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The Reaction of Oxygen Difluoride with Some Lewis Acids. The Preparation of Dioxygenyl Salts[1]

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Both oxygen difluoride and a mixture of oxygen and fluorine react with AsF_5 and SbF_5 to give dioxygenyl salts under moderate pressure and elevated temperature.

Introduction

The first detailed investigation of reactions of OF_2 was made by Ruff.[2] He found that OF_2 would react so as to introduce either fluorine or oxygen or both into a molecule depending upon the conditions used.

In 1934, Schumacher[3] studied the kinetics of the thermal decomposition of OF_2 and concluded that it is decomposed in a first step to $F\cdot$ and $OF\cdot$ radicals which decomposed to O_2 and F_2. In several photochemical reactions[4,5] it was demonstrated that OF_2 could react with inorganic compounds as $OF\cdot$ and $F\cdot$ radicals. Franz and Neumayr[6] investigated similar reactions. Thermal reactions carried out by Cady[7] and by Engelbrecht[8] showed that OF_2 reacts as a mixture of O_2 and F_2 at elevated temperatures.

An objective of this work was to find conditions under which OF_2 would react as OF^+ and F^- to give products containing an OF^+ moiety. The most promising type of reaction seemed to be that which might be stabilized by some Lewis acids, *e.g.*

$$OF^+ + F^- + BF_3 \rightarrow OF^+BF_4^-$$

OF^+ salts were not prepared, but dioxygenyl salts were obtained in the AsF_5 and SbF_5 reactions.

The first dioxygenyl salt was discovered by Bartlett in 1962.[9] He found that PtF_6 was able to oxidize molecular oxygen to form O_2PtF_6. In 1963, Solomon[10] and Young[11] in independent work reported the preparation of O_2BF_4 and O_2PF_6 and O_2PF_6, O_2AsF_6, and O_2SbF_6, respectively, using O_2F_2 and the appropriate Lewis acid.

Since it appeared that OF_2 was behaving as though it were a mixture of oxygen and fluorine, fluorine–oxygen mixtures were made to react with AsF_5 and SbF_5. By this simple and convenient route the dioxygenyl salts have been obtained in high yields and purities. These salts have been identified by chemical, infrared, and X-ray analyses.

Attempts to prepare dioxygenyl salts from BF_3, PF_5, SiF_4, BrF_3, BrF_5, and IF_5 were unsuccessful.

Discussion

Dioxygenyl Hexafluoroarsenate and -antimonate.—The first evidence for the formation of a dioxygenyl salt from OF_2 came from a high-pressure reaction. In this experiment, OF_2 and AsF_5 were allowed to react in an autoclave (3 cm^3) at 200° and 717 atm. (Pressures were calculated assuming ideality.) The major products were those formed by the reaction of the gases with the reactor. There was a small amount of a material, however, which behaved as an oxidizer and reacted vigorously with water with evolution of ozone.

The reaction was repeated in a larger reactor (30 cm^3) at 100° and 200 atm. The mole ratio was 1:1. There was no detectable reaction after 3 days. The temperature was raised to 200° for a like period, when a salt was formed, in a yield of about 40% based on AsF_5. The gaseous products were fractionated and found to be O_2, F_2, and AsF_5. The ratio of reactants was changed to 2:1 (OF_2:AsF_5) and the experiment repeated at 200° and 200 atm. The yield of salt in this case was approximately 80%. Again the gaseous products were fractionated and identified by infrared spectra, molecular weights, or both, as O_2, F_2, and AsF_5. Material balances were determined by *PVT* relationships and weight differences. The data indicate that the reaction occurred as

$$4OF_2 + 2AsF_5 \rightarrow 2O_2AsF_6 + 3F_2$$

In an attempt to gain an insight as to the reaction mechanism and in view of the fact that the temperature of 200° was above the decomposition temperature for OF_2, an experiment was made using fluorine, oxygen, and AsF_5 ($^1/_2$:1:1) at a pressure of about 150 atm. After 5 days at 200° it was found that O_2AsF_6 had formed in 97% yield. A similar yield was obtained at

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130°; however, at room temperature only a trace of O_2AsF_6 had formed in 10 days.

Similar findings were obtained with SbF_5 in place of AsF_5.

It seems that the dioxygenyl salt formation in these reactions involves, primarily, molecular oxygen, fluorine, and the Lewis acid. The following mechanism is consistent with the findings

$$F_2 \rightarrow 2F\cdot$$

$$O_2 + F\cdot \rightarrow O_2F\cdot$$

$$O_2F\cdot + AsF_5 \rightarrow O_2F\cdot AsF_5 \rightarrow O_2^+AsF_6^-$$

The existence of the $O_2F\cdot$ radical in O_2F_2 at low temperatures has been demonstrated by Arkell.[12] Thus, the presence of $O_2F\cdot$ in O_2F_2 must be significant in the formation of dioxygenyl salts. The instability[13] of O_2F_2 at temperature above −80° precludes it as a likely intermediate in the mechanism.

