[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Ozone Fluoride or Trioxygen Difluoride, O_3F_2[1]

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The existence of ozone fluoride, O_3F_2, has been put on a solid foundation by isolating the pure compound and analyzing it. O_3F_2 is a deep blood-red liquid, solidifying at 83°K. and decomposing at about 116° or higher in a clean cut reaction to O_2 and O_2F_2. It is an endothermic compound and is one of the most potent oxidizers known. It is more reactive than either F_2, OF_2 or mixtures of O_2 and F_2.

Introduction

Two fluorides of oxygen are well known in Western chemical literature. Oxygen fluoride, or OF_2, discovered by Lebeau and Damiens[2] is a colorless gas at room temperature and a pale yellow liquid, boiling at 128.4°K. Dioxygen difluoride, or O_2F_2, discovered by Ruff and Menzel[3] is an orange solid, melting at 109.7°K. to a red liquid; it decomposes rapidly into O_2 and F_2 close to its normal boiling point of 216°K.

A third fluoride, of the formula O_3F_2, was claimed by two Japanese scientists, Aoyama and Sakuraba, nearly twenty years ago. They described their investigations in detail in two papers.[4,5] Nevertheless their claims have not been accepted in our standard reference books; thus there is no mention of O_3F_2, for example, in Sidgwick's "Chemical Elements and Their Compounds,"[6] or in Simons' "Fluorine Chemistry."[7] Only in the handbook of Sneed, Maynard and Brasted[8] is any reference made. This is

> "The evidence for both OF[9] and O_3F_2 is not sufficiently conclusive to permit their acceptance as well-defined oxy-compounds of fluorine." (p. 124)
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> ".... to give a compound corresponding to the formula O_3F_2; the existence of this compound as well as OF[9] must be regarded with skepticism." (p. 125)

According to the Japanese scientists, O_3F_2 is formed when mixtures of oxygen and fluorine are subjected to an electrical discharge or to ultraviolet light at low temperatures. Aoyama and Sakuraba[4,5] did not give a quantitative analysis of a *weighed* sample of their product; they showed, however, that the mole ratio of O_2 to F_2 in their product, depending upon conditions, ranged from 1.0 to 1.5. Possibly the absence of a quantitative analysis and the fact that the solubility of oxygen in the known O_2F_2 was not excluded by them has been responsible for the skepticism regarding their claims.

We have repeated and confirmed the Japanese work. O_3F_2, trioxygen difluoride or, more simply, *ozone fluoride*, is a definite compound. It is a blood-red viscous liquid which can be refluxed and distilled with only slight decomposition in the range of 96 to 114°K. and at a pressure of 0.1 to 1.5 mm. It remains liquid at 90°K. and can thus be easily distinguished from O_2F_2. The composition has now been established unambiguously by chemical analysis.

It is a very strong oxidizer, very similar to O_2F_2. It is also an endothermic compound; it decomposes, with heat evolution, at about 115°K., quantitatively, according to the equation

$$2O_3F_2 \longrightarrow O_2 + 2O_2F_2$$

At about 200°K., O_2F_2 dissociates quantitatively, again under heat evolution, to $O_2 + F_2$. These two reactions provide a simple and convenient method for quantitative analysis of the compound.

Experimental

Preparation.—Ozone fluoride was prepared essentially by the method described by Aoyama and Sakuraba,[5] *i.e.*, a gaseous mixture of O_2 and F_2 was passed through a high voltage electrical discharge at either 77 or 90°K., and at a 12 ± 1 mm. total pressure. The discharge varied from 2100–2400 volts and 25–30 milliamperes. Instead of the equimolar gas mixture of the Japanese scientists, a $3O_2{:}2F_2$ mixture was used. It was found to combine quantitatively to O_3F_2 at a rate of 3–4 grams of O_3F_2 per hour in our apparatus, while the pressure remained constant.

The fluorine used in the preparation was obtained from Pennsylvania Salt Manufacturing Co. and contained 99.4% F_2, 0.4% N_2 and 0.2% HF. The oxygen from standard cylinders had a purity of at least 99.6% O_2.

The fluorine was premixed with the oxygen in a magnetic type stainless steel cylinder (obtained from A. C. Tank Co., Burlington, Wis.), after the cylinder was prefluorinated. Before use, this gaseous mixture was passed through a trap cooled to 77°K. in order to remove any hydrogen fluoride present as an impurity in the fluorine. Sodium fluoride pellets were put into the reaction vessel to remove any SiF_4 formed.

