193–196°, was prepared. The pyridine analog, $AsCl_3 \cdot 2py$, m.p. 64°, has been reported previously.[16]

Recent work on the preparation of Tl(III) adducts of the type $TlX_3 \cdot 2D$ and $[Q^+][TlX_4^-]$[17] further illustrates the general applicability of the methods outlined in this paper. Particularly noteworthy is the stabilization of thallium(III) iodide by complexation with triphenylphosphine oxide to give $TlI_3 \cdot 3OP(C_6H_5)_3$. Whereas solid TlI_3 is most surely thallium(I) triiodide,[18] in the presence of certain neutral ligands the Tl(III) state is stabilized.

It should be borne in mind that solvent molecules may also serve as stabilizing ligands. By the appropriate selection of a solvent it should be possible to stabilize species of desired oxidation states. An example serves to illustrate this point. Thallium(I) triiodide, when placed in methanol or ethanol, behaves as though it were a solution of thallium(III) iodide.[19] The stabilization of the thallium(III) state may be viewed in terms of complexation stabilization by the solvent according to the idealized equations

$$x\text{ROH} + \text{TlI}_3(\text{s}) = \text{Tl(ROH)}_x{}^+ + \text{I}_3{}^- \qquad (4)$$

$$y\text{ROH} + \text{Tl(ROH)}_x{}^+ + \text{I}_3{}^- = [\text{Tl(ROH)}_{x+y-n}\text{I}_n{}^{+(3-n)}] + (3-n)\text{I}^- \qquad (5)$$

Other explanations are possible,[19] but the complexation model should not be ignored.

Experimental

Reagents.—All reagents were used without further purification except those for which purification procedures are given. Reagent grade carbon tetrachloride was fractionally distilled from potassium hydroxide and stored over anhydrous sodium sulfate until used. Reagent grade chloroform was shaken repeatedly with concentrated sulfuric acid, washed with water, dried over P_2O_5, and fractionally distilled.

Chlorine gas (Matheson) was dehydrated by passing through a sulfuric acid scrubbing tower.

Practical grade acetonitrile (Eastman Kodak) was fractionally distilled from phosphorus pentoxide. The constant-boiling center fraction was retained and shaken for several days with Linde Molecular Sieve, Type 3A, to remove the last traces of moisture.

Preparation of $AsCl_5 \cdot 2OP(C_6H_5)_3$.—In a typical reaction chlorine was added to 350 ml. of a carbon tetrachloride solution of 10.7 g. (0.0590 mole) of arsenic trichloride (Matheson Coleman and Bell) and 16.5 g. (0.0593 mole) of triphenylphosphine oxide (Metal and Thermit Corp.), m.p. 155.5–156.5°. The reaction temperature was held between −7 and 0° with a sodium chloride–ice bath. Within a short period after the introduction of the chlorine an orange solid separated from the solution. The solid was filtered, washed with chilled carbon tetrachloride, and dried under vacuum at room temperature for 3 hr. The yield was 17.4 g., 73.0%. The orange crystals evolve chloride slowly at room temperature. The compound melts partially at 42° with decomposition. At 70° the solid is completely melted to a yellow liquid that becomes colorless at 95°. The compound is slowly hydrolyzed by atmospheric moisture.

Anal. Calcd. for $C_{36}H_{30}P_2O_2AsCl_5$: C, 53.46; H, 3.74; P, 7.66; O, 3.96; As, 9.26; Cl, 21.92. Found: C, 53.38; H, 4.04; P, 8.70; O (by difference), 4.20; As, 9.53; Cl, 20.15.

All melting points reported herein are for samples in open capillary tubes and are uncorrected.

