoxide. The -OF group also bonds to sulfur and to selenium to form hypofluorite compounds. Pentafluorosulfur hypofluorite is more stable than the corresponding selenium compound, and the tellurium analog appears to be very unstable as attempts (18) to prepare the compound

have been unsuccessful. This stability gradation, of the essentially covalent hypofluorites, is, no doubt, due to the increase of metallic character of the group VI elements with increasing atomic weight.

A. FLUOROSULFURYL FLUOROPEROXIDE, $F(SO_2)OOF$

On irradiating a mixture of fluorine monoxide and sulfur trioxide at room temperature with light of 365 $m\mu$ wave length, fluorosulfonyl fluoroperoxide is obtained (34) in almost quantitative yield. The compound is a pale yellow-green liquid with a 0° boiling point and is thermally stable at temperatures below 50° . The vapor pressure (mm.) varies as (temperature in $^\circ K.$)

$$\log P = 6.781 - \frac{1063}{T}$$

B. FLUORINE FLUOROSULFONATE, FSO_2OF

Fluorine fluorosulfonate is readily produced (26, 27) in approximately 40% yields by treating sulfur trioxide with an excess of fluorine in the presence of a heated catalyst composed of copper ribbon or wire coated with fluorides of silver. Direct fluorination of peroxydisulfonyl difluoride (59) and of sulfamic acid (27) also produces fluorine fluorosulfonate.

Fluorine fluorosulfonate, a colorless gas, with an odor resembling that of oxygen difluoride, condenses (27) to a colorless liquid, b.p. -31.3° and f.p. -158.5° . The temperature dependence of its vapor pressure (mm.) is represented (27) by the equation

$$\log P = 6.56476 - \frac{6.2687 \times 10^2}{T} - \frac{6.3906 \times 10^4}{T^2}$$

The heat of vaporization at the boiling point, calculated from the above data, using the Clapeyron equation, is 5350 cal./mole. This value corresponds to a Trouton constant of 22.2. The temperature dependence (27) of the liquid density (g./cc.) is given by the equation

$$d_{liq} = 2.4314 + 0.00325T$$

From the densities, the volume coefficient at -70° is calculated to be 0.00181 cc./cc.-deg.

Structural investigations of fluorine fluorosulfonate using infrared (27) and nuclear magnetic resonance (17, 29) are consistent with the structure FSO_2OF . The fluorine n.m.r. spectrum of fluorine fluorosulfonate contains two equal peaks; both resolve to doublets under high resolution indicating that each fluorine is coupled to a nucleus of spin $1/2$, *i.e.*, the other fluorine atom.

At temperatures near 250° , fluorine fluorosulfonate undergoes homogeneous, quantitative thermal decomposition (25) to sulfonyl fluoride and oxygen. The hypofluorite is highly reactive, liberating (27) oxygen from aqueous sodium hydroxide and iodine from aqueous iodide solutions, but is, however, unreac-

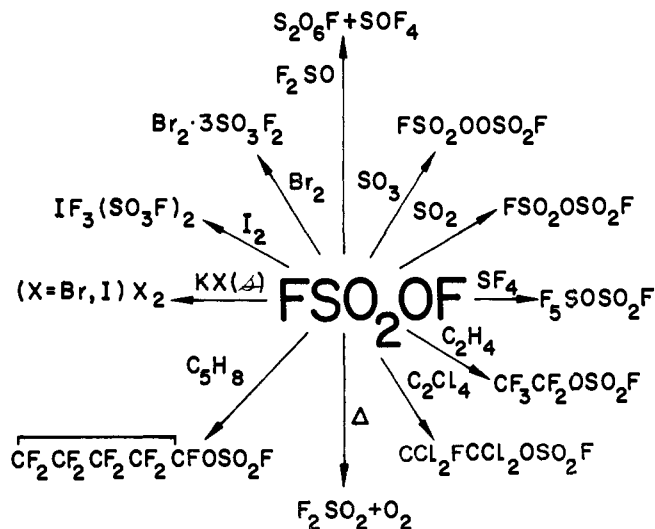


Fig. 3.—Some reactions of fluorine fluorosulfonate.

tive to chlorine (60). Halogens (27) are liberated from solid potassium bromide and from solid potassium iodide by fluorine fluorosulfonate. Bromine reacts (36) with the fluorosulfonate to give $Br_2 \cdot 3SO_3F_2$, a golden yellow liquid, and iodine (60) reacts to yield iodine trifluoride bisfluorosulfonate, $IF_3(SO_3F)_2$. Fluorine fluorosulfonate reacts with the sulfur compounds sulfur tetrafluoride (36), sulfur dioxide (60), sulfur trioxide (26), and thionyl fluoride (60) to give, respectively, pentafluorosulfur fluorosulfate, pyrosulfonyl fluoride, peroxydisulfonyl difluoride, and, with the thionyl fluoride, a mixture of peroxydisulfonyl difluoride and thionyl tetrafluoride. Fluorine fluorosulfonate adds (36) across the carbon-carbon double bond of tetrafluoroethylene, tetrachloroethylene, perfluorocyclopentene, and, perhaps, ethylene to attach the fluorine atom to one of the carbon atoms and the fluorosulfonate group to the other. The chemical reactions of fluorine fluorosulfonate are summarized in Fig. 3.

