PROPERTIES OF SF4 AND ITS ADDUCT WITH BF3

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Abstract-Some new data on the adduct of SF4 with BF3 are reported and arguments are given, based on these and other data, to indicate that the adduct is quite unlikely to be a donor-acceptor complex. Infra-red examination proved inconclusive due to the instability and reactivity of the adduct. SF₄ has been found to react with F_2 producing SF₆ but is unreactive toward BrF₃ and Cl₂. It reacts rapidly with BCl₃ producing BF₃, SCl₂ and Cl₂ when in excess.

WHILE the formation of sulphur tetrafluoride had been reported by a number of workers, only a few attempted to characterize the compound chemically and physically; its properties and even, by some authors, its existence, were considered uncertain until the definitive study of BROWN and ROBINSON.⁽¹⁾ These authors described a tedious but reliable method of preparation of the pure material and measured a number of its physical properties. Shortly thereafter, a study of the infra-red and Raman spectra⁽²⁾ led to the conclusion that the molecule possesses C_{2n} symmetry. DODD et $al^{(2)}$ further commented that this is the symmetry of the general structure to be expected by analogy with other halides of group V, VI and VII elements. In this case the structure may be considered to be derived from a trigonal-bipyramidal disposition of five pairs of valence shell electrons in a $3s_3p^33d$ set of orbitals around the sulphur atom. By assuming one of the equatorial pairs of electrons to be the unshared pair, a structure of C_{2v} symmetry is obtained from this formalism. Strong and independent evidence for this structure has been obtained from studies of the fluorine nuclear resonance spectrum.⁽³⁾ These nuclear resonance studies are completely conclusive in eliminating any higher symmetry (e.g. T_d , D_{4h} , C_{3v}) and very strongly, although not with absolute rigor, support the kind of C_{2v} structure described above.

In succeeding notes, BARTLETT and ROBINSON⁽⁴⁾ reported observations on the formation by SF₄ of adducts with BF₃, AsF₅ and SbF₅ and also reported that compounds of analogous stoicheiometry are formed by SeF₄. It has further been stated by BARTLETT and ROBINSON^(4a) that "there is evidence from electrical conductivity that SeF₄ ionizes to SeF₃⁺ and SeF₅⁻ but very little that a similar fluorine transfer takes place in SF4." They also advanced the tentative hypothesis that the SF4 adducts with BF₃, AsF₅ and SbF₅ are simple donor-acceptor compounds while allowing that the compounds of SeF₄ having similar stoicheiometry might be ionic, e.g. [SeF₃+BF₄-], etc.

In this communication some chemical and physical evidence bearing on the constitution of the adduct of SF_4 with BF_3 is presented and discussed. Other observations on the reactivity of SF₄ are also reported.

⁽¹⁾ F. BROWN and P. L. ROBINSON, J. Chem. Soc. 3147 (1955).

R. E. DODD, L. A. WOODWARD and H. L. ROBERTS, Trans. Faraday Soc. 52, 1052 (1956).
 F. A. COTTON, J. W. GEORGE and J. S. WAUGH, J. Chem. Phys. 28, 994 (1958).
 N. BARTLETT and P. L. ROBINSON, Chem. & Ind. 1351 (1956); ^(b) Proc. Chem. Soc. 230 (1957).

DISCUSSION

The constitution of the SF_4 -BF₃ adduct.* Certain of the data and observations reported in this communication as well as those previously given by ROBINSON *et al.* will be considered in regard to their bearing on the constitution of the SF_4 -BF₃ adduct. Only the two extreme cases, viz. a simple Lewis acid-Lewis base complex, $F_4S \rightarrow BF_3$ and an ionic salt $[SF_3^+BF_4^-]$ will be considered here.[†] The principal evidence concerning the constitution of the SF_4 -BF₃ adduct can be summarized as follows:

(1) Comparing SF₄ with PF₃ there are two reasons to expect that SF₄ would be much the poorer donor. Firstly, in PF₃ there are only three fluorine atoms tending to decrease the lability of the lone pair whereas in SF₄ there are four. Secondly, there should be less steric hindrance in PF₃ than in SF₄. Nevertheless, while the SF₄ adduct has a dissociation pressure of only ~115 mm at 300°K. BOOTH and WALKUP⁽⁵⁾ have shown by thermal analysis that even in the range of -140 to -165° C PF₃ forms no adduct with BF₃.