Preparation of $[(C_2H_5)_4N^+][AsCl_6^-]$.—In a typical reaction a 10.7-g. (0.0590 mole) sample of arsenic trichloride was dissolved in 200 ml. of freshly distilled chloroform and the solution chilled to 0°. Chlorine gas was passed into the solution until the solution became saturated with the gas. A chloroform solution containing 5.33 g. (0.0321 mole) of tetraethylammonium chloride (Eastman Kodak White Label) in 100 ml. of solvent was added dropwise to the deep yellow $AsCl_3$–Cl_2 solution. Immediately an orange precipitate developed. The addition of the ammonium chloride solution required 30 min. An excess of chlorine was maintained at all times. The solid material was filtered and washed with chloroform under a nitrogen atmosphere. The yield of crude product was 12.5 g., 93.0% of theoretical.

The compound was recrystallized from acetonitrile to give orange platelets, m.p. 146.5–149.0° with decomposition. The dissolution of the crude material was carried out at room temperature and crystallization was immediately induced at 0° in order to reduce the amount of decomposition that spectral studies reveal takes place in acetonitrile.

Anal. Calcd. for $C_8H_{20}NAsCl_6$: C, 22.99; H, 4.82; N, 3.43; As, 17.92; Cl, 50.90. Found: C, 23.08; H, 4.78; N, 3.35; As, 17.99; Cl, 50.74.

Preparation of $AsCl_3$.—The yellow solid adduct, m.p. 193–196°, was obtained in essentially quantitative yields by the addition of arsenic trichloride to 2,2′-dipyridine (Eastman Kodak White Label) in carbon tetrachloride.

Anal. Calcd. for $C_{10}H_8N_2AsCl_3$: C, 35.59; H, 2.39; N, 8.30; Cl, 31.52. Found: C, 35.46; H, 2.51; N, 8.27; Cl, 31.38.

Elemental Analyses and Spectral Analyses.—All elemental analyses were performed by the Galbraith Laboratories, Knoxville, Tenn.

Infrared spectra in the 4000–650 cm.$^{-1}$ region were taken on a Beckman spectrophotometer, Model IR8. All spectra were of samples in potassium bromide pellets except where stated otherwise.

The Perkin-Elmer Model 521 grating spectrophotometer was used for measuring spectra in the 650–200 cm.$^{-1}$ region.

Ultraviolet spectra were measured on a Cary Model 15 spectrophotometer.

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The Radical Decomposition of Peroxysulfuryl Difluoride, FSO_2OOF, and Related Compounds by Chemical and Electron Paramagnetic Resonance Methods

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The synthesis of peroxysulfuryl difluoride (FSO_2-OOF) by the reaction of sulfur trioxide and oxygen di-

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(17) F. A. Cotton and B. F. G. Johnson, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30–Sept. 4, 1964, p. 15-O.

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TABLE I

E.p.r. DATA OF RADICALS TRAPPED IN CCl_3F MATRIX

Compd., % in CCl_3F	Radical	Temp., °C.	hfs, gauss A	hfs, gauss B	Isotropic g value
FSO_2OOSO_2F (pure)	FSO_2O	−196	9.9	0.43[a]	2.0133
FSO_2OOSO_2F (25%)	FSO_2O	−196	9.4		2.0131
FSO_2OF, ultraviolet (15%)	FSO_2O	−132 to −175	9.5		2.0132
FSO_2OOF, ultraviolet (10%)	FSO_2	−40 to −150	14.6		2.0050
FSO_2OOF, ultraviolet (10%)	OOF	−160 to −180	48.0	25.2[b]	2.0042
OF_2, ultraviolet (0.7%)	OF	−134 to −184	13.8		2.0046

[a] Observed values: $hfs_\perp = 9.5$, $hfs_{||} = 10.8$, $g_\perp = 2.0122$, $g_{||} = 2.0155$. [b] Observed values: $hfs_\perp = 22.8$, $hfs_{||} = 98.3$, $g_\perp = 2.0024$, $g_{||} = 2.0080$.

fluoride was recently reported.[1-3] This compound decomposed under various conditions using ultraviolet irradiation.[2] However, intermediate free radicals and final products were not identified.

