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Reaction of Octasulfur Bis(hexafluoroarsenate), $S_8(AsF_6)_2$, with Tetrafluoroethylene. A Novel Synthesis of Bis(perfluoroethyl) Polysulfides[1]

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Received August 28, 1972

Solid $S_8(AsF_6)_2$ reacts with gaseous C_2F_4 at room temperature to form $(C_2F_5)_2S_x$, $x = 2$-6. In SO_2, the same reactants yield $(C_2F_5)_2S_x$, $C_2F_5S_xCF_3$, and $C_2F_5S_xCF_2COF$, $x = 2$-3. A reaction mechanism is proposed.

Group VI elements can be oxidized by a variety of reagents to form several polyatomic cationic species,[2] *viz.* S_4^{2+}, S_8^{2+}, S_{16}^{2+}, Se_4^{2+}, Se_8^{2+}, Te_4^{2+}, Te_6^{2+}, and Te_n^{n+}. Much has been learned about these cations by X-ray diffraction, vibrational spectroscopy, and other physical techniques. Their chemical properties, however, have not been systematically investigated.

The sulfur rings in $S_8(AsF_6)_2$ have the endo,exo conformation[3] shown in Figure 1. The interatomic distances for the two crystallographically distinct sulfur rings, given in Table I, suggest that there are bonds across the ring between adjacent pairs of sulfur atoms, the interaction between S(3) and S(7) being slightly greater than that between the other pairs. It was of interest, therefore, to determine if the sulfur ring would undergo reactions which could be interpreted as manifestations of this unusual bonding situation. The results reported herein involve the reaction of tetrafluoroethylene with $S_8(AsF_6)_2$.

Experimental Section

Tetrafluoroethylene was purchased from Columbia Organic Chemicals, sulfuryl fluoride, from Chemicals Procurement Laboratories, thionyl fluoride, from Peninsular ChemResearch, and sulfur, from McArthur Chemical Co. All were used without further purification. Sulfur dioxide and hydrogen fluoride were purchased from the Matheson Co. and dried over calcium hydride and K_2NiF_6, respectively, and redistilled prior to use. Arsenic pentafluoride was prepared by fluorination of arsenic trifluoride purchased from Ozark-Mahoning. $S_8(AsF_6)_2$ was prepared in anhydrous hydrogen fluoride according to the published procedure[4] and $S_{16}(AsF_6)_2$ was prepared by disproportionation of equimolar amounts of $S_8(AsF_6)_2$ and S_8 in sulfur dioxide.

Low-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D spectrometer using an ionizing voltage of 70 eV except where confirmation of molecular ions required reduced voltage High-resolution spectra were obtained by Shrader Analytical and Consulting Laboratories, Detroit, Mich. ^{19}F nmr spectra were obtained on a Varian HA-60 spectrometer operating at 56.4 MHz or a Varian HA-100 spectrometer operating at 94.08 MHz. Vapor-phase chromatographic analyses were accomplished using a column of 10% DC-200 Silicone oil on Chromosorb W.

Neat Reaction between $S_8(AsF_6)_2$ and C_2F_4. In a typical reaction, $S_8(AsF_6)_2$ (9.7 g, 0.015 mol) was measured into a metal reaction vessel whose closure was made leak tight by use of a Telfon "O" ring. After evacuating the container, the solid was exposed to approximately 0.075 mol of C_2F_4, at initially 3 atm pressure. After 2 days, the pressure of C_2F_4 and the gaseous products dropped to 1.5 atm where it stabilized. The products were separated first by fractional condensation in a vacuum line constructed with "Rotoflo" Teflon valves. In addition to unreacted C_2F_4, the most volatile fraction contained a small amount of C_2F_6. The remaining less volatile products consisted of two layers, the more dense being arsenic trifluoride and the less dense a mixture of bis(perfluoroethyl) polysulfides. It was found by vpc that the solubilities of the two layers in each other were very small. Thus, the products were easily separated by freezing the AsF_3 and decanting the liquid polysulfides into an isolatable side arm of a specially designed glass vessel. The 3.2 g of AsF_3 represented 80% of the total arsenic. The 7.4 g of sulfides was found by vpc to be 80% $(C_2F_5)_2S_2$, 19% $(C_2F_5)_2S_3$, and approximately 0.5% $(C_2F_5)_2S_4$. Thus, the products incorporated 53% of the fluorine available from the hexafluoroarsenate ion (*i.e.*, 3 fluorine atoms per AsF_6^-) and 43% of the total sulfur.

