TABLE V

FORCE CONSTANTS AND PARAMETERS USED IN THEIR CALCULATION

Ion	r_0, Å.	m^c	B'^c dynes·Å.[9]	dynes·Å.[10]	n^d	B^e dynes·Å.[9]	dynes·Å.[10]	k_1, md./Å.	k_2, md./Å.	k', md./Å.
					9	0.573		0.1883	0.8005	−0.0576
$[ZnCl_4]^{2-}$	2.24[a]	9	4.48							
					10		1.284	.1883	.9808	− .0576
					9	0.877		.1740	.6177	− .0484
$[ZnBr_4]^{2-}$	2.39[b]	10		30.86						
					10		2.095	.1740	.7658	− .0484

[a] In solid $(Me_4N)_2[ZnCl_4]$ (ref. 2). [b] Mean value of Zn–Br distances in solid Cs_2ZnBr_4 (B. Morosin and E. C. Lingafelter, Acta Cryst., 12, 744 (1959). [c] From ref. 8. [d] Assumed. [e] Calculated (see text).

TABLE VI

OBSERVED AND CALCULATED VIBRATIONAL FREQUENCIES FOR $[ZnCl_4]^{2-}$ AND $[ZnBr_4]^{2-}$ IONS

	$[ZnCl_4]^{2-}$				$[ZnBr_4]^{2-}$			
	Obsd. frequencies		Calcd. frequencies		Obsd. frequencies		Calcd. frequencies	
Assignment	Raman[a]	Infrared[b]	$n = 9$	$n = 10$	Raman[a]	Infrared[c]	$n = 9$	$n = 10$
ν_1 (A$_1$)	282		275	290	172		167	176
ν_2 (E)	82	84?	109	109	61		69	69
ν_3 (F$_2$)		276	282	307	210	207	215	233
ν_4 (F$_2$)	116	133	167	167	82	92	109	110

[a] Aqueous solution (ref. 6). [b] Solid $(Me_4N)_2[ZnCl_4]$. [c] Solid $(Et_4N)_2[ZnBr_4]$.

and the observed values is surprisingly good, especially for $n = 9$. We feel that a more elaborate calculation of the vibrational frequencies of these complex ions is not warranted as a direct comparison of the calculated and observed values is not possible. In fact, the calculated values refer to the $[ZnX_4]^{2-}$ ion in the gaseous state whereas the observed values are influenced by solid state interactions in the case of infrared spectra and by solvent interactions for the Raman spectra.

[CONTRIBUTION FROM REACTION MOTORS DIVISION, THIOKOL CHEMICAL CORP., DENVILLE, N. J.]

The Preparation of Dioxygenyl Salts from Dioxygen Difluoride

BY A. R. YOUNG, II, T. HIRATA, AND S. I. MORROW

Dioxygen difluoride reacts at temperatures near its melting point ($-163.5°$) with the pentafluorides of phosphorus, arsenic, and antimony to give solid products which behave as strong oxidizers. Chemical evidence as well as infrared and X-ray diffraction data support a characterization of these solids as dioxygenyl salts, O_2MF_6 ($M = P$, As, or Sb). O_2PF_6 is unstable at room temperature, but O_2AsF_6 and O_2SbF_6 are stable to above $100°$ in an inert atmosphere.

Introduction

The synthesis of the thermally unstable compound, dioxygen difluoride, was first reported by Ruff and Menzel[1] in 1933. Nothing was published about its chemical properties until the recent appearance of reports of its reactions with tetrafluoroethylene,[2] with chlorine monofluoride,[3] and with a variety of inorganic reagents.[4] During the course of a continuing investigation of its chemical properties in our laboratories, dioxygen difluoride has been observed to undergo reactions with the pentafluorides of phosphorus, arsenic and antimony, yielding solid products having moderate thermal stability and considerable oxidizing power. Qualitative studies of the properties of these solids indicated that they might be structurally related to the recently reported[5] dioxygenyl salt, O_2PtF_6. The results of quantitative studies of reactions with water and with nitrogen dioxide, as well as infrared and X-ray data, appear to support a characterization of the dioxygen difluoride–group V pentafluoride reaction products as dioxygenyl salts of composition O_2MF_6 (M = P, As, Sb).[5a]

