also. Gillespie's approach accounts for certain trends in a formally different way from Rundle's. According to Rundle's model variations in polarity and bond lengths stem in a straightforward way from variations in the atomic populations and bonding characteristics of the filled molecular orbitals. In Gillespie's scheme the forms of the orbitals are ignored and the trends correlate, through considerations of geometry, with the magnitudes of repulsions between the various valence-shell electron pairs.

In summary, the stereochemistry and bonding trends in the series $(CH_3)_nPF_{5-n}$ can be qualitatively understood on the basis of Rundle's formulation which neglects d orbitals or Gillespie's approach which neglects hybridization altogether.[33] The quantitative interpretation of results, however, remains an interesting challenge.

[33] NOTE ADDED IN PROOF.—For the molecules studied in this research Rundle's and Gillespie's models give similar structural implications. In the case of XeF_6, however, Rundle's model has been widely interpreted as predicting that the molecule is a regular octahedron, whereas Gillespie's model requires that it be distorted from O_h symmetry. A preliminary analysis of electron diffraction data for XeF_6 has just been carried out in our laboratory. It shows that the molecule is indeed distorted, but that it is distorted much less than demanded by Gillespie's hypotheses. The truth seems to lie somewhere between the two simple models.

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Chemical Properties of Disulfur Decafluoride[1,2]

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Disulfur decafluoride, S_2F_{10}, has been found to react with Cl_2 at approximately 150° in a borosilicate glass vessel to give almost quantitative yields of SF_5Cl. With Br_2, high yields of SF_5Br were obtained. Disulfur decafluoride also underwent reaction with BCl_3 under similar conditions to give SF_5Cl, and with NH_3 to give NSF_3. The interaction of S_2F_{10} with $(CN)_2$, Al_2Cl_6, NO, C_2H_4, and $(CH_3)_2NH$ was also investigated.

Although the chemical inertness of sulfur hexafluoride, SF_6, to a large variety of reagents is well known,[3,4] relatively little information is available concerning the chemical properties of the related compound, disulfur decafluoride, S_2F_{10}.[3] The properties of the sulfur–sulfur bond in S_2F_{10} are of particular interest, since this is the only sulfur–sulfur bond known in which both sulfur atoms exhibit a coordination number of six.

Disulfur decafluoride is less stable thermally and more reactive chemically than SF_6. It decomposes slowly in an inert container above 150° to give SF_6 and SF_4[5]; it reacts upon heating with certain olefins and benzene to give small quantities of derivatives containing the $-SF_5$ group[6] and with N_2F_4 to give SF_5NF_2.[7] When streamed with chlorine through a heated tube, trace amounts of SF_5Cl have been observed.[8] Under the influence of ultraviolet irradiation, S_2F_{10} reacts with SO_2 to give SF_5OSO_2F.[9]

In the present investigation it was found that S_2F_{10} underwent reaction with excess chlorine in a glass container at 150° during 29 hr. to give almost quantitative yields of SF_5Cl (eq. 1). Essentially no attack of the glass was observed. The reaction was slow, and a heating period of less than 20 hr. resulted in incomplete consumption of the S_2F_{10}. When the heating was carried out during a period of 50 hr., some of the SF_5Cl underwent reaction with the glass reaction vessel to form SiF_4 and unidentified materials.

$$S_2F_{10} + Cl_2 \longrightarrow 2SF_5Cl \qquad (1)$$

When S_2F_{10} was heated with bromine at 138° for 24 hr. in a glass vessel, a reaction analogous to that observed with chlorine took place, and a 77% yield of SF_5Br, based on the quantity of S_2F_{10} consumed, was obtained (eq. 2). The reaction differed markedly from that with chlorine in that nearly 53% of the S_2F_{10} did not react, even though an almost threefold molar excess of bromine was used. Even when the molar ratio of Br_2 to S_2F_{10} was increased to 5:1 and the temperature was raised to 150°, a large fraction of the S_2F_{10} remained unreacted. It therefore appears that the reaction is reversible and that SF_5Br partly decomposes at 135–150° to form S_2F_{10} and bromine. The reaction appears to be a useful method for the preparation of SF_5Br, which has been synthesized previously only by the very

$$S_2F_{10} + Br_2 \rightleftarrows 2SF_5Br \qquad (2)$$

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[1] This report is based on portions of a thesis submitted by Bernard Cohen to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This research was supported by the Advanced Research Projects Agency, Office of the Secretary of Defense.