Table I. Some Interatomic Distances[a] in S_8^{2+}

Sulfur atoms	Interatomic distances,[b] Å		Av, Å
	Ring I	Ring II	
S(2)-S(8)	3.010 (11)	2.866 (11)	2.94
S(3)-S(7)	2.832 (10)	2.889 (12)	2.86
S(4)-S(6)	2.942 (10)	3.053 (12)	3.00

[a] See ref 3. [b] *Cf.* van der Waals contact distance 3.7 Å and the S-S bond distance in S_8 2.05 Å.

The high-resolution mass spectra gave molecular ions at 301.9301 (calcd for $C_4F_{10}{}^{32}S_2$, 301.9280), 333.9034 (calcd for $C_4F_{10}{}^{32}S_3$, 333.9001), and 365.8729 (calcd for $C_4F_{10}{}^{32}S_4$, 365.8722). The isotopic ratios and fragmentation patterns were consistent with the assigned structures and in agreement with reported data.[5] The ^{19}F nmr spectrum of $(C_2F_5)_2S_2$ gave CF_2 (97.0 ppm, q) and CF_3 (84.3 ppm, t) and that of $(C_2F_5)_2S_3$ gave CF_2 (95.2 ppm, q) and CF_3 (84.0 ppm, t), all relative to an external (capillary) CCl_3F standard. All coupling constants were 2.5 Hz. These data are also in substantial agreement with the data published by others.[5]

In addition to the volatile products, a yellow-green solid was found in the reaction vessel. Of the 1.6 g of solid, 1.2 g was an unidentified green SO_2-soluble substance showing only AsF_6^- in significant amounts in the infrared spectrum. The remaining 0.4 g was found to consist mainly of elemental sulfur.

Other neat reactions at pressures of 0.5-3 atm and temperatures from ambient to 100° gave similar results with the disulfide always constituting at least 60% of the product and the tetrasulfide never exceeding 1%. In some cases, traces of $(C_2F_5)_2S_5$ and $(C_2F_5)_2S_6$ were detected by low-resolution mass spectrometry and vpc but conditions favoring the higher sulfides in the neat reaction were not found. At −78°, there was no indication that a reaction had taken place between C_2F_4 and $S_8(AsF_6)_2$ after 4 days.

A neat reaction employing $S_{16}(AsF_6)_2$ also resulted in a mixture of polysulfides. The vpc analysis of the mixture showed 88% $(C_2F_5)_2S_2$, 11% $(C_2F_5)_2S_3$, and less than 1% $(C_2F_5)_2S_4$. Traces of $(C_2F_5)_2S_5$ and $(C_2F_5)_2S_6$ were also found in the vpc and mass spectral analyses of the mixture. In this case, too, an unidentified solid remained.

Reaction between $S_8(AsF_6)_2$ and C_2F_4 in the Presence of Liquid Sulfuryl Fluoride. In a typical reaction, $S_8(AsF_6)_2$ (9.1 g, 0.014 mol) was measured into a 35-cm³ metal reactor. To this were added about 5 cm³ of SO_2F_2 and 0.042 mol of C_2F_4. After 2 days at room temperature, the products were separated by fractional condensation to remove C_2F_4, C_2F_6, and SO_2F_2. By the method previously described, the polysulfides were decanted and found to weigh 5.1 g. A vpc analysis showed the polysulfides consisted of 79% $(C_2F_5)_2S_2$, 18% $(C_2F_5)_2S_3$, and 3% $(C_2F_4)_2S_4$. Thus, 38% of the available fluorine and 32% of the total sulfur were incorporated into the

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[1] Presented in part at the American Chemical Society Winter Fluorine Conference, St. Petersburg, Fla., Jan 23-28, 1972.

