Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, OXYGEN

1. Oxygen Difluoride

Oxygen difluoride [7783-41-7], OF_2, is the most stable binary compound of oxygen and fluorine. Under ambient conditions, it is a colorless gas that condenses to a pale yellow liquid at −145°C (1) and freezes at −224°C (2). Oxygen difluoride is a powerful oxidizer that has attracted considerable attention as an ingredient of high energy rocket propellant systems (see Explosives and propellants). Several comprehensive reviews of the physical and chemical properties of OF_2 (3–5) and its handling (6) are available.

1.1. Physical Properties

An extensive tabulation of the physical properties of OF_2 is available (4). Selected data are mp −224°C (2); bp, −145°C (1); critical temperature −58°C (7); density of liquid, in g/mL from −145 to −153°C, t in K, $d = 2.190 - 0.00523\ t$ (8); heat of formation 31.8 kJ/mol (7.6 kcal/mol) (9); and heat of vaporization 11.1 kJ/mol (2.65 kcal/mol) (10).

Spectroscopic investigations have shown that OF_2 is bent and has equivalent O—F bonds. The O—F distance is 0.139–0.141 nm and the FOF angle is 103–104° (11–13). Measurements of the dipole moment have yielded values of $0.6 - 1.3 \times 10^{-30}$ C·m (0.18–0.40 D) (12, 14, 15). The ir (16–18), uv (19), mass (20), and nmr (21) spectra of OF_2 have been reported.

1.2. Chemical Properties

The kinetics of decomposition of OF_2 by pyrolysis in a shock tube are different, as a result of surface effects, from those obtained by conventional decomposition studies. Dry OF_2 is stable up to 250°C (22).

1.2.1. Reactions with Metals

Many common metals react with OF_2, but the reaction stops after a passive metal fluoride coating is formed (3, 4).

1.2.2. Reactions with Nonmetallic Elements and Inorganic Compounds

Mixtures of OF_2 with carbon, CO, CH_4, H_2, or H_2O vapor explode when ignited with an electrical shock. Elemental B, Si, P, As, Sb, S, Se, and Te react vigorously on slight warming to produce fluorides and oxyfluorides. Oxides such as CrO_3, WO_3, As_2O_3, and CaO react with OF_2 to form fluorides. The corresponding chlorides react with OF_2 to form the respective fluorides and liberate free chlorine in the process (3, 4).

In aqueous solution, OF_2 oxidizes HCl, HBr, and HI (and their salts), liberating the free halogens. Oxygen difluoride reacts slowly with water and a dilute aqueous base to form oxygen and fluorine. The rate of this hydrolysis reaction has been determined (23).

Nitric oxide and OF_2 inflame on contact; emission and absorption spectra of the flame have been studied (24). Oxygen difluoride oxidizes SO_2 to SO_3, but under the influence of uv irradiation it forms sulfuryl fluoride [2699-79-8], SO_2F_2, and pyrosulfuryl fluoride [37240-33-8], $S_2O_5F_2$ (25). Photolysis of SO_3–OF_2 mixtures yields the peroxy compound FSO_2OOF [13997-94-9] (25, 26).

1.2.3. Oxygen Difluoride as a Source of the of Radical

The existence of the ·OF radical [12061-70-0] was first reported in 1934 (27). This work was later refuted (28). The ·OF radical was produced by photolysis of OF_2 in a nitrogen or argon matrix at 4 K. The existence of the ·OF species was deduced from a study of the kinetics of decomposition of OF_2 and the kinetics of the photochemical reaction (25, 26):

$$OF_2 + SO_3 \xrightarrow[350\text{ nm}]{hv} FSO_2OOF$$

The existence of the ·OF radical was further established by use of ^{17}O-labeled compounds and ^{17}O nmr studies to verify the mechanism (29):

$$OF_2 + hv \longrightarrow F + \cdot OF$$

$$F + SO_3 \longrightarrow FSO_3\cdot$$

$$FSO_3 + \cdot OF \longrightarrow FSO_2OOF$$

The ·OF radical has also been detected by CO_2 laser magnetic resonance (30). The O—F bond length is 0.135789 nm.

Carbonyl fluoride, COF_2, and oxygen difluoride react in the presence of cesium fluoride catalyst to give bis(trifluorylmethyl)trioxide [1718-18-9], CF_3OOOCF_3 (31). CF_3OOF has been isolated from the reaction in the presence of excess OF_2 (32).