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slow interaction of SF_4 with BrF_3 and Br_2 in a metal apparatus.[10]

A similar experiment in which cyanogen, $(CN)_2$, was used in place of the free halogen gave no SF_5CN but only the thermal decomposition products of S_2F_{10}. The apparent inability of $(CN)_2$ to react in an analogous fashion to chlorine and bromine might lie in the fact that the energy required to break the carbon–carbon bond in $(CN)_2$ (C–C bond dissociation energy in $(CN)_2$, 112 kcal./mole[11]) is greater than that required to cleave the bond in chlorine (57.1 kcal./mole[11]) or in bromine (45.5 kcal./mole[11]). No new reaction products were observed when S_2F_{10} was heated with AgCN or AgOCN.

Since it appears likely that S_2F_{10} decomposes on heating by a process involving the formation of $\cdot SF_5$ radicals,[5] the following free radical mechanism based upon cleavage of the sulfur–sulfur bond in S_2F_{10} is postulated for the reaction of S_2F_{10} with chlorine and bromine

$$S_2F_{10} \longrightarrow 2\cdot SF_5 \tag{3}$$

$$\cdot SF_5 + X_2 \longrightarrow SF_5X + \cdot X \tag{4}$$

$$\cdot SF_5 + \cdot X \longrightarrow SF_5X \tag{5}$$

where X is chlorine or bromine.

Since SF_6 is known to react with Al_2Cl_6 at 180 to 200°[12] to form aluminum fluoride, sulfur chlorides, and chlorine, it was not surprising that S_2F_{10} underwent what appeared to be a somewhat analogous reaction to give SF_6 and Cl_2 as identifiable products. However, it was interesting to find that BCl_3, which does not react with SF_6 at 200°,[12] did react with S_2F_{10} during 17 hr. at 150° to give SF_5Cl, BF_3, and Cl_2, together with SF_6, SO_2, and SOF_2. The latter two compounds were presumably formed by reactions involving the walls of the glass reaction vessel. Of the SF_5 groups present in the S_2F_{10} employed, 58.4% were isolated as SF_5Cl. The difference in reactivity of SF_6 and S_2F_{10} toward BCl_3 is apparently related to the presence of a sulfur–sulfur bond in the S_2F_{10}. Although it is possible to formulate a number of reaction mechanisms, based on the primary production of $\cdot SF_5$ radicals, to account for the products obtained, there is no obvious preference for any particular reaction scheme.

When NH_3 was heated with excess S_2F_{10} in a glass container at 150° for 14 hr., a 53% yield of NSF_3, based on the quantity of S_2F_{10} consumed, was obtained, assuming that reaction occurred according to eq. 6.

$$S_2F_{10} + NH_3 \longrightarrow NSF_3 + SF_4 + 3HF \tag{6}$$

Since a sample of S_2F_{10}, alone, was found to decompose to the extent of approximately 30% when heated at 150° for 23 hr. in a borosilicate glass container, the yield of NSF_3 would probably be greater if the reaction were carried out in an inert metal container. No HF or SF_4 was found among the reaction products. The HF would react with NH_3 to give ammonium fluorides or with the glass to give SiF_4, which would then react further with NH_3. The absence of SF_4 is consistent with the observation that, in a separate experiment, SF_4 was found to react with NH_3, even at low temperatures, to form solid materials which contained S_4N_4.