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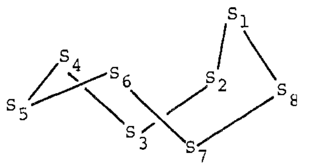


Figure 1. Structure of S_8^{2+}.

polysulfides. The 2.4 g of AsF_3 represented 62% of the total arsenic. Remaining was a gray-green solid which partially dissolved in SO_2. The green SO_2-soluble portion (2.2 g) was indistinguishable from the corresponding product of the neat reaction. The insoluble portion (1.1 g) was found to contain a substantial amount of elemental sulfur.

Reaction between $S_8(AsF_6)_2$ and C_2F_4 in the Presence of Liquid Thionyl Fluoride. In an experiment identical with the one previously described, $S_8(AsF_6)_2$ (3.2 g, 0.051 mol) was allowed to react with 0.020 mol of C_2F_4 in about 1.5 cm³ of SOF_2. The 1.6 g of sulfides formed was found to consist of 64% $(C_2F_5)_2S_2$ and 36% $(C_2F_5)_2S_3$ with a trace of $(C_2F_5)_2S_4$. Thus, the sulfides formed incorporated 34% of the available fluorine and 30% of the sulfur. The 0.8 g of AsF_3 represented 50% of the total arsenic. There remained a red-brown solid consisting of 0.8 g of SO_2-soluble material and 0.4 g of sulfur-containing insoluble material. The unidentified SO_2-soluble material showed only AsF_6^- as a significant peak in the infrared spectrum.

Reaction between C_2F_4 and $S_8(AsF_6)_2$ in SO_2 Solution. In a typical reaction, $S_8(AsF_6)_2$ (9.1 g, 0.014 mol) was measured into a 35-cm³ metal reactor. To this were added about 4 cm³ of dry SO_2 and 0.058 mol of C_2F_4. After 1 day, the most volatile products were removed by fractional condensation and found to contain C_2F_6, SOF_2, and CF_3COF, in addition to unreacted C_2F_4 and solvent. These products were identified by comparison of the infrared spectra to those of authentic samples. The less volatile products were found to contain 1.6 g of AsF_3 representing 43% of the arsenic and 1.6 g of sulfur-containing products. Unlike the neat reactions and the reactions in the other solvents, a component of the less volatile products of the reaction in SO_2 appeared to react with hydrocarbon grease and with glass (more than the usual reaction with AsF_3). In addition, the infrared spectrum of the mixed products had a strong band at 1870 cm^{-1}. Low-resolution mass spectrometry showed that the products included $(C_2F_5)_2S_x$, $C_2F_5S_xCF_3$, and $C_2F_5S_xC_2F_3O$, $x = 2, 3$. The vpc analysis of the mixture indicated that additional products were also present. It is likely that higher sulfides were present, but not observed in the mass spectrum due to the combined effects of low volatilities and low concentrations. A low-resolution ^{19}F spectrum was consistent with the proposed perfluoroalkyl compounds and, in addition, had a peak at −16 ppm (*cf.* CF_3COF, ϕ −15 ppm[6]). This information, combined with the infrared spectrum and the chemical reactivity, supports the structure $C_2F_5S_xCF_2COF$ for the oxygen-containing compound. The analogous diselenium compound has been isolated and identified.[7]

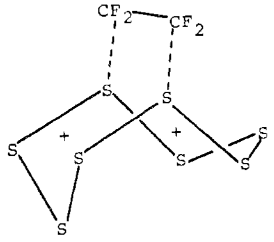
A red-brown solid remaining after the reaction was found to weigh 5.8 g. This solid was separated into 0.9 g of an SO_2-soluble substance and 4.9 g of an insoluble substance, both unidentified.

Results and Discussion

Solid $S_8(AsF_6)_2$ reacts with gaseous tetrafluoroethylene at room temperature and moderate pressures to give arsenic trifluoride, bis(perfluoroethyl) di-, tri-, and tetrasulfides, and, in some cases, traces of penta- and hexasulfides. Substantially the same results are obtained when the reaction is carried out in the presence of liquid SOF_2 and SO_2F_2, in which $S_8(AsF_6)_2$ is not detectably soluble at 0°.