1.2.4. Reactions with Organic Compounds

Tetrafluoroethylene and OF_2 react spontaneously to form C_2F_6 and COF_2. Ethylene and OF_2 may react explosively, but under controlled conditions monofluoroethane and 1,2-difluoroethane can be recovered (33). Benzene is oxidized to quinone and hydroquinone by OF_2. Methanol and ethanol are oxidized at room temperature (4). Organic amines are extensively degraded by OF_2 at room temperature, but primary aliphatic amines in a fluorocarbon solvent at $-42^\circ C$ are smoothly oxidized to the corresponding nitroso compounds (34).

The reaction of OF_2 and various unsaturated fluorocarbons has been examined (35, 36) and it is claimed that OF_2 can be used to chain-extend fluoropolyenes, convert functional perfluorovinyl groups to acyl fluorides and/or epoxide groups, and act as a monomer for an addition-type copolymerization with diolefins.

1.3. Preparation

The synthesis of OF_2 was first achieved by the electrolysis of molten KHF_2 in the presence of water (37). The electrolysis of aqueous HF in the presence of O_2 and O_3 was also found to produce OF_2 (38–40).

The most satisfactory method of OF_2 generation is probably the fluorination of aqueous NaOH (3, 22, 41–45):

$$2\ F_2 + 2\ NaOH \longrightarrow OF_2 + 2\ NaF + H_2O$$

Yields of greater than 60% are obtained (46). This method has been used for the commercial production of OF_2 (8). The NaOH concentration, however, must be kept low to avoid the loss of product by a secondary reaction:

$$OF_2 + 2\ OH^- \longrightarrow O_2 + F^- + H_2O$$

An economic study of the preparation of OF_2 is available (47).

1.4. Analytical Procedures

Oxygen difluoride may be determined conveniently by quantitative application of ir, nmr, and mass spectroscopy. Purity may also be assessed by vapor pressure measurements. Wet-chemical analyses can be conducted either by digestion with excess NaOH, followed by measurement of the excess base (2) and the fluoride ion (48, 49), or by reaction with acidified KI solution, followed by measurement of the liberated I_2 (4).

1.5. Handling and Safety Factors

Oxygen difluoride can be handled easily and safely in glass and in common metals such as stainless steel, copper, aluminum, Monel, and nickel, from cryogenic temperatures to 200°C (4). At higher temperatures only nickel and Monel are recommended. The compatibility of OF_2 with process equipment depends largely on the cleanliness of the equipment; contaminants such as dirt, moisture, oil, grease, scale slag, and pipe dope must be avoided. Equipment should be passivated with elemental fluorine before contact with OF_2.

Oxygen difluoride must be regarded as a highly poisonous gas, somewhat more toxic than fluorine. It has a foul odor with a limit of detectability of 0.1–0.5 ppm. Repeated exposure of rats to 0.5 ppm OF_2 produced death; repeated exposure to 0.1 ppm, however, caused no discernible effects.

2. Dioxygen Difluoride

Dioxygen difluoride[7783-44-0], O_2F_2, prepared by passing a 1:1 mixture of O_2 and F_2 through a high voltage electric discharge tube cooled by liquid nitrogen, has also been prepared by uv irradiation of O_2 and F_2 (50, 51) and by radiolysis of liquid mixtures of O_2 and F_2 at 77 K using 3 MeV bremsstrahlung (52). Heating an O_2/F_2 mixture to 700°C in stainless steel tubes followed by rapid cooling produces O_2F_2 (53). This compound is also obtained in high yield by subjecting a flowing gas mixture of F_2 to microwave, then downstream and outside of the region of discharge, introducing molecular oxygen (54).

2.1. Physical Properties

Because O_2F_2 is unstable, it is difficult to purify. Consequently, some of the reported physical properties are open to question. Selected data are density, in g/mL, from -87 to $-156^\circ C$, $d = 2.074 - 0.00291\ t$ (50); heat of formation 19.8 kJ/mol (4.73 kcal/mol) (55); and heat of vaporization 19.2 kJ/mol (4.58 kcal/mol) at $-57^\circ C$ (55).

The structure of O_2F_2 is that of a nonlinear FOOF chain, having the following molecular constants (56, 57): O—O distance, 0.122 nm; OOF angle, $109^\circ 30'$; dihedral angle, $87^\circ 30'$; dipole moment, 4.8×10^{-30} C·m (1.44 D). Additional physical and spectral data are summarized in References 4 and 58.