Discussion

The reactions of O_2F_2 with the group V pentafluorides occur at temperatures slightly above the melting point of dioxygen difluoride ($-163.5°$). After completion of the reactions, as indicated by a rapid increase in pressure and the disappearance of the orange color of dioxygen difluoride, the gaseous fraction which is not condensable at $-196°$ contains an excess of fluorine over oxygen. The solid products obtained in these reactions are white at room temperature, but at $-80°$ or lower they develop violet-colored areas on their surfaces. They fume in moist air and react violently with water and organic solvents.

Thermal Decomposition.—The products derived from arsenic and antimony pentafluorides are stable at room temperature and ordinary pressures. Rapid decomposition occurs only at temperatures above $100°$. When samples of the O_2F_2–AsF_5 or O_2F_2–SbF_5 reaction products are evacuated to 10^{-6} mm. pressure, small mass peaks due to the $O_2{}^+$ are observed in the mass spectra of the vapors above the solids. The $O_2{}^+$ mass peaks increase in intensity as the samples are heated, and eventually peaks are observed which can be attributed to

(1) O. Ruff and W. Menzel, Z. anorg. allgem. Chem., **211**, 204 (1933).
(2) R. T. Holzmann and M. S. Cohen, Inorg. Chem., **1**, 972 (1962).
(3) A. G. Streng and A. V. Grosse, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, pp. 159-164.
(4) A. G. Streng, J. Am. Chem. Soc., **85**, 1380 (1963).
(5) N. Bartlett and D. Lohmann, J. Chem. Soc., 5253 (1962).

(5a) NOTE ADDED IN PROOF.—The dioxygenyl salts, O_2BF_4 and O_2PF_6, were recently reported by I. J. Solomon, et al., of the Illinois Institute of Technology Research Institute. "Reactions of O_2F_2 with Lewis Acids," Symposium on Inorganic Fluorine Chemistry, Argonne National Laboratory, Sept. 4-6, 1963.

mass fragments derived from arsenic pentafluoride and antimony pentafluoride, respectively (Table I). Aliquots of the noncondensable (at $-196°$) decomposition gas from the O_2F_2–AsF_5 product were shown by reaction with mercury to contain fluorine as well as oxygen.
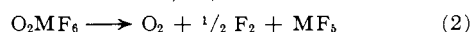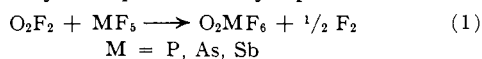
TABLE I

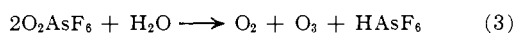THERMAL DECOMPOSITION OF O_2F_2–MF_5 REACTION PRODUCTS

	O_2F_2–AsF_5 reacn. prod.		O_2F_2–SbF_5 reacn. prod.
T, °C.	Obsd. ions	T, °C.	Obsd. ions
Ambient	$O_2{}^+$	Ambient	$O_2{}^+$
40	F^+, $O_2{}^+$, $AsF_n{}^+$		
	$(n = 0 \longrightarrow 4)$	50	$O_2{}^+$
50	F^+, $O_2{}^+$, $AsF_n{}^+$	125	F^+, $O_2{}^+$, $SbF_3{}^+$,
			$SbF_4{}^+$
	$(n = 0 \longrightarrow 4)$		
75	F^+, $O_2{}^+$, $AsF_n{}^+$	150	F^+, $O_2{}^+$, $SbF_n{}^+$,
			$Sb_4{}^+$
	$(n = 0 \longrightarrow 4)$		$(n = 0 \longrightarrow 4)$

The product derived from phosphorus pentafluoride decomposes rapidly at room temperature and even at $-80°$ undergoes slow decomposition. The decomposition gas consists of phosphorus pentafluoride, oxygen, and fluorine, the ratio of oxygen to fluorine being approximately 2:1.