Previous methods used for preparing fluorocarbon polysulfides have been reviewed[8] and generally involve the reaction of an active fluorocarbon moiety and elemental sulfur. For example, trifluoromethyl radicals produced by heating trifluoromethyl iodide react with elemental sulfur to form bis(trifluoromethyl) polysulfides containing 2, 3, and 4 sulfur atoms.[9] Perfluoroisobutylene reacts with elemental sulfur in the presence of fluoride ion at 60-70° in DMF *via* the intermediate $(CF_3)_3C^-$ to form $(CF_3)_3CS_xC(CF_3)_3$,[10] $x = 3, 4$. (Bis(trifluoromethyl)thioketene dimer is also formed but by a different pathway.)

The present reaction occurs under mild conditions implying a facile reaction pathway. That tetrafluoroethylene is a weak nucleophile,[11] however, argues against a simple nucleophilic attack on the sulfur cation. Thus, it is possible that the reaction is initiated by interaction between a weak transannular bond in the sulfur cation and tetrafluoroethylene, which is known to have diradical character.[12] The intermediate, such as **1**, may then abstract a fluoride ion from a hexafluoroarsenate ion to form a perfluoroethylsulfur ion.



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Reaction of tetrafluoroethylene with this species followed by fluoride ion abstraction from a hexafluoroarsenate ion leads to bis(perfluoroethyl) polysulfides. Free arsenic pentafluoride may oxidize sulfur chains present to form **2** as well as other fragments, itself being reduced to arsenic trifluoride.

$$C_2F_5S_xF$$

2

Alternatively, the arsenic pentafluoride may form a hexafluoroarsenate ion with an existing fluorinated species to form the unidentified solid by-product.

The S-F bond of **2** may add across the double bond of a tetrafluoroethylene molecule also forming the observed product, bis(perfluoroethyl) polysulfide. Support for this reaction is provided by the observation that S_2F_2 formed in the presence of tetrafluoroethylene by the reaction between silver(I) fluoride and sulfur[13] yielded bis(perfluoroethyl) disulfide.[14] The trisulfide homolog was also observed in trace quantities consistent with the recent report[15] that S_3F_2 is formed in low yield in the above preparation of S_2F_2.

This mechanism also is applicable to the reaction between $S_{16}(AsF_6)_2$ and tetrafluoroethylene yielding bis(perfluoroethyl) polysulfides. The S_{16}^{2+} ion probably consists of two S_8^+ rings joined by a weak sulfur-sulfur bond[16] which may interact with the olefin.

Solid samples of $S_8(AsF_6)_2$ and $S_{16}(AsF_6)_2$ both have a very slight temperature-independent paramagnetism.[4,16] Gillespie and Ummat[17] suggested that the paramagnetism is

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due to S_4^+ and S_8^+ respectively either trapped in the crystals or adsorbed on the surfaces. It is noted that $(C_2F_5)_2S_5$ and $(C_2F_5)_2S_6$ were observed as reaction products in the C_2F_4-$S_8(AsF_6)_2$ reaction and that they can be simply derived from **1**, $S_8C_2F_4^+$, but not $S_4C_2F_4^+$.

The reaction of $S_8(AsF_6)_2$ and tetrafluoroethylene in SO_2 gave in addition to arsenic trifluoride and bis(perfluoroethyl) polysulfides, $C_2F_5S_xCF_3$, $C_2F_5S_xCF_2COF$ ($x = 2, 3$), CF_3COF, and SOF_2. The reaction is clearly more complicated than the neat reaction and would appear to involve reaction with the solvent. The reaction using sulfur dioxide was carried out in well-dried glass and Kel-F apparatus and in a thoroughly passivated metal vessel, the results being essentially the same in all cases. It appears highly unlikely, therefore, that moisture or adhering oxides could have provided the oxygen for the carbonyl species. The sulfur dioxide itself was carefully dried over fresh P_4O_{10} and in other cases over CaH_2 for several weeks. The presence of thionyl fluoride supports the claim that sulfur dioxide participates in the reaction, perhaps in a manner analogous to the reaction between carbon tetrachloride and sulfur dioxide in the presence of aluminum chloride. In this reaction, thionyl chloride is formed in good yield along with phosgene and, presumably, other products.[18]