C. PENTAFLUOROSULFUR HYPOFLUORITE, F_5SOF

Pentafluorosulfur hypofluorite is obtained (28) by the reaction of excess fluorine either with thionyl fluoride or with sulfur dioxide at 200° in a reactor filled with "catalytic" silver(II) fluoride. Approximately 35 g. of pentafluorosulfur hypofluorite is obtained from the fluorination of a 63-g. thionyl fluoride sample.

Pentafluorosulfur hypofluorite condenses to form a faintly yellow liquid (28) freezing at -86.0° and boiling at -35.1° . The temperature ($^\circ K.$) dependence (28) of its vapor pressure (mm.) is given by the equation

$$\log P = 6.03633 - \frac{4.2035 \times 10^2}{T} - \frac{7.836 \times 10^4}{T^2}$$

The calculated heat of vaporization at the normal boiling point is 5210 cal./mole, and the Trouton con-

stant is 21.9. The temperature dependence of the liquid density (g./cc.) over the temperature range -64 to -47° is

$$d_{liq} = 2.788 - 3.722 \times 10^{-5}T$$

and the volume coefficient of expansion at -56° is 0.001872 cc./cc.-deg.

The structure of pentafluorosulfur hypofluorite has been investigated using infrared (28, 79) and n.m.r. (17, 29, 38) spectra and electron diffraction (19). The configuration of the molecule consists of an octahedrally coordinated sulfur with a staggered hypofluorite bond. The five fluorine atoms of the pentafluorosulfur group are not magnetically equivalent.

Pentafluorosulfur hypofluorite begins to thermally decompose at 210° to give sulfur hexafluoride and oxygen. Exposure of the hypofluorite to ultraviolet (49) results in the formation of bis(pentafluorosulfur) peroxide, F_5SOOSF_5 . The peroxide is also formed (49) by the reaction of pentafluorosulfur hypofluorite with either thionyl fluoride or with thionyl tetrafluoride. Reaction (54) of pentafluorosulfur hypofluorite with sulfur dioxide in the liquid phase gives sulfur hexafluoride, sulfuryl fluoride, sulfur trioxide, and F_5SOSO_2F . The reaction corresponds to that of the higher temperature gas-phase reaction (75) of trifluoromethyl hypofluorite with sulfur dioxide, and it seems likely that both the reactions occur by similar mechanisms. Pentafluorosulfur hypofluorite reacts with sulfur tetrafluoride in the liquid phase (54) to give F_5SOSF_6 , F_5SOOSF_5 , and $F_5SOSF_4OSF_5$, whereas, a similar reaction in the presence of oxygen gives $F_5SOSF_4OOSF_5$ and $F_5SOSF_4OOSF_4OSF_5$ as additional products. The gas-phase reaction (80) at 140° of pentafluorosulfur hypofluorite with sulfur tetrafluoride yields products similar to those obtained from the corresponding liquid-phase reaction, except no $F_5SOSF_4OSF_5$ is formed. Pentafluorosulfur hypofluorite also reacts (80) with carbon monoxide to give carbonyl fluoride and thionyl tetrafluoride, and with carbon tetrachloride to yield carbonyl fluoride, chlorine, and F_5SOSF_5 . The unsaturated organic compounds perfluorocyclopentene, tetrafluoroethylene, tetrachloroethylene, ethylene, and vinyl chloride react (80) with pentafluorosulfur hypofluorite at room temperature to yield compounds achieved by heterolysis of the O-F bond of the hypofluorite. In these reactions, the hypofluorite fluorine combines with one of the double-bonded carbons of the alkene, and the residual F_5SO -group bonds to the other. In many respects, the reactions of the alkenes with either pentafluorosulfur hypofluorite, fluorine fluorosulfonate, or trifluoromethyl hypofluorite are similar. The reactions of pentafluorosulfur hypofluorite are depicted in Fig. 4.

D. PENTAFLUROSELENIUM HYPOFLUORITE, F_5SeOF

The reaction (51) of nitrogen-diluted fluorine with

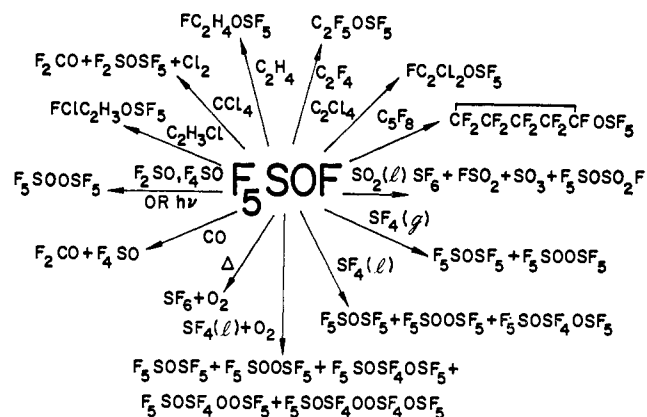


Fig. 4.—Some reactions of pentafluorosulfur hypofluorite.

selenium dioxide, at approximately 100° , yields a mixture of volatile fluorides containing small amounts of pentafluoroselenium hypofluorite. Reported yields of the hypofluorite are low, the maximum being about 14% of the theoretical value based on the amount of dioxide consumed. Direct fluorination of bis(pentafluoroselenium) peroxide, $F_5SeOOSeF_5$, results in a product containing selenium hexafluoride and pentafluoroselenium hypofluorite. Trace amounts of pentafluoroselenium hypofluorite are also formed by the action of fluorine on selenium oxychloride.