2.2. Chemical Properties

The bond distance of O—O is relatively short (121.7 ± 0.3 pm) and that of O—F is relatively long (157.5 ± 0.3 pm) (56). The weakest bond in O_2F_2 is thus the O—F bond and the mechanisms of reaction of O_2F_2 can probably be explained by the formation of F· and ·OOF and not two ·OF radicals. The ·OOF radical [15499-23-7] is a feasible intermediate as it has been shown to exist at low temperatures (56, 59–61). If O_2F_2 is allowed to react quickly with other compounds, simple fluorination usually results. The controlled reactions of O_2F_2, however, yield products that appear to be formed via an ·OOF intermediate.

2.3. Simple Fluorination Reactions

Some examples (62) of O_2F_2 acting mainly as a fluorinating agent are

$$\mathrm{Xe} \xrightarrow{\mathrm{O_2F_2}} \mathrm{XeF_4}$$

$$\mathrm{ClF_3} \xrightarrow{\mathrm{O_2F_2}} \mathrm{ClF_5}$$

$$\mathrm{Ag} + \mathrm{ClF_5} \xrightarrow{\mathrm{O_2F_2}} \mathrm{AgF_3}$$

$$\mathrm{PuF_4} \xrightarrow{\mathrm{O_2F_2}} \mathrm{PuF_6}$$

2.4. Reactions Involving an $\cdot OOF$ Intermediate

In controlled reactions of O_2F_2 and various compounds, ^{17}O tracer studies and other techniques have shown that the first step in the reaction appears to be

$$\mathrm{FOOF} \longrightarrow \cdot\mathrm{OOF} + \mathrm{F}\cdot$$

For example:

$$\mathrm{SO_2} + \mathrm{O_2F_2} \longrightarrow \mathrm{FSO_2OOF}$$

where the proposed mechanism (63) is

$$\mathrm{SO_2} + \mathrm{F}\cdot \longrightarrow \mathrm{FSO_2}\cdot$$

$$\mathrm{FSO_2} + \cdot\mathrm{OOF} \longrightarrow \mathrm{FSO_2OOF}$$

Also:

$$2\ \mathrm{CF_3CF{=}CF_2} + 2\ \mathrm{O_2F_2} \longrightarrow \mathrm{CF_3CF(OOF)CF_3} + \mathrm{CF_3CF_2CF_2OOF}$$

in which the proposed mechanism (64) involves the transfer of an OOF group.

The formation of a new class of compounds, dioxygenyls, containing $O^{+}{}_2$, is also thought to take place via an ·OOF intermediate (65).

$$O_2F_2 \longrightarrow \cdot OOF + F\cdot$$

$$\cdot O_2F + BF_3 \longrightarrow O_2^+BF^-{}_4$$

A number of fluorides have been shown to form $O^{+}{}_2$ compounds upon reaction with O_2F_2.

3. Uses

Oxygen difluoride is mainly a laboratory chemical. It has been suggested as an oxidizer for rocket applications and has been used for small tests in this area.

Dioxygen difluoride has found some application in the conversion of uranium oxides to UF_6 (66), in fluorination of actinide fluorides and oxyfluorides to AcF_6 (67), and in the recovery of actinides from nuclear wastes (68) (see Actinides and transactinides; Nuclear reaction, waste management).

4. Higher Oxygen Fluorides

Several higher oxygen fluorides, O_3F_2 [16829-28-0] (50, 69), O_4F_2 [12020-93-8] (70), O_5F_2 [12191-79-6] (71), and O_6F_2 [12191-80-9] (71), and radicals such as $\cdot O_3F$ (72, 73) have been reported. Only ·OF, OF_2, O_2F_2, ·OOF, and O_4F_2, however, have been satisfactorily characterized. From cryogenic mass spectroscopy, it appears that O_3F_2 consists of loosely bonded $\cdot O_2F$ and ·OF radicals (74). The ^{19}F nmr spectrum of O_3F_2 suggests an O_3F_2 model consisting of O_2F_2 and interstitial oxygen (75). However, ^{19}F and ^{17}O nmr (7, 76), and other studies have shown that O_3F_2, as reported in the literature, is actually a mixture of O_4F_2 and O_2F_2.

Little is known about O_4F_2. It has been reported to behave similarly to O_2F_2 in that it can act as a fluorinating agent or a source of the ·OOF radical. In fact, it appears to be a better source of the ·OOF radical than O_2F_2 in its reactions with SO_2 and BF_3.

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