Since SF_6 does not react with NH_3 under the experimental conditions employed, and since S_2F_{10} probably decomposes on heating by a mechanism involving the formation of $\cdot SF_5$ radicals,[5] it is likely that $\cdot SF_5$ radicals may first react with NH_3 to give SF_5H and SF_5NH_2. It is to be expected[13,14] that these species would be unstable and that each would spontaneously eliminate HF to form SF_4 and NSF_3, respectively. Decomposition of this type, for H_2NSF_5, is supported by the observation that CF_3NHSF_5 eliminates HF on heating to form $CF_3N{=}SF_4$.[14]

When S_2F_{10} was heated with an excess of NH_3, no NSF_3 was obtained. Instead, solid materials were formed which appeared to contain $SiF_4\cdot 2NH_3$, NH_4HF_2, and S_4N_4. This is consistent with an observation that NSF_3 and NH_3 underwent rapid reaction at low temperatures to yield an unidentified solid. The formation of NSF_3 in the reaction might well depend on the fact that the postulated H_2NSF_5 does not react readily with NH_3 and that it exists for an appreciable time in the reaction system, at least until most of the NH_3 is consumed, before decomposing to give NSF_3.

The interaction of S_2F_{10} with $(CH_3)_2NH$, NO, and C_2H_4 under varying reaction conditions did not result in the formation of any interesting species; however, it would appear that because of the presence of the relatively reactive sulfur–sulfur bond, S_2F_{10} might prove to be a useful reagent for the synthesis of many types of compounds containing sulfur–fluorine linkages.

Experimental

All experimental work was performed in a borosilicate glass vacuum system fitted with glass stopcocks lubricated with fluorocarbon (Kel-F 90) grease. Reactions of S_2F_{10} were studied at elevated temperatures in all-glass (borosilicate) containers fitted with glass break-seals. Gas chromatographic separations were carried out with a preparative scale column containing fluorocarbon oil (Kel-F 3) absorbed on "Chromosorb-W."[15] A helium pressure of 25 p.s.i. at a flow rate of 290 cc./min. was employed. Mass spectra were obtained with a Consolidated Electrodynamics Model 21-130 spectrometer at an ionizing voltage of 77 v. and an ionizing current of 20 μa.

The S_2F_{10}[16] used in the experiments was purified by gas chromatography and by slow distillation out of a trap held at −96° (mol. wt. found 254.0, calcd. 254.1; confirmed by infrared[17] and mass spectra). The commercial SF_4 (94% minimum purity) employed, which contained small quantities of chlorine and SOF_2, was freed from the chlorine before use by shaking with mercury. Other volatile reagents were purified, where necessary, in the vacuum system or by gas chromatography until a molecular

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weight determination in the vapor phase gave a percentage error of less than 1%. Where appropriate, the purity of each reagent was also confirmed by examining its infrared and/or mass spectrum.

Reaction of S_2F_{10} with Borosilicate Glass.—Disulfur decafluoride (0.2274 g., 0.8949 mmole) was heated at 150° for 23 hr. in a 30-ml. Pyrex glass tube. The contents of the tube were then distilled through a trap held at $-112°$ in which the S_2F_{10} condensed (0.1574 g., 0.6194 mmole, 69.2% recovery; mol. wt. found 254.1, calcd. 254.1; confirmed by infrared[17] and mass spectra). The material which passed through the $-112°$ trap weighed 0.0824 g., and after separation by passage through the gas chromatography column, it was found to consist of SF_6, SiF_4, and SOF_2, all of which were identified by their infrared[18–20] spectra. Since S_2F_{10} decomposes thermally to give SF_6 and SF_4,[5] it seems likely that the formation of the SiF_4 and SOF_2 might have resulted from the reaction of SF_4, produced from the S_2F_{10}, with the glass.

Reaction of S_2F_{10} with Cl_2.—Disulfur decafluoride (0.1263 g., 0.4970 mmole) and Cl_2 (0.1612 g., 2.274 mmoles) were heated in a 30-ml. borosilicate glass break-seal tube for 29 hr. at 150°. Separation by gas chromatographic techniques[15] gave SF_5Cl (0.1560 g., 0.9600 mmole, 96.5% yield; mol. wt. found 161.3, calcd. 162.5; confirmed by infrared spectrum[21]) and Cl_2 (0.1250 g., 1.763 mmoles; mol. wt. found 69.2, calcd. 70.9). The mass spectrum of SF_5Cl has not been reported in the literature. Possible assignments (for the most abundant isotope) in decreasing order of intensity are SF_5^+, 100%; SF_3^+, 62.9%; SF_4^+, 23.7%; SF_4Cl^+, 15.7%; S^+, 13.4%; SF_2^+, 13.1%; Cl^+, 6.5%; SF_4^{2+}, 3.5%; SCl^+, 3.3%; SF^+, 2.9%; F^+, 2.5%; $SFCl^+$, 2.3%; SCl^{2+}, 1.0%; $SFCl^{2+}$, 0.9%; S^{2+}, 0.8%; SF_2Cl^+, 0.5%; SF^{2+}, 0.3%.