The composition of the decomposition gases from the solid products suggests that their preparation and decomposition may be represented by eq. 1 and 2.

$$O_2F_2 + MF_5 \longrightarrow O_2MF_6 + {}^1/_2 F_2 \qquad (1)$$
$$M = P, As, Sb$$

$$O_2MF_6 \longrightarrow O_2 + {}^1/_2 F_2 + MF_5 \qquad (2)$$

Reaction with Water.—All of the dioxygen difluoride–group V pentafluoride reaction products evolve a mixture of oxygen and ozone when treated with water, and the resultant solutions are acidic. A quantitative study of the reaction of water with the AsF_5 product shows that the total number of moles of oxygen and ozone liberated is equivalent to the number of moles of dioxygenyl hexafluoroarsenate reacted. This result is in agreement with the reaction shown in eq. 3. Convincing chemical evidence was obtained for the existence of the hexafluoroarsenate ion in the residual aqueous solution. When the solution is treated with hydrogen sulfide it fails to form a precipitate of arsenic pentasulfide, but it immediately forms a white precipitate when treated with tetraphenylarsonium chloride. This behavior has been reported previously for the hexafluoroarsenate ion.[6,7]

$$2O_2AsF_6 + H_2O \longrightarrow O_2 + O_3 + HAsF_6 \qquad (3)$$

Reaction with Nitrogen Dioxide.—The dioxygenyl compounds oxidize nitrogen dioxide to the nitronium ion, oxygen is liberated and the residual solids may be identified as nitronium salts by their infrared spectra. Quantitative determinations (carried out on the arsenic compound) of the oxygen liberated during this reaction are in agreement with values predicted by eq. 4.

$$O_2AsF_6 + NO_2 \longrightarrow O_2 + NO_2AsF_6 \qquad (4)$$
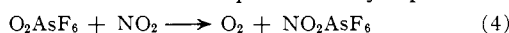
Infrared Spectra.—Infrared spectra of dioxygenyl hexafluoroarsenate and of dioxygenyl hexafluoroantimonate show characteristic absorptions[8,9] for the hexafluoroarsenate ion at 705 cm.$^{-1}$ and the hexafluoroantimonate ion at 669 cm.$^{-1}$, respectively.

X-Ray Diffraction Patterns.—The powder diffraction spacings obtained for dioxygenyl hexafluoroarsenate (Table II) may be correlated on the basis of a cubic unit cell with $a_0 = 8.00$ Å. The powder diffraction

(6) H. M. Dess and R. W. Parry, J. Am. Chem. Soc., **79**, 1589 (1957).

(7) H. M. Dess, Ph.D. Thesis, University of Michigan, 1959.

(8) G. A. Olah, et al., J. Am. Chem. Soc., **84**, 2733 (1962).

(9) H. C. Clark and R. J. O'Brien, Proc. Chem. Soc., 113 (1963).

pattern of nitrosyl hexafluoroarsenate was photographed for comparison and it appears (Table II) that the two compounds are isomorphous. In view of the similarity in size of the nitrosyl (NO$^+$) and dioxygenyl (O$_2{}^+$) cations,[5] this result further supports the characterization of the dioxygen difluoride–arsenic pentafluoride product as a dioxygenyl salt, O_2AsF_6.