Apparatus.—The Pyrex glass apparatus used is shown, drawn to scale, in Fig. 1. A controlled electrical discharge can be passed between the two copper electrodes. The electrical apparatus consisted of a 110–5000 v., 60 cycle, one phase transformer, in series, with a 1000 ohm Ohmite vitreous enameled limiting resister, together with a 0–100 milliammeter and a 0–5000 voltmeter.

The copper electrodes were kept 10 cm. apart; they were sealed to the reaction vessel by means of Teflon plugs, coated by Glyptal.

Analysis.—As mentioned in the Introduction, this was based on the quantitative decomposition to gaseous elementary fluorine and oxygen. The fluorine was determined by the classical method of H. Moissan by absorption with mercury in a gas buret; the oxygen in a standard Orsat gas analysis apparatus.

Two typical analyses are as follows.

(a) A 1.10 ± 0.05 gram sample was decomposed by warming to 25°. The volume of gas formed equalled 644.1 cm.^{3} S.T.P., and consisted of

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(1) This work financed by the Army Ballistic Missile Agency, Redstone Arsenal, Huntsville, Alabama.

(2) P. Lebeau and A. Damiens, *Compt. rend.*, **185**, 652 (1927).

(3) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **211**, 204 (1933).

(4) S. Aoyama and S. Sakuraba, *J. Chem. Soc. Japan*, **59**, 1321 (1938); *C. A.*, **33**, 1576^7 (1939).

(5) S. Aoyama and S. Sakuraba, *ibid.*, **62**, 208 (1941); *C. A.*, **35**, 4699^6 (1941).

(6) N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford, at the Clarendon Press, 1950.

(7) J. H. Simons, "Fluorine Chemistry," Vols. I and II, Academic Press, Inc., New York, N. Y., 1950.

(8) Sneed, Maynard and Brasted, "Comprehensive Inorganic Chemistry, III, The Halogens," Van Nostrand Co., New York, N. Y., 1954, pp. 124–125.

(9) OF has been shown by P. Frisch and H. J. Schumacher, *Z. anorg. Chem.*, **229**, 423 (1936), to be but an equimolar *mixture* of $O_2 + F_2$!

	Vol., %	Vol. at S.T.P., cm.³	Wt., g.
F_2 =	40.6	261.5	0.452
O_2 =	59.4	382.6	0.557
Total =	100.0	644.1	1.009

The molar ratio $O_2{:}F_2$ was 1.464, while theory for O_3F_2 = 1.500.

(b) A second sample (0.951 g.) was decomposed to 0.534 g. of O_2 and 0.417 g. of F_2. The $O_2{:}F_2$ ratio was 1.525.

The average ratio for the two samples was 1.495 ± 0.030, in good agreement for the formula O_3F_2.

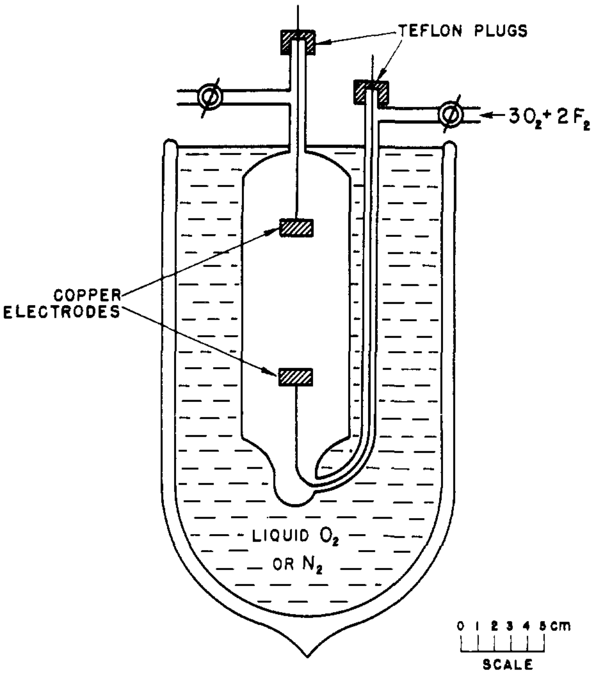

Fig. 1.—Reaction vessel for electrical discharge.

Reaction of O_3F_2 with Fluorine.—Gaseous fluorine did not react with liquid O_3F_2 at 77°K. If the fluorine gas was activated, however, by an electrical discharge of 3000–4000 v. at 30–60 milliamp., it reacted and was converted quantitatively to O_2F_2, in line with the equation

$$2O_3F_2 + F_2^* \longrightarrow 3O_2F_2$$

5.46 millimoles of O_3F_2 was distributed on the walls of the reaction vessel (see Fig. 1) at 77°K. and treated with 2.51 mmoles of "activated" F_2^*. Over a period of 0.5 hr., the O_3F_2 was converted into the red-orange solid O_2F_2. The latter, on analysis, showed an $O_2{:}F_2$ ratio of 1.04, thus proving that over 90% of the O_3F_2 was fluorinated to O_2F_2. Without a discharge, no conversion to O_2F_2 takes place.