In this work, the ultraviolet- and radical-induced decomposition reactions of FSO_2OOF and related compounds were investigated. Free radicals produced in these reactions were identified and studied by electron paramagnetic resonance (e.p.r.) techniques. The final products were usually separated by fractional codistillation[4] and identified by infrared and F^{19} n.m.r. analyses.[3]

Experimental

Radical-Induced Decomposition of FSO_2OOF.—A 1-l. nickel flask was charged with 110 mm. pressure of FSO_2OOF (0.86 g., 0.0064 mole) and 40 mm. pressure of dinitrogen tetroxide. The mixture was allowed to stand overnight at room temperature, and the products were separated by fractional codistillation. The main products were 0.080 g. (0.00078 mole) of sulfuryl fluoride (F_2SO_2), 0.32 g. (0.0018 mole) of pyrosulfuryl difluoride (FSO_2OSO_2F), and a small amount of silicon tetrafluoride. Essentially, all of the dinitrogen tetroxide was recovered. A large quantity of "noncondensable" gas was observed but was not analyzed.

Ultraviolet-Induced Decomposition of FSO_2OOF.—Approximately 0.6 g. of gaseous FSO_2OOF in a 1-l. Pyrex flask was irradiated for 40 min. with a high-pressure mercury vapor lamp. Fractional codistillation of the decomposition products gave 0.082 g. (0.00080 mole) of F_2SO_2 and 0.31 g. (0.0017 mole) of FSO_2OSO_2F. A small amount of silicon tetrafluoride and 0.011 g. (0.000082 mole) of unreacted FSO_2OOF were collected. Again, a large quantity of "noncondensable" gas was observed but was not analyzed.

E.p.r. Studies of Decomposition Reactions.—The compounds listed in Table I were studied by e.p.r. techniques. Studies of radicals formed in the pure compounds and in $CFCl_3$ matrices containing the compounds were carried out with a Varian Model 4500-10A e.p.r. spectrometer, equipped with a 9.2-kMc. wave meter and a crystal controlled fluxmeter. The $CFCl_3$ solutions were frozen (m.p. −110°) and irradiated with ultraviolet light inside the e.p.r. cavity. In most cases, spectra were recorded repetitively, in order to detect any changes with time or temperature. The temperature ranges, concentrations, hyperfine splittings (hfs), and g values for each system are listed in Table I.

Results

Peroxysulfuryl Difluoride (FSO_2OOF).—The decomposition of gaseous FSO_2OOF by radical or ultraviolet treatment resulted in moderate yields of FSO_2OSO_2F and F_2SO_2. Also, a considerable quantity of "noncondensable" gas was produced. The product distribution for both the radical-induced and the ultraviolet-induced reactions was approximately the same; that is, the ratio of moles of FSO_2OSO_2F to F_2SO_2 was approximately 2.

The ultraviolet decomposition of FSO_2OOF in a $CFCl_3$ matrix was monitored by e.p.r. techniques. The matrix was continuously irradiated while the spectra were observed at various temperatures. Above −110° FSO_2 was readily observed in liquid $CFCl_3$ as an isotropic doublet. Below −135° the FSO_2 spectrum was considerably broadened. At −160° the spectra of the FSO_2 and O_2F radicals[5] were superimposed. At lower temperatures, only the O_2F signal was observed, and the FSO_2 signal presumably became too broad for detection.

The spectrum of O_2F in a $CFCl_3$ matrix at −180° is shown in Figure 1. It shows a highly anisotropic doublet. The small peak indicated with an asterisk at the center of the spectrum may be due to the decomposition of the O_2F since it was more intense when pure FSO_2OOF was irradiated. This spectrum is identical (including the peak indicated with an asterisk) with the one obtained by Grosse, *et al.*, by the decomposition of O_3F_2 and O_2F_2[5] and identified as the O_2F radical. Measurements were made as indicated for the parallel and perpendicular directions. The isotropic (*A*) and

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(1) R. Gatti, E. H. Staricco, J. E. Sicre, and H. J. Schumacher, *Angew. Chem.*, **75**, 137 (1963).