TABLE II

DIFFRACTION PATTERNS OF O_2AsF_6 AND NOAsF$_6$

Cubic unit cell		O_2AsF_6		NOAsF$_6$	
$a_0 = 8.00 \pm 0.02$ Å.					
h,k,l	d, Å. (calcd.)	d, Å.	I/I_0 (rel.)	d, Å.	I/I_0 (rel.)
111	4.62	4.60	100	4.61	100
200	4.00	3.99	100	4.00	100
220	2.83	2.83	50	2.84	40
311	2.41	2.43	10	2.43	5
222	2.31	2.32	20	2.32	20
. . .	. . .	2.10	5	. . .	. . .
400	2.00	2.01	10	2.01	5
. . .	. . .	1.93	4	. . .	. . .
331	1.83	1.85	10	1.85	10
420	1.79	1.80	20	1.80	20
422	1.63	1.64	20	1.65	20
333,511	1.54	1.55	15	1.55	15
. . .	. . .	1.49	6	. . .	. . .
440	1.42	1.42	6	1.42	2
531	1.35	1.36	10	1.36	5
442,600	1.33	1.34	10	1.34	5
620	1.27	1.27	5	1.28	2
. . .	. . .	. . .	. . .	1.25	2
533	1.22	. . .	. . .	1.24	2

Some difficulty was encountered in obtaining a satisfactory diffraction pattern for O_2SbF_6; most of the photographs showed only one or two lines. It is believed that the difficulty in obtaining satisfactory patterns was due to reaction of the powder samples with the glass capillary walls. The data shown in Table III

TABLE III

DIFFRACTION PATTERN OF O_2SbF_6

Cubic unit cell		O_2SbF_6	
$a_0 = 10.71 \pm 0.15$ Å.			
h,k,l	d, Å. (calcd.)	d, Å.	I/I_0 (rel.)
. . .	. . .	5.45	20
200	5.35	5.33	20
. . .	. . .	5.11	15
210	4.79	4.87	8
. . .	. . .	4.11	20
220	3.84	3.84	100
300,221	3.52	3.53	35
310	3.39	3.39	5
311	3.23	3.23	10
222	3.09	3.16	15
321	2.86	2.80	8
400	2.68	2.68	12
410,322	2.60	2.61	5
331	2.46	2.43	10
422	2.19	2.24	5
500,430	2.14	2.13	5
511,333	2.06	2.05	10
440	1.89	1.84	10
522,441	1.82	1.81	10
620	1.69	1.70	10
621,540,443	1.67	1.67	5
631	1.58	1.59	5
711,551	1.50	1.51	5

are a composite of two fairly sharp patterns. The lines correlate roughly with calculated values for a cubic unit cell, $a_0 = 10.71$ Å. The reported unit cell dimension for NOSbF$_6$[5] is 10.19 Å.

Experimental

A Bendix time-of-flight mass spectrometer (Model 12-101) was used to identify gaseous products obtained in the thermal decomposition studies and from reactions of the dioxygenyl salts with water and NO_2. Infrared spectra were obtained on sodium fluoride pellets using a Perkin–Elmer Model 21 spectrophotometer. Positive identification of the nitronium ion by its absorption at 2350 cm.$^{-1}$ was accomplished by scanning fluorocarbon mulls of the O_2MF_6–NO_2 reaction products from 1 to 7 μ. Powder diffraction patterns were photographed with Cu Kα radiation from a nickel filter. The X-ray samples were sealed under nitrogen in Pyrex capillaries.

Oxygen, fluorine, and nitrogen dioxide were purchased from the Matheson Company, Inc., East Rutherford, N. J. Phosphorus pentafluoride, arsenic pentafluoride, antimony pentafluoride, and nitrosyl hexafluoroarsenate were purchased from the Ozark–Mahoning Co., Tulsa, Okla.