Pentafluoroselenium hypofluorite is a colorless gas with a strong, characteristic, irritating hypofluorite odor. Condensation of the gas results in a liquid which freezes at -54° and has a normal boiling point of -29° . Vapor pressures (51) of the liquid over a temperature range of -52 to -33° are reported.

The infrared absorption spectrum (51) of pentafluoroselenium hypofluorite is rather simple and displays a weak band at 925 cm.^{-1} , which may be assigned to the O-F vibration. A very broad and strong absorption with a maximum at 758 cm.^{-1} corresponds to the Se-F stretch. The mass spectrum (51) of pentafluoroselenium hypofluorite is very complex and much like that of bis(pentafluoroselenium) peroxide.

Pentafluoroselenium hypofluorite is reasonably stable but is extremely reactive with many substances. It reacts with traces of water vapor and liberates oxygen from water or alkali solutions. Iodide ion in acidic solution reduces the selenium in this hypofluorite to a number of oxidation states including that of the element selenium.

V. GROUP VII HYPOFLUORITES

Discussion of the hypofluorites of hydrogen and of chlorine is made difficult by a number of conflicting reports. A considerable amount of the disagreement arises from the difficult identification of these very unstable compounds. In the case of the chlorine hypofluorites (47), the existence of isomers containing no -OF groups further complicates the problem.

The simplest oxy acid of fluorine (hypofluorous acid, HOF) has not been prepared or isolated. However, a value of -26 ± 5 kcal./mole has been calculated (39) for the heat of formation of this hypothetical molecule. The existence of the ionic fluoric acid, HFO_3 , and its silver salt, AgFO_3 , is reported (23, 24); however, some doubt is expressed (11, 68) concerning the existence of the anion as well as the possible (21) formation of the ionic perfluoric acid, HFO_4 .

The formation (65, 67) of chlorine hypofluorite, ClOF , is reported; however, no structural information concerning the compound is available. No hypofluorite isomer of the fairly stable (69) chloryl fluoride, FClO_2 , is reported. The preparation of chloryl hypofluorite, $\text{O}_2\text{Cl}\cdot\text{OF}$, by the fluorination of potassium chlorate (7) has been questioned (30) and later revised (8). Only small amounts of a Cl-O-F compound, probably the $\text{O}_2\text{Cl}\cdot\text{OF}$, are obtained from the fluorination of potassium chlorate (8, 30) and from the reaction (5) of fluorine with chlorine hexaoxide. The hypofluorite has not been completely isolated. Its presence is inferred by its explosive nature, which is in contrast to the stability of the isomer, perchloryl fluoride, FClO_3 . Thus, the only hypofluorite compound of this group known to exist with a degree of certainty is fluorine perchlorate.

A. FLUORINE PERCHLORATE, O_3ClOF

Fluorine perchlorate is formed (63), with oxygen difluoride, by the reaction of undiluted fluorine on 70% perchloric acid. Yields, based on the quantity of acid consumed, are approximately 90% of theoretical. Smaller amounts of fluorine perchlorate are obtained by the fluorination of various metal perchlorates (3, 4), and trace amounts are probably formed by the reaction of fluorine with dilute perchloric acid (33), with solid potassium chlorate (7) at temperatures below -40° , and with chlorine hexaoxide (22).

Fluorine perchlorate is an unstable, colorless gas possessing (63) a sharp, acid-like odor. It condenses (63) to a colorless liquid boiling at -15.9° (755 mm.) and to a solid melting at -167.3° . Using Guldberg's rule, a critical temperature of 113° is computed (32) for fluorine perchlorate. Four infrared absorption bands in the sodium chloride region are reported (1) for the gas. The fluorine n.m.r. spectrum (1) of fluorine perchlorate consists of a single line. The fluorine chemical shifts of the three compounds, fluorine perchlorate, perchloryl fluoride, and oxygen difluoride, appear to be of the right order of magnitude, and are in the order predicted by theory (37). A value of $+37.6 \pm 9$ kcal./mole for the heat of formation of fluorine perchlorate was computed (10) from the measured heat of hydrolysis.

Fluorine perchlorate is highly reactive (63); grease, dirt, or contact with rubber will cause sharp explosions.

In the presence (10) of excess gaseous hydrogen, fluorine perchlorate ignites spontaneously. The hypofluorite liberates (63) iodine from aqueous iodide and reacts with hydroxyl ion to produce oxygen (63) and small amounts (10) of oxygen difluoride.

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