Reaction of S_2F_{10} with Br_2.—Disulfur decafluoride (0.1038 g., 0.4085 mmole) and Br_2 (0.1857 g., 1.162 mmoles) were heated in a 30-ml. borosilicate glass break-seal tube for 24 hr. at 138°. Distillation from a glass low-temperature fractionating column[22] yielded four fractions as the temperature of the column was raised slowly. Fraction 1 (~0.0025 g.) consisted of SOF_2, SF_6, and SiF_4, which were identified by their infrared spectra.[18–20] Fraction 2 was pure SF_5Br (0.0274 g., 0.132 mmole; mol. wt. found 209.2, calcd. 207.0; confirmed by infrared and mass spectra[10]). Infrared examination of fraction 3 showed that it consisted of a mixture of only S_2F_{10}[17] and SF_5Br[10] (0.0889 g.; mol. wt. found 233.6). The molecular weight indicated the presence of 0.215 mmole of S_2F_{10} and 0.166 mmole of SF_5Br in this fraction. The yield of SF_5Br, based on the S_2F_{10} consumed, was 77.1%. Fraction 4 was unreacted Br_2 (0.1707 g., 1.068 mmoles; mol. wt. found 156.4, calcd. 159.8; confirmed by the absence of absorption bands in the infrared spectrum). Reaction of S_2F_{10} with Br_2 during longer periods of time or at higher temperatures (150°) did not give increased yields of SF_5Br; instead, more extensive decomposition of the S_2F_{10} and SF_5Br took place. Pentafluorosulfur bromide reacts readily with mercury at room temperature. It may be handled in a Pyrex glass vacuum system if the glass is very clean and well-dried.

Reaction of S_2F_{10} with $(CN)_2$.—Disulfur decafluoride and $(CN)_2$ in the molar ratio of 1.0:3.7 were heated in a 30-ml. borosilicate glass break-seal tube for 24 hr. at 150°. No solid product was formed. Infrared and gas chromatographic examination of the reaction products showed only the presence of S_2F_{10},[17] $(CN)_2$,[23] SOF_2,[20] and SiF_4.[19]

Reaction of S_2F_{10} with AgCN or AgOCN.—When S_2F_{10} was heated with either AgCN or AgOCN for 17–24 hr. at 150–200°, the only volatile compounds isolated were SF_6, SO_2F_2, SOF_2, SO_2, and SiF_4.

Reaction of S_2F_{10} with Al_2Cl_6.—Disulfur decafluoride (0.1250 g., 0.4919 mmole) was heated with Al_2Cl_6 (~0.2 g.) for 17 hr. in a 30-ml. borosilicate glass break-seal tube at 200°. Gas chromatographic separation of the volatile material showed the presence of only SF_6 (identified by retention time and infrared spectrum[18]) and Cl_2 (identified by retention time). Since SF_6 reacts only slowly with Al_2Cl_6 under these conditions,[12] it is not surprising to find it in the products.