Preparation of Dioxygenyl Salts. (a) O_2PF_6 and O_2AsF_6.—The reactions of dioxygen difluoride with phosphorus pentafluoride and arsenic pentafluoride were conducted in an all-glass vacuum apparatus. Approximately 1 mmole of phosphorus pentafluoride or arsenic pentafluoride was distilled into an evacuated U-shaped trap at $-196°$. Copper electrodes had been sealed into both legs of the trap so that it could be used as a discharge tube. Excess dioxygen difluoride was generated at $-196°$ according to the procedure of Kirshenbaum and Grosse[10] and was condensed in the legs of the trap as an orange solid. As the liquid nitrogen ($-196°$) bath was lowered the dioxygen difluoride melted and flowed to the bottom of the trap where it came into contact with arsenic pentafluoride or phosphorus pentafluoride. After the orange color of the dioxygen difluoride had been discharged due to thermal decomposition, as well as reaction with the group V pentafluoride, the trap was again cooled to $-196°$, and the gas present at that temperature was sampled for fluorine analysis by absorption in mercury. The solid products were then pumped at $-80°$ for 1 hr., and, in the case of the arsenic pentafluoride product, at room temperature for an additional 2 hr. The products were white solids at room temperature, but developed violet colored areas on their surfaces when cooled to $-80°$. O_2PF_6 was stored in the reactor at $-80°$, O_2AsF_6 was sufficiently stable at room temperature to permit the transfer of the solid, in a drybox, to a Kel-F sample vial.

(b) O_2SbF_6.—The preparation of O_2SbF_6 was carried out in a vacuum apparatus constructed of Kel-F and brass. Antimony pentafluoride was weighed into a Kel-F tube in a dry atmosphere box. The tube was attached to the vacuum system at a distance of about 3 in. from the O_2F_2 generator, which was a Kel-F U-trap with copper electrodes. Excess dioxygen difluoride was generated at $-196°$, warmed to $-80°$, and vacuum distilled into the tube containing the solid antimony pentafluoride at $-196°$. The reagents were allowed to mix by replacing the liquid nitrogen bath with a Dry Ice–Trichlor bath ($-80°$), so that the dioxygen difluoride could melt and flow onto the solid antimony pentafluoride. The O_2SbF_6 was pumped for several hours and then stored under dry nitrogen at room temperature.

Analytical Determinations.—Arsenic, antimony, and fluorine were determined on solutions obtained by the reaction of weighed samples of O_2AsF_6 and O_2SbF_6 with water as described below. In the case of O_2AsF_6, perchloric acid was added to the solutions and they were boiled in order to break up the hexafluoroarsenate complex.[7] The solutions were distilled until fumes of perchloric acid were observed in the distillation flask. Fluorine was determined in the distillates by titration with thorium nitrate solution. Arsenic was determined gravimetrically on the pot residues as the pentasulfide.

Anal. Calcd. for O_2AsF_6: As, 33.91; F, 51.60. Found: As, 33.86; F, 51.11.

The hexafluoroantimonate complex could be destroyed simply by adding H_2S to an aliquot of the solution obtained by the reaction of O_2SbF_6 with water. The precipitate was dried at 280° and weighed as Sb_2S_3. Fluoride was determined on a separate aliquot by titrating with thorium nitrate.

Anal. Calcd. for O_2SbF_6: Sb, 45.47; F, 42.59. Found: Sb, 46.05; F, 39.22.

Reaction with Water.—All three O_2F_2–group V pentafluoride reaction products liberated a mixture of oxygen and ozone when allowed to react with water. Samples of O_2AsF_6 were weighed under dry nitrogen in a 50-ml. round-bottom Pyrex flask. The flask was attached to the vacuum system of calibrated volume, water was distilled into the flask at $-196°$, and the flask was then allowed to warm to room temperature, where a vigorous reaction occurred. The total pressure was measured and a sample of the gas evolved by the reaction was identified as a mixture of oxygen and ozone by mass spectroscopy. The results of two determinations are

(10) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959).