Attempts to Prepare Other Dioxygenyl Salts.—Attempts were made to extend this reaction to other compounds, particularly SiF_4, BF_3, PF_5, and IF_5, and the findings are summarized in Table I.

TABLE I

REACTIONS OF OF_2 WITH VARIOUS LEWIS ACIDS

Reactants	Temp, °C	Results
$OF_2 + BF_3$	$\leqq 320$	OF_2 decomposed, no combination with BF_3
$OF_2 + IF_5$	$\leqq 150$	IF_7 produced
$OF_2 + BrF_3$	$\leqq 200$	BrF_5 produced
$OF_2 + BrF_5$	$\leqq 200$	No reaction
$OF_2 + SiF_4$	150	No reaction
$OF_2 + PF_5$	$\leqq 200$	Small amount of a white solid
$OF_2 + AsF_5$	$\leqq 200$	O_2AsF_6 obtained
$OF_2 + SbF_5$	$\leqq 200$	O_2SbF_6 obtained

Infrared Spectra.—The only absorption observed for O_2AsF_6 in the range 2–25 μ is at 14.2 μ which is characteristic for the AsF_6^- ion.[14,15] Spectra of the antimony salt showed absorption at 15 μ, characteristic of SbF_6^-.[15,16]

X-Ray Data.—The X-ray diffraction powder pattern for O_2AsF_6 is in accord with that reported by Young, *et al.*; however, the pattern obtained for O_2SbF_6 is significantly different from theirs. Since it appeared likely that O_2SbF_6 and $NOSbF_6$ would be isomorphous, X-ray diffraction powder patterns were made for both salts. These data appear in Table II and Table III. The observed pattern of O_2SbF_6 agrees quite well with that calculated for a face-centered cubic unit cell, a_0 = 10.13 Å. The differences in the cell parameters that were reported by Young and by us cannot be explained either by minor impurities or by X-ray technique. The product of Young must have been highly contaminated as was suggested by them.

TABLE II

DIFFRACTION PATTERN OF O_2SbF_6[a]

	d, Å				d, Å		
hkl	Calcd	Obsd	I/I_0	*hkl*	Calcd	Obsd	I/I_0
200	5.065	5.092	2	662	1.162	1.160	2
220	3.581	3.593	8	840	1.133	1.131	2
222	2.924	2.934	2	842	1.105	1.103	5
400	2.532	2.533	1	664	1.080	1.077	2
...	...	2.405	1	844	1.034	1.032	2
420	2.265	2.265	4	10,0,0	1.013	1.011	2
422	2.068	2.067	10	10,2,0	0.993	0.992	7
440	1.791	1.798	6	666	0.975	0.974	3
600	1.688	1.685	8	10,4,0	0.941	0.940	6
620	1.602	1.600	7	10,4,2	0.925	0.924	4
622	1.527	1.524	7	10,4,4	0.882	0.881	3
444	1.462	1.460	2	10,6,0	0.869	0.868	4
640	1.405	1.402	6	10,6,2	0.856	0.856	5
642	1.354	1.352	9	884	0.844	0.844	5
820	1.228	1.227	6	12,2,2	0.822	0.821	5
660	1.194	1.193	5				

[a] Face-centered cubic unit cell, a_o = 10.130Å.

TABLE III

DIFFRACTION PATTERN OF $NOSbF_6$[a]

	d, Å				d, Å		
hkl	Calcd	Obsd	I/I_0	*hkl*	Calcd	Obsd	I/I_0
200	5.095	5.092	2	820	1.236	1.234	7
220	3.603	3.598	8	660	1.201	1.198	6
222	2.942	2.942	2	662	1.169	1.167	2
400	2.547	2.536	1	840	1.139	1.138	3
(411)	(2.402)	2.402	1	842	1.112	1.111	3
420	2.279	2.272	5	664	1.086	1.086	2
(332)	(2.173)	2.165	2	844	1.040	1.039	3
422	2.080	2.074	10	10,0,0	1.019	1.018	3
(510)	(1.999)	1.994	1	10,2,0	0.999	0.999	7
440	1.801	1.796	7	666	0.981	0.980	3
600	1.698	1.693	8	10,4,0	0.946	0.946	7
620	1.611	1.607	7	10,4,2	0.930	0.930	6
622	1.536	1.533	6	10,4,4	0.887	0.887	6
444	1.471	1.469	2	10,6,0	0.874	0.873	7
640	1.413	1.409	7	10,6,2	0.861	0.861	7
642	1.359	1.362	9	884	0.849	0.849	5
(732)	(1.294)	1.290	1	12,2,0	0.838	0.838	4
800	1.274	1.272	1	12,2,2	0.827	0.826	7

[a] Face-centered cubic unit cell, a_o = 10.190Å.