Reaction of S_2F_{10} with BCl_3.—Disulfur decafluoride (0.1092 g., 0.4298 mmole) and BCl_3 (0.0459 g., 0.392 mmole) were heated in a 30-ml. borosilicate glass break-seal tube for 17 hr. at 150°. A very small quantity of nonvolatile solid had formed in the reaction vessel after this time. Gas chromatographic separation of the volatile material gave SiF_4 (0.0107 g., 0.103 mmole; confirmed by infrared spectrum[19]), SOF_2 (0.0120 g., 0.139 mmole; confirmed by infrared spectrum[20]), and SF_5Cl (0.0817 g., 0.503 mmole; mol. wt. found 161.0, calcd. 162.5; confirmed by infrared[21] and mass spectra). All species were further confirmed by their retention times. An unknown quantity of chlorine, which had a very similar retention time to SO_2 on the column employed, was also recovered in a Cl_2–SO_2 fraction. The chlorine was removed from the SO_2 (0.0080 g., 0.12 mmole; confirmed by infrared spectrum[23]) by shaking the mixture with mercury. The solid which formed contained chloride ion. The infrared spectrum of the mixture of products from the reaction before passage through the gas chromatography column showed the presence of BF_3. This compound did not elute from the column; however, a subsequent quantitative infrared examination showed that 0.0260 g. (0.383 mmole) of BF_3 was present in the original products.

Reaction of S_2F_{10} with NH_3. (A) With Excess S_2F_{10}.—Disulfur decafluoride (1.8681 g., 7.3518 mmoles) and NH_3 (0.1117 g., 6.571 mmoles) were distilled into a 500-ml. borosilicate glass flask. After warming to room temperature, an infrared spectrum of the gaseous mixture showed the presence of only the unreacted starting materials. The mixture was then heated in the glass flask at 150° for 14 hr. After 2 hr., a thin film of white solid, the density of which continued to increase throughout the experiment, had formed on the walls of the flask. The volatile products were then passed through two traps immersed in $-134°$ baths and thence into a trap immersed in liquid nitrogen. The condensate in the $-134°$ traps was next passed through the gas chromatography column to remove SO_2, SF_6, and unreacted S_2F_{10} (1.1649 g., 4.5844 mmoles, 62.4% recovery; mol. wt. found 254.0, calcd. 254.1; confirmed by infrared[17] and mass spectra) from pure NSF_3 (0.1519 g., 1.4620 mmoles, yield 53.2%; mol. wt. found 103.9, calcd. 103.9; confirmed by infrared spectrum[24]). The infrared spectrum of the material (~0.1 g.) which passed through the $-134°$ traps showed the presence of SF_6,[18] SiF_4,[19] and an unidentified material (possibly H_2NSF_5) which could not be isolated in the pure state.

Possible assignments of the fragments in the mass spectrum of NSF_3 (values are given only for the most abundant isotope) are NSF_3^+, 100%; SF_3^+, 30.2%; SF_2^+, 22.2%; S^+, 20.3%; NSF^+, 20.2%; N_2^+, 19.1%; NSF_2^+, 18.3%; NS^+, 14.1%; SF^+, 9.8%; N^+, 6.5%; F^+, 2.7%; SF^{2+}, 1.0%; SF_2^{2+}, 0.8%; S^{2+}, 0.6%.

(B) **With Excess NH_3.**—Disulfur decafluoride (0.1220 g., 0.4801 mmole) and NH_3 (0.1146 g., 6.741 mmoles) were heated at 150° for 18 hr. in a 30-ml. borosilicate glass tube. The only volatile materials present after this time were an unidentified gas which could not be condensed at liquid nitrogen temperature and excess NH_3 (0.0592 g., 3.48 mmoles; mol. wt. found 17.0, calcd. 17.0; confirmed by infrared spectrum[23]). An infrared examination of the solid material suggested the presence of $SiF_4 \cdot 2NH_3$[25] and S_4N_4.[23,27] An X-ray power photograph was also

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consistent with the presence of $SiF_4{\cdot}2NH_3$[28] and NH_4HF_2.[28] Sulfur nitride was further identified by direct comparison of the X-ray film to a film prepared from a sample of pure S_4N_4.[29]

Reaction of SF_4 with NH_3.—Sulfur tetrafluoride (0.5815 g., 5.379 mmoles) and NH_3 (0.1467 g., 1.629 mmoles) were distilled into a reaction vessel, and upon allowing the vessel to warm from liquid nitrogen temperature, reaction was observed to occur while the reactants were still very cold. The infrared spectrum of the gas which was removed at room temperature showed the presence of SF_4[30] (~0.176 g.) and SOF_2.[20] Benzene was distilled into the multicolored solid remaining in the reactor. Evaporation of the filtered benzene solution yielded an orange solid, which was shown by infrared[26,27] and X-ray powder pattern examination to be S_4N_4. When the experiment was repeated using a large excess of NH_3, similar results were obtained, except that the volatile material at the conclusion of the reaction consisted only of unreacted NH_3.