(2) According to current views of the nature of the co-ordinate link between donor ligands and transition metal atoms or ions, the ability of the ligand to participate in metal-ligand dative π -bonding is often essential to the overall stability of the metal-ligand bonding. Presumably it is always necessary that the ligand have some ability to form a σ -donor bond, but in many cases the π -bond seems to be by far the more important. Thus in PF₃ the phosphorus atom can form $d\pi$ -d π -bonds with metals by using its unfilled $3d_{xy}$ and $3d_{yz}$ orbitals which under the C_{3v} symmetry of PF_{3} itself form a doubly degenerate pair of π symmetry. It appears that while the three highly electronegative fluorine atoms greatly reduce the donor power of the phosphorus atom as evidenced by the inability of PF₃ to form complexes with even strong but simple acceptors such as BF₃, they also markedly increase the stability of $d\pi$ - $d\pi$ dative bonds. Now in SF₄ the $3d_{xy}$ and $3d_{yz}$ orbitals are again available for π -bonding just as in PF₃ (although they are no longer degenerate). Moreover, the presence of an additional fluorine atom in SF₄ might be expected to further enhance the ability of the sulphur to participate in dative $d\pi$ -d π -bonding. If then it is assumed that the SF_4 -BF₃ adduct demonstrated the marked ability of SF_4 to function as a simple σ -donor while the ability of PF₃ to do so is marginal, it is very difficult to understand why PF₃ readily forms stable adducts with PtCl₂ whereas BARTLETT and ROBINSON^(4a) were unable to effect any combination between $PtCl_2$ and SF_4 or SeF_4 .

(3) While BF₃ can function as a fluoride acceptor giving BF_4^- and as a general Lewis acid, and AsF_5 and SbF_5 are known to be very strong F^- acceptors, i.e., acids in the HF system, there is little evidence to show that the latter are also good general Lewis acids. Consequently, it seems reasonable to postulate that the AsF_5

⁽⁵⁾ H. S. BOOTH and J. H. WALKUP, J. Amer. Chem. Soc. 65, 2334 (1943).

^{*} The term adduct, unmodified by any adjective, is used here with no intended connotation as to the constitution of the substance, since it is the constitution which is at issue.

[†] It is possible to envision a semi-ionic or ion-pair case in which there are fluoride bridges, viz. F

 F_3S or something similar. Other than the report that the SeF₄-BF₃ adduct is soluble in ether,

there is nothing in the literature on SF_4 - BF_3 or similar compounds to explicitly suggest the existence of fluorine bridges, nor do we have any such evidence to offer. Consequently, only the two extreme cases are considered. It should be borne in mind however that the essence of arguments favouring the ionic structure or using an ionic structure to explain the course of a reaction would be preserved if some kind of ion-pairing or fluorine bridging exists.

and SbF_5 adducts of SF_4 are actually $[SF_3^+AsF_6^-]$ and $[SF_3^+SbF_6^-]$ and therefore that these compounds imply the ability of SF_4 to form ionic adducts containing SF_3^+ ions. Moreover, it has recently been shown⁽⁶⁾ that the strongest acids in HF, i.e. the best F^- acceptors are AsF_5 , SbF_5 and BF_3 .

(4) Arguments from conductivity data as to the ability of SF_4 to produce SF_3^+ by ionization must be used with caution. The absence of appreciable self-ionization according to

$$2SF_4 = SF_3^+ + SF_5^-$$

could be due entirely to the inability of SF_4 to add a fluoride ion to form SF_5^- and thus not indicate any marked inability to form SF_3^+ . For example, the electrical conductivity of BF_3 is very low $(5 \times 10^{-10} \text{ cm}^{-1} \text{ ohm}^{-1})^{(7)}$ despite the ready formation of BF_4^- because of its inability to dissociate to give BF_2^+ . It is not at all improbable that the inverse situation occurs with SF_4 .

(5) Professor F. G. A. STONE of Harvard University has kindly drawn our attention to an additional consideration. If both the SF_4 and SeF_4 adducts with BF_3 are donor-acceptor complexes, the order of stability in this case (Se > S) would be contrary to the general rule that Lewis basicity decreases in descending a group of analogous donors. Of course, if SF_4 and SeF_4 are electron donors, they are unusual in so many other ways that this anomaly would not be very singular. It must be added too that this stability order argument would be irrelevant if the SF_4 adduct is a donor-acceptor complex while the SeF_4 adduct is ionic.