Wt. O_2AsF_6, g.	Total O_2 and O_3, found, mmole	Total O_2 and O_3, calcd. by eq. 3, mmole
0.1728	0.790	0.785
0.1608	0.701	0.729

Reaction with Nitrogen Dioxide. (a) O_2PF_6.—Phosphorus pentafluoride (1.31 mmoles) was allowed to react with excess O_2F_2 as described above. The reactor was warmed to $-80°$ and evacuated through a trap at $-196°$. The gas (0.705 mmole) condensed in the $-196°$ trap was identified by mass spectroscopy as a mixture of POF_3, SiF_4, and PF_5. The reactor was then cooled to $-196°$, and approximately 2 mmoles of NO_2 was condensed onto the solid. A carbon tetrachloride slush bath ($-23°$) was placed under the reactor for approximately 3 hr. and then replaced by a $-196°$ bath. The residual gas was transferred to a bulb of known volume by means of a Toepler pump. The quantity of gas thus removed from the reactor was found to be 1.05 mmoles. It was identified as pure oxygen by mass spectroscopy. The solid residue was removed from the reactor in a drybox in order to obtain an infrared spectrum. It was identified as NO_2PF_6 by absorptions at 2350 (NO_2^+) and at 837 cm.$^{-1}$ (PF_6^-).

(b) O_2AsF_6.—Weighed samples of O_2AsF_6 were allowed to react with excess NO_2 by a procedure identical with that used to carry out the reaction with water. The noncondensable (at $-196°$) gas produced by the reaction was measured in a calibrated bulb and identified as oxygen by mass spectroscopy. The results of two determinations are

Wt. O_2AsF_6, g.	O_2, found, mmoles	O_2, calcd. (eq. 4), mmole	Wt. NO_2AsF_6 found, g.	Wt. NO_2AsF_6, calcd. (eq. 4), g.
0.2160	1.08	0.970	. . .	. . .
0.1926	0.897	0.872	0.2043	0.2048

Thermal Decomposition. (a) O_2PF_6.—The product obtained by the reaction of PF_5 with O_2F_2 decomposed slowly on standing at $-80°$ *in vacuo*. After a 24-hr. period at $-80°$, the trap containing the O_2PF_6 was cooled to $-196°$. The noncondensable gas at $-196°$ was pumped by means of a Toepler pump, through a U-trap containing sodium chloride at 100°. Chlorine was produced by reaction of the sodium chloride with the fluorine present in the decomposition gas. The chlorine was condensed in a second U-trap at $-196°$. The oxygen in the decomposition gas passed through both traps and was transferred into a bulb of known volume. The quantity of oxygen measured was 0.116 mmole and the quantity of chlorine (equivalent to the initial fluorine) found was 0.063 mmole. The oxygen to fluorine ratio in the decomposition gas was therefore 1.85/1.00.

(b) O_2AsF_6.—Determination of the oxygen fluorine ratio in the noncondensable decomposition gas from pyrolyzed samples of O_2AsF_6 consistently gave high results (theoretical $O_2/F_2 = 2$). This was due to the consumption of fluorine by reaction with the walls of the pyrolysis and gas measuring apparatus at the temperatures required to induce rapid decomposition (130–180°). The pyrolysis tubes were constructed from 13 mm.-diameter copper or Teflon tubing fitted by means of a Swagelock connection to a monel valve and balljoint. Samples of O_2AsF_6 (30–100 mg.) were loaded into the tubes under dry nitrogen, the Swagelock connection was tightened, and the tubes were attached to a Pyrex vacuum system and evacuated. Included in the Pyrex vacuum system were a U-trap, a manometer having a 1-cm. protective layer of Fluorolube oil on the surface of the mercury, and a tube of known volume into which mercury could be admitted in order to absorb fluorine. The pyrolysis tubes were heated for several hours at approximately 180° with the valves open to the U-trap (at $-196°$) and manometer. Aliquots of the noncondensable decomposition gas were admitted to the calibrated tube where they were shaken over mercury to absorb the fluorine. The pressure of residual gas was measured and it was identified as oxygen by mass spectroscopy. The results obtained in three typical runs are

Noncondensable aliquot, mmole	O_2, found, mmole	F_2, by difference, mmole	O_2/F_2
0.060	0.047	0.013	3.6
0.275	0.205	0.070	2.9
0.112	0.085	0.027	3.1