It has been reported that SF_4 and NH_3 interact to give NSF[31]; however, only trace amounts were observed spectroscopically among the gaseous products of the reaction, and none of the pure material was isolated.[32] A more extensive examination of this reaction indicates that up to 70% yields of S_4N_4 may be obtained.[33]

Reaction of S_2F_{10} with $(CH_3)_2NH$.—Disulfur decafluoride (0.1320 g., 0.5195 mmole) and $(CH_3)_2NH$ (0.0235 g., 0.521 mmole) were heated in a 30-ml. borosilicate glass break-seal tube for 19 hr. at 160°. A nonvolatile yellow solid was deposited on the walls of the reaction vessel. Gas chromatographic separation of the volatile material showed the presence of S_2F_{10}, SiF_4, and SO_2, which were identified by their retention times and by their infrared spectra. All the $(CH_3)_2NH$ was consumed.

Reaction of S_2F_{10} with C_2H_4.—Disulfur decafluoride (0.2607 g., 1.026 mmoles) and C_2H_4 (2.9954 g., 106.98 mmoles) were vaporized in a 2-l. bulb and irradiated with ultraviolet light for a total period of 10 hr. The composition of the gaseous products was examined from time to time. A nonvolatile tarry material formed on the walls of the bulb. The volatile products which condensed in a trap held at −78° had an infrared spectrum similar to that found for hydrocarbons containing some SF_5 groups.[34] The molecular weight of the material ranged from 100 to 120. The infrared and mass spectra suggested that the material consisted primarily of short-chain hydrocarbons containing some SF_5 end groups.

Reaction of S_2F_{10} with NO.—A number of experiments were carried out in which S_2F_{10}, mixed with a large excess of NO, was either heated to temperatures up to 200° or exposed to ultraviolet light. Although reaction occurred and unidentified absorption bands were observed in the infrared spectra of the volatile products, no pure compound apart from SiF_4 and SOF_2 could be obtained. Extensive decomposition of many of the products appeared to take place when gas chromatographic separations were attempted.

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Difluorochlorates(I) of Cesium, Rubidium, and Potassium

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The difluorochlorates(I) of cesium, rubidium, and potassium were successfully prepared by the reaction of the corresponding fluorides with chlorine monofluoride or $NO^+ClF_2^-$. These white solids are the first known difluorochlorate(I) salts stable at 25°. They decompose exothermally at temperatures higher than 230°. Their composition and structure were established by elemental analysis, infrared, and X-ray studies. The salts are ionic and contain linear ClF_2^- anions. Attempts to prepare $LiClF_2$ and $Ca(ClF_2)_2$ failed, while $NaClF_2$, $Ba(ClF_2)_2$, and $Sr(ClF_2)_2$ may have formed to a very small extent.

Introduction

The existence of ionic complexes containing species such as ClF_2^+,[1-5] and ClF_4^-,[6-9] derived from chlorine trifluoride, is well-established. However, complexes containing such species as Cl^+ and ClF_2^-, formed from chlorine monofluoride, have not been investigated until recently. Schmeisser[10] isolated $Cl^+AsF_6^-$ and $Cl^+SbF_6^-$, prepared by the interaction of ClF with the corresponding Lewis acid, AsF_5 or SbF_5. We[11] have reported the existence of the ClF_2^- anion in the form of its nitrosyl salt, $NO^+ClF_2^-$. Nitrosyl difluorochlorate(I) was shown to be ionic in solution and in the solid state. The ClF_2^- anion was assigned a linear structure based on infrared investigation. Since $NO^+ClF_2^-$ is stable only at low temperature we have investigated the replacement of the NO^+ cation by an alkali or alkaline earth metal cation with the hope of

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