Bartlett has reported[9] $NOSbF_6$ as having a cubic cell, a_0 = 10.193 Å. This value was in a table comparing cell dimensions of several salts of the general formula $A^+[BF_6^-]$ for which diffraction patterns were not given. We now present the powder pattern in Table III which shows $NOSbF_6$ to be a face-centered cubic unit cell in which a_0 = 10.19 Å. Attempts have been made to fit the data to more primitive cells but without success. The extra lines in Table III, which are identified by parenthetical enclosure, are attributed to NO_2SbF_6 which is present as an impurity (unpublished data).

Experimental Section

Pressure Reactions. (a) With OF_2.—The least volatile reactant was charged first to the reactor, which was a Hoke 4 HSM-30 Monel cylinder rated at 5000 psi. Then OF_2 was added by condensing with liquid nitrogen N_2(l). (OF_2 is a highly toxic gas and should be handled in an adequate fume hood. Before undertaking experiments with OF_2 it is recommended that one become familiar with the safety precautions described in the product data sheet of the Industrial Chemical Division of Allied Chemical Corp.) The materials were in mole ratios of 1:1 or 2:1 (OF_2:Lewis acid). The quantities used were those calculated to give the desired pressure at a given temperature;

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e.g., for OF_2 and AsF_5 (1:1) at 200 atm and 200° the cylinder would be charged with $\sim$0.064 mol of OF_2 and $\sim$0.064 mol of AsF_5. The reactor was then placed in an oven. After the reaction period the remaining gases were pumped off through traps in $N_2(l)$ followed by a scrubber containing a NaOH–CaO mixture to protect the pump. The white solid products were removed and handled in a drybox. Yields (based on AsF_5) varied from 40% in the 1:1 case to 81% in the 2:1 case at 200° for 6 days.

(b) **With Oxygen and Fluorine.**—Reactants were charged to the cylinder as above in the Lewis acid:O_2:F_2 ratio of $1{:}1{:}{}^1/_2$. After 1 week at temperatures in the range of 130–200°, a yield of 97–98% of the salt was realized.

Anal. Calcd for O_2AsF_6: As, 33.91; F, 51.6. Found: As, 33.56; F, 51.8. Calcd for O_2SbF_6: Sb, 45.47; F, 42.59. Found: Sb, 45.8; F, 41.3.

Analytical Methods. (1) Fluoride.—This was steam distilled from sulfuric acid at 155°. The distillate was buffered to pH 3.1 and titrated with $Th(NO_3)_4$ using alizarin red S as the indicator. The procedure used was a modification of that of Willard and Winter.[17–20]

(2) Antimony and Arsenic.—These elements were reduced to the +3 oxidation state with sulfur and then determined by titration with $KBrO_3$.[21,22]

(3) Infrared Spectra.—A Perkin-Elmer 337 spectrophotometer was used to record ir spectra in the range 2.5–25 μ. Spectra of solids were made by using mulls of Kel-F oil between AgCl disks or by using KCl pellets. Spectra of gases were made using a 5-cm length cell made from 1-in. nickel pipe fitted with a valve. Windows were 25-mm diameter rolled AgCl and were sealed to the cell with Kel-F 200 wax.

(4) X-Ray Powder Patterns.—Samples were transferred to Pyrex capillary tubes and sealed. These operations were made in a drybox. The photographs were made using a GE 143.2-mm camera and Cu Kα irradiation through a nickel filter.

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Molecular Beam Mass Spectrum, Pyrolysis, and Structure of Octaborane(18)[1]

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The molecular beam mass spectrum of octaborane(18) and the appearance potential of the ion $B_4H_9^+$ were measured. These measurements support a proposed structure for the compound in which two tetraborane fragments are joined by a single B–B bond. In addition, a pyrolysis study was made to determine the nature of the thermal decomposition of this unusual boron hydride; both tetraborane(8) and tetraborane(10) appear to be formed in the initial steps of the decomposition.

Introduction

Reaction of the unstable boron hydride octaborane(18) with hydrogen and with carbon monoxide results in cleavage to tetraborane(10) and tetraborane carbonyl, respectively.[3] Formation of these compounds is suggestive that octaborane(18) is comprised of two tetraborane(9) units connected by a B–B bond. This structure is one of two which are compatible with observed nmr data for the compound. The second structure is a belt-line icosahedral fragment.[3]

Neither a crystal structure nor a mass spectrum for octaborane(18) has been published. Since the ion fragmentation patterns of the two diverse structures that have been proposed for this boron hydride should be distinctly different,[4,5,6] the mass spectrum of octaborane(18) is expected to give evidence for its structure.

Because of the thermal instability of the boron hydrides, pyrolysis of a compound in the room-temperature inlet or on the hot-ion source of a conven-

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