Solubility of O_2 in O_2F_2 and O_3F_2.—In order to eliminate the possibility that O_3F_2 is in reality O_2 dissolved in O_2F_2, the following experiments were performed.

(1) Some of the blood-red liquid was refluxed while pumping at 116°K. in order to remove any dissolved oxygen. The refluxed material was then decomposed and analyzed for F_2 and O_2. The molar ratio of $O_2{:}F_2$ was 1.49, proving it to be O_3F_2.

(2) A sample of O_2F_2 was mixed with gaseous O_2 (pres. = 760 mm.) at 195°K. After shaking, the sample was rapidly frozen to 90°K. The pressure dropped to 350 mm. which corresponds to the original 760 mm. at 195°K. and did not change after standing for 18 hr. The gas was pumped off and the product decomposed to O_2 and F_2; the molar ratio of $O_2{:}F_2$ was equal to 1.01. Similar results were obtained when liquid O_2 was mixed with O_2F_2 at 90°K.; thus ozone fluoride is O_3F_2 and not O_2 dissolved in O_2F_2. Furthermore, it is not a mixture of ozone and fluorine. Both these liquids mix in any proportion at 77–85°K.; the 1:1 molar mixture is deep blue in color.

Density.—The density of liquid O_3F_2 was determined, for various temperatures, from the loss in weight of an immersed sinker. Both Pyrex glass and stainless steel sinkers were used.

Vapor Pressure.—The "vapor pressure" of O_3F_2 was determined between 79 and 114°K., with some difficulty due to the slow decomposition of O_3F_2 to $^1/_2\ O_2 + O_2F_2$ in the higher temperature range. The same difficulty was encountered in the case of O_2F_2.[3] To eliminate any error due to irreversible decomposition, as much as possible, time-pressure measurements were made over a period of ≃30 min. and then extrapolated to zero time.

At the higher temperatures O_3F_2 can be boiled under reflux, or distilled, and the pressure measurements are reproducible (see Table III). We consider them, however, of a preliminary nature until the effect of decomposition is entirely eliminated. The actual vapor pressure of O_3F_2 may be *lower* than the measured values.

Chemical Properties.—Although ozone fluoride, like all endothermic compounds, is very reactive even at 90°K., it is safer to handle than ozone, O_3. Liquid O_3F_2 can be evaporated rapidly, refluxed or thermally decomposed without any explosions. Even an electric spark will not cause it to explode. When in contact with organic or any oxidizable matter, however, it will either burn immediately, explode or detonate.

Thus, the addition of one drop of O_3F_2 to solid anhydrous ammonia (both at 90°K.) resulted in an instantaneous yellow-white flame accompanied by mild explosions. When one drop was added to a few drops of either liquid methane or solid hydrazine at 90°K., an instantaneous loud, sharp, powerful explosion occurred, shattering the reaction vessel into fine glass powder.

A mild explosion and bright white flame resulted upon contact of a drop of liquid O_3F_2 and red phosphorus powder at 90°K. while an instantaneous blue flame was produced upon adding liquid O_3F_2 to flowers of sulfur at 90°K., which after a while turned white with occasional mild explosions.

The addition of liquid O_3F_2 to powdered wood charcoal resulted immediately in a yellow flame at 90°K. As the temperature rose, the mixture exploded.

Ozone fluoride did not react with solid ethyl alcohol when added at 90°K. When removed from the liquid oxygen bath, however, it immediately burst into a blue-white flame accompanied by mild explosions.

When liquid O_3F_2 came into contact with solid bromine or iodine at 90°K., a white flash and mild explosions occurred.

TABLE I

DENSITY OF LIQUID OZONE FLUORIDE

Temp., °K.	Density, g./cm.³
82.3	1.800
83.75	1.790
85.4	1.782
87.4	1.768
89.4	1.750
89.5	1.756

TABLE II

DENSITY AND MOLAR VOLUME OF VARIOUS LIQUID OXIDIZERS

Oxidizer	Temp., °K.	Density, g./cm.³	Mol. wt., g./mole	Molar vol. cm.³/mole
O_3F_2	90.3	1.747	86	49.3
O_2F_2	116	1.736[10]	70	40.4
OF_2	90.3	1.709[11]	54	31.6
F_2	85 (b.p.)	1.505[12,13]	38	25.2
O_2	90.3	1.143[14]	32	28.0
O_3	90.3	1.575[15]	48	30.4

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(10) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **217**, 85 (1934).