Obviously, direct evidence on the constitution of the SF_4-BF_3 adduct would be desirable. We have attempted to ascertain whether or not BF_4^- ions are present in the solid by infra-red spectroscopy, but the ready dissociation and reactivity toward water have made it impossible to obtain conclusive results. Spectra of both mulls and alkali halide pressings prepared in a nitrogen atmosphere showed bands due to BF_4^- but there is no doubt that decomposition, hydrolytic and otherwise, occurred in the preparation of these mounts. It is rather certain that hydrolysis will lead to the formation of BF_4^- . Attempts to obtain spectra of thin films sublimed onto a silver chloride plate in a vacuum cell also failed to provide useful results. Details will be found in the experimental section.

Physical properties of the SF₄-BF₃ adduct. Examination of the infra-red spectrum of the gaseous compound indicated that it is at least 95 per cent dissociated into BF₃ and SF₄ around room temperature and at low pressures. This was confirmed by measurement of the vapour-density at room temperature from which an apparent molecular weight of 85 ± 5 was calculated. The average of the molecular weights of SF₄ and BF₃ is 88. The vapour-pressure as a function of temperature in the range 0-25° was found to follow the equation

$$\log_{10} p_{(\rm mm)} = 12.8_4 - \frac{3230}{T}$$

from which the enthalpy of the process

$$(SF_4 - BF_3)_{(s)} = SF_{4(g)} + BF_{3(g)}$$

⁽⁶⁾ A. F. CLIFFORD, H. C. BEACHELL and W. M. JACK, J. Inorg. Nucl. Chem. 5, 57 (1957).

⁽⁷⁾ Woolf and GREENWOOD, J. Chem. Soc. 2200 (1950).

is calculated to be $14\cdot8 \pm 1$ kcal/mole. This is about the order of magnitude to be expected for $(SF_3^+BF_4^-)$ by comparison with similar systems. Thus we have

$$[PtCl_4^+, PCl_6^-]_{(s)} = 2PCl_{5(g)} \qquad \Delta H = 21.5 \text{ kcal/mole}^{(8)} \\ [NO_2^+, NO_3^-]_{(s)} = N_2O_{5(g)} \qquad \Delta H = 13.5 \text{ kcal/mole}^{(9)}$$

and from the data of SHEFT et al.(10)

 $[BrF_{2}^{+}, SbF_{6}^{-}]_{(s)} = BrF_{3(g)} + SbF_{5(g)} \qquad \Delta H = 13.9 \text{ kcal/mole}$

In the last case it was not proven that the vapour is fully dissociated but the authors stated that they believed it was and this would certainly seem likely.

Chemical properties of SF₄. Some other chemical properties of SF₄ have been investigated. SF₄ reacts quantitatively with excess F₂ at room temperature and up to at least 250°C to give SF₆. At temperatures up to 300°C no reaction of SF₄ with Cl₂ occurs. SF₄ is apparently not fluorinated by BrF₃ upon bubbling the gas through liquid BrF₃ at room temperature, or after passing the mixed gases through a 15 cm length of monel tubing heated to 300°C, nor does it appear to be more than slightly soluble in BrF₃. This experiment was undertaken to determine whether an adduct such as [SF₃+BrF₄⁻] could be readily prepared. It is possible, if SF₄ is sufficiently soluble in BrF₃, that conductivity studies might indicate whether or not SF₃⁺ and BrF₄⁻ ions are present.

 SF_4 reacts with BCl_3 at $-75^{\circ}C$; at this temperature no evidence of a complex is obtained. Instead SF_4 functions as a fluorinating agent. With SF_4 in excess, the principle reaction is the following:

$$7SF_4 + 4BCl_3 = 4(SF_4 - BF_3) + 3SCl_2 + 3Cl_2$$

With BCl₃ in excess, mixed halides of boron result. The following equation represents a typical reaction:

$$3SF_4 + 8BCl_3 = 3SCl_2 + 3Cl_2 + 4BF_2Cl + 4BFCl_2$$

The products in these reactions were detected but not quantitatively estimated by their infra-red spectra. It is quite possible that SCl_4 is produced initially but under the experimental conditions it would be expected to decompose rapidly to SCl_2 and Cl_2 . With excess BCl_3 a small amount of the (SF_4-BF_3) adduct was also obtained