$S_8(AsF_6)_2$ is very soluble in sulfur dioxide, and it has been shown that in solution S_8^{2+} is in equilibrium with a paramagnetic species, most probably S_4^+.[4,16,17,19] This could, wholly or in part, be the species involved in the initial reaction with tetrafluoroethylene in sulfur dioxide forming the intermediate $S_4C_2F_4^+$. This, or intermediate **1**, may react as in the neat reaction yielding bis(perfluoroethyl) polysulfides or undergo reactions, some of which involve sulfur dioxide, leading to $CF_3S_xC_2F_5$, $C_2F_5S_xCF_2COF$ ($x = 2, 3$), CF_3COF, and SOF_2. A study of the mechanism of this reaction and the isolation and characterization of the interesting perfluoroethyldi- and trisulfanylperfluoroacetyl fluorides will be the subject of further investigation.

While our work was in progress, Belen'kii, *et al.*, reported a reaction between tetrafluoroethylene and sulfur in sulfur dioxide in the presence of antimony pentafluoride giving compounds of the type $C_2F_5S_xC_2F_5$ and $C_2F_5S_xCF_3$ ($x = 2, 3, 4$).[5] Sulfur poly cations were postulated as intermediates, and it was suggested that they react with the olefin to form a cationic intermediate. They did not, however, report carbonyl-containing products.

Registry No. $S_8(AsF_6)_2$, 33248-05-4; C_2F_4, 116-14-3.

Acknowledgments. The authors wish to thank the National Research Council of Canada, the Research Corp., and the University of New Brunswick Research Fund for the financial support of this work. We are also indebted to Dr. P. A. W. Dean of the University of Western Ontario for the ^{19}F nmr data.

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The Platinum-Oxygen Electrode in Dichromate-Chromate Solutions of Alkali Nitrate Melts

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Received June 22, 1972

A platinum electrode dipping into a nitrate melt buffered with respect to oxide ions and bathed in an atmosphere of dry nitrogen follows Nernstian behavior toward oxide ions. It is proposed that the platinum-oxygen electrode in the absence of oxygen gas is an electrode of the second kind, *i.e.*, $Pt|PtO|O^{2-}$, in dichromate-chromate solutions of alkali nitrate melts. The standard emf of this indicator electrode *vs.* $Ag|Ag^+$ (1.0 *m*) reference electrode is 0.547 V at 250° and its temperature dependence is −0.111 mV/deg. Replacing Pt with Au gives potential readings 80 mV larger and approximate Nernst behavior is observed with Au. In $Cr_2O_7^{2-}$-CrO_4^{2-} solutions of nitrate melts, these indicator electrodes are electrodes of the second kind and the half-reaction is the oxidation of the metal to its oxide.

In 1963 Kust and Duke[1] reported that a platinum electrode bathed in an atmosphere of oxygen responds reversibly to both oxide ion and oxygen gas in alkali nitrate melts according to the half-reaction $^1/_2O_2 = O^{2-} + 2e^-$. Their findings have most recently been confirmed by Temple, *et al.*[2] Shams El Din and coworkers[3-6] have been using this electrode as an indicator electrode to carry out Lux-Flood titrations in molten nitrates and they have based many of their arguments concerning the stable polymeric species of chromate, molybdate, arsenate, phosphate, etc., upon the reversibility of the above half-reaction in distinctly basic nitrate melts as well as in acidic nitrate melts. However, Jordan and his group[7] have used voltammetry at a rotating platinum disk electrode to show that oxide ion is not stable [except possibly at very low concentrations] in fused nitrates because the addition of Na_2O to the nitrate melts results in its oxidation by NO_3^- to give an "equilibrium mixture" of O_2^{2-} and O_2^-. In view of their findings and a report by Inman[8] that a one-electron process involving O_2 and O^{2-} occurs at a gold electrode in molten halides, Jordan[9] sug-

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