(11) O. Ruff and W. Menzel, *ibid.*, **198**, 39 (1931).

(12) R. L. Jarry and H. C. Miller, THIS JOURNAL, **78**, 1552 (1956).

(13) D. White, J. Hu and H. L. Johnston, *ibid.*, **76**, 2584 (1954).

(14) E. C. C. Baly and E. G. Donnan, *J. Chem. Soc.*, **81**, 907 (1902).

(15) R. J. Brobels and J. M. McDonough, *J. Chem. Phys.*, **27**, 880 (1957).

Results and Discussion

The experimental data for the liquid density of O_2F_2 are given in Table I; they fall on a straight line when plotted against temperature. The density for the liquid follows the equation

$$D = 2.357 - 0.00676T°\text{K.}$$

A comparison of the density and molar volumes of O_3F_2, O_2F_2, OF_2, F_2, O_2 and O_3 at 90.3°K. (except O_2F_2 at its melting point) is presented in Table II.

Ozone fluoride, as readily can be seen, has the highest density of all of these substances. The increase in molar volume for the oxygen fluorides seems to be constant and = 9 cc./mole.

Preliminary "vapor pressure" values[16] for liquid O_3F_2 are given in Table III and follow the equation

$$\log P_{\text{mm}} = 4.7277 - \frac{520.7}{T°\text{K.}}$$

Preliminary data show that O_3F_2 solidifies at 83°K. and melts at 84°K.; it is always liquid at 90°K., but may be supercooled to 77°K. The substantially higher melting point of 98°K., claimed for pure O_3F_2 by Aoyama and Sakuraba,[4,5] is due to the fact that they actually had mixtures with O_2F_2 (m.p. 110°K.) in their hands.

TABLE III

VAPOR PRESSURE OF LIQUID O_3F_2

Temp., °K.	Vapor pressure, mm.
79.44	0.0052
80.80	.0054
80.80	.0048
89.47	.0365
89.60	.0385
103.7	.31
113.8	1.63
113.8	1.30

The rate of decomposition, following the equation

$$2O_3F_2 \longrightarrow O_2 + 2O_2F_2$$

was determined at temperatures between 77 and 116°K. The values obtained are listed in Table IV and show that O_3F_2 is quite stable at the lower temperatures. Thus the half decomposition time is ≃2.0 years at 77°K. The data of Table IV show a straight line when plotting the log of decomposition rate *vs.* $1/T$°K.; the activation energy of O_3F_2 decomposition is 3.7 kcal./mole. Purification of the O_3F_2 is likely to make it still more stable because impurities tend to catalyze the decomposition of endothermic compounds.

TABLE IV

RATE OF DECOMPOSITION OF OZONE FLUORIDE

Temp., °K.	Fraction decomposed/hr.
77.3	3.6×10^{-5}
77.8	6.2×10^{-5}
79.4	8.3×10^{-5}
89.5	1.6×10^{-3}
89.5	1.3×10^{-3}
89.7	1.6×10^{-3}
113.8	7.2×10^{-2}
116.0	6.12×10^{-2}

O_3F_2 is insoluble in liquid fluorine, nitrogen and oxygen at 77°K.; at 90°K. it is noticeably, but only slightly, soluble in liquid oxygen, forming a pale yellow solution (concentration probably less than 1:1000). It is miscible with OF_2 in all proportions at 116°K. but only slightly soluble at 90°K. It is slightly soluble in tetrafluoromethane (CF_4) at 116°K. It is readily soluble in dichlorodifluoromethane (CCl_2F_2) and monochlorotrifluoromethane ($CClF_3$), forming homogeneous solutions over the whole range of concentrations at 116°K. At 90°K. it is still completely soluble if the volume ratio of these solvents to O_3F_2 is 2:1 or greater. At a lower ratio than 2:1 two layers are formed; the lower one is a cherry-red solution of O_3F_2 in the halocarbon, while the upper blood-red layer is essentially O_3F_2.

Chemically, as demonstrated in the Experimental part, ozone fluoride is one of the most potent oxidizers known. It is definitely more reactive than fluorine, OF_2, or mixtures of O_2 and F_2, which is most likely due to its endothermic nature.

It will be of interest to determine the bond strengths and the structure of the O_3F_2 molecule (infrared spectrum), particularly in relation to OF_2, O_2F_2, O_3 and H_2O_2. In view of its known behavior it is unlikely that it will have the simple structure F–O–O–O–F with O–F bonds as in OF_2 and O–O bonds as in H_2O_2.

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[16] See remarks on "vapor pressure" above.