(2) R. Gatti, E. H. Staricco, J. E. Sicre, and H. J. Schumacher, *Z. physik. Chem.* (Frankfurt), **36**, 211 (1963).

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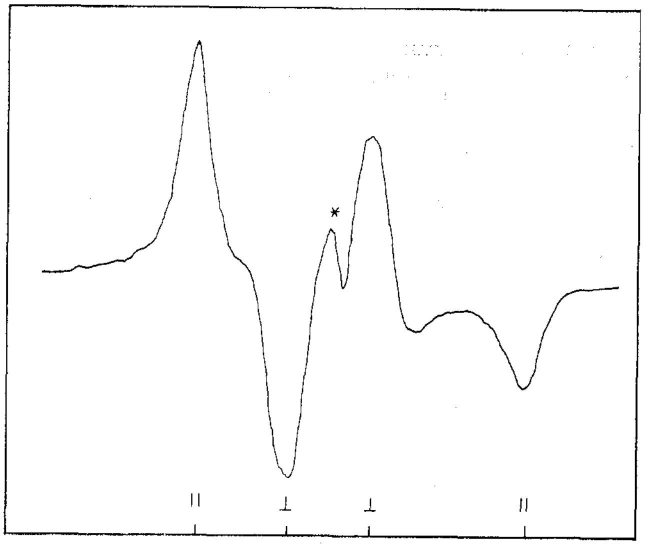

Figure 1.—E.p.r. spectrum of the O_2F radical formed by the ultraviolet irradiation of 5–10% FSO_2OOF in a $CFCl_3$ matrix at −180°.

anisotropic (*B*) hyperfine splittings were calculated from $hfs_{\parallel} = |A + 2B|$ and $hfs_{\perp} = |A - B|$, and the relative signs were not determined. The isotropic *g* value was calculated from $^1/_3 g_{\parallel} + {}^2/_3 g_{\perp}$.

The decomposition of FSO_2OOF in both the pure solid and in the $CFCl_3$ matrix gave rise to the same radicals. Under both conditions the O_2F radical was relatively long-lived at −190°. Approximately 80% of the FSO_2 radical disappeared within 14 min. at −120°.

Peroxydisulfuryl Difluoride (FSO_2OOSO_2F).—FSO_2OOSO_2F has been shown by spectrophotometric and pressure–temperature studies to be in equilibrium with the FSO_2O radical at room temperature.[6] When the low-pressure, room temperature gas was condensed on a cold finger at −196°, FSO_2O radicals were trapped in solid FSO_2OOSO_2F and observed as a slightly anisotropic doublet. The same radical was observed when a gaseous mixture of FSO_2OOSO_2F and $CFCl_3$ was condensed at −196°, but its spectrum was more isotropic. However, upon irradiation at −196° the radical disappeared, as indicated by the disappearance of the e.p.r. signal.

Fluorine Fluorosulfonate (FSO_2OF).—Irradiation of FSO_2OF produced the FSO_2O radical. In addition an unidentified radical with a *g* value of 1.99 was observed. The latter may have arisen from the reaction of fluorine atoms with the matrix material or the Pyrex sample tube. The FSO_2O radical does not recombine at −196°.

Oxygen Difluoride (OF_2).—Irradiation of both pure liquid OF_2 at −196° and OF_2 in a $CFCl_3$ matrix gave the same resolved isotropic doublet. The hyperfine splitting, *g* value, and relative stability were entirely different from those of the other radicals. The radical was relatively unstable at −184°, decomposing to the extent of 70% in 19 min. in the $CFCl_3$ matrix.

The observed free radicals were not due to a reaction with the CCl_3F matrix since similar spectra were obtained with the pure compounds.

Discussion

The initial step in the decomposition of FSO_2OOF could involve the breaking of any one of three bonds. The radicals FSO_2OO, FSO_2O, or FSO_2 could be formed (accompanied by F, OF, or O_2F, respectively).

The formation of FSO_2F and FSO_2OSO_2F as final products by reaction with NO_2 or under ultraviolet irradiation suggests that FSO_2O and/or FSO_2 radicals were formed. The e.p.r. data showed the formation of FSO_2 and O_2F radicals and that OF, FSO_2O, and FSO_2OO radicals were not formed. Therefore, the initial step in the decomposition appears to be the breaking of the S–O bond to yield the FSO_2 and O_2F radicals. A mechanism for this decomposition must account for the initial formation of the FSO_2 and O_2F radicals, the 2:1 mole ratio of FSO_2OSO_2F to FSO_2F as products, and the formation of noncondensable products (probably O_2 and F_2).

It is not within the scope of this work to give a precise explanation for the larger hyperfine splitting observed for FSO_2 relative to FSO_2O. However, this result may be qualitatively accounted for by considering the relative amounts of s-character expected at the fluorine nuclei in these two radicals. Since FSO_2 and FSO_2O have similar hybridization, the smaller FSO_2 radical would be expected to have a higher electron spin density per atom. Also, the FSO_2 has one less electronegative oxygen atom which probably would give more s-character in the orbitals at the fluorine nucleus. These effects would lead one to predict a smaller hyperfine interaction in FSO_2O than in FSO_2, since the splitting is determined by the magnitude of the unpaired electron spin density and s-character at the fluorine nucleus. By this same reasoning, the FSO_2OO radical would be expected to have a smaller hyperfine interaction than the FSO_2O radical.

It is of interest to note that the relative strengths of bonds in the FSO_2 system vary, depending on the groups which are attached to the FSO_2 group. The O–O and O–F bonds are the weakest ones in FSO_2OOSO_2F and FSO_2OF, respectively. In contrast the S–O bond is the weaker one in FSO_2OOF.

It would seem likely that the initial step in the dissociation of OF_2 involves the breaking of an O–F bond to form the OF radical, as indicated by our gas-phase e.p.r. studies. However, the e.p.r. evidence for the existence of the OF radical is not very conclusive. Our observations of stability, concentration, and temperature effects observed with pure liquid OF_2 and with OF_2 in a matrix indicate that the e.p.r. spectrum could arise from either the OF radical or a fairly unstable paramagnetic molecule. The existence and identification of the OF radical will be the subject of a forthcoming publication. Of primary interest here is the fact that the radical observed from OF_2 was not formed in the decomposition of any of the sulfuryl compounds. Also, the O_2F radical is unique and can only be obtained

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(6) F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **85**, 3375 (1963).

from the decomposition of FSO_2OOF, O_3F_2, or O_2F_2 and not from FSO_2OOSO_2F, FSO_2OF, or OF_2.

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CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA,
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Plutonium Borides[1]

BY HARRY A. EICK[2]

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Although the chemistry of many refractory plutonium compounds has been investigated extensively in the past 10 years, little effort has been directed toward study of the plutonium borides. The first report of these borides appeared in 1960 in a communication[3] which lists four compounds, PuB, PuB_2, PuB_4, and PuB_6, together with the crystal structure, lattice parameters, and interatomic distances of each species. The melting points of nominal compositions corresponding to the above have been reported,[4] but no additional information is available.

Since McDonald and Stuart[3] report the presence of extra unidentified lines in their X-ray powder diffraction photographs, and since the existence of PuB_{12} was suspected, the system was re-examined. Another point of interest was the NaCl-type monoboride which they report. No other metal has been shown unequivocally to form a monoboride with this type of structure; thus if it indeed exists, it would be most interesting.

Experimental

Two procedures were followed. In the first method, which differed from that reported by McDonald and Stuart only in the use of a vacuum instead of an argon atmosphere, plutonium (99.99% pure) was heated with elemental boron (98.7% pure; 0.5% Mg and Si, 0.05% Al, Cu, Mn, Fe, Ni, and Ca) in various atom ratios in either a BN or a ZrB_2 container in an evacuated tantalum resistance-heated tube furnace. The product was removed from the cell, crushed, ground in an Alundum mortar, and reheated in the furnace to achieve homogeneity. Temperatures ranging from 800 to 2060° were used. The BN crucible was found to react with plutonium at 1200° to form PuB_2 and thus was not a satisfactory container.

The second method consisted of arc melting in a purified argon atmosphere samples of plutonium and boron in the atom percentages, plutonium to boron, 67:33, 50:50, 33:67, 20:80, 14:86, 12:88, 10:90, 5:95, and 0.8:99.2

The products of both preparations were examined by X-ray powder diffraction using a 114.59-mm. diameter Debye–Scherrer powder camera and copper Kα radiation (λ_{α_1} 1.54050 Å.). In addition, the arc-cast specimens were examined micrographically. The 1:1 specimen was annealed for 8 hr. at 1600° and 8 hr. at 1700° to check for monoboride formation.

As a check for homogeneity ranges, the lattice parameters of a large number of preparations were determined using the extrapolation procedure described by Vogel and Kempter.[5]

Results and Discussion

Table I lists the phases present in the arc-cast samples, as determined by X-ray powder diffraction analysis and confirmed by micrography. The 1:6 and 1:12 compositions may have been somewhat deficient in boron because of its volatility and the difficulty involved in collecting into the arc-cast button that material which had distilled onto the cold hearth. These particular compositions were sensitive to thermal shock and (usually) fractured violently during cooling after the arc had been extinguished. The boride X-ray diffraction patterns of all specimens were sharp; large single crystals were present in the 14:86 preparation. In those preparations containing metallic plutonium, the metal pattern was diffuse and weak, but clearly present. Lines present in the photographs of all but the 95:5 composition were explainable on the basis of the phases listed in Table I.

TABLE I
PHASES OBSERVED IN ARC-CAST SPECIMENS
OF PLUTONIUM AND BORON

Compn., Pu:B atom ratio	Measured density, g./cc.	Phases present by X-ray	Phases present by micrography
67:33	...	α-Pu, PuB_2	α-Pu, PuB_2
50:50	...	α-Pu, PuB_2	α-Pu, PuB_2
33.3:66.7	12.06	PuB_2, PuB_4 (trace)	PuB_2, PuB_4 (trace)
20:80	9.21	PuB_4, PuB_6 (trace)	PuB_4, PuB_6
14:86	7.21	PuB_4, PuB_6	PuB_4, PuB_6
12:88	6.79	PuB_6, PuB_{12}	3 phases, see text
10:90	6.25	PuB_6, PuB_{12}	3 phases, see text
5:95	5.63	PuB_6, PuB_{12}	3 phases, see text
0.8:99.2	2.73	PuB_{12}, PuB_{100}	PuB_{100}, PuB_{12} (trace)

The micrographic examination of the 12:88, 10:90, and 5:95 specimens indicated the presence of three constituents, while the X-ray patterns showed only two phases, PuB_6 and PuB_{12}. All the observed microstructures are compatible with the following construction for the temperature–composition phase diagram: PuB_4 melts congruently, while PuB_2, PuB_6, PuB_{12}, and "PuB_{100}" melt peritectically. A eutectic exists between PuB_{12} and "PuB_{100}." The eutectic composition is greater than 95 atomic % boron. Thus the above three alloys, listed in Table I as showing three phases under the microscope, consisted of primary PuB_6 and secondary PuB_{12} surrounding the PuB_6. The third constituent was the last liquid to solidify and consisted of a eutectic mixture of PuB_{12} and "PuB_{100}." The eutectic mixture either was too fine to resolve

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) On leave from Department of Chemistry, Michigan State University, East Lansing, Mich.

(3) B. S. McDonald and W. I. Stuart, *Acta Cryst.*, **13**, 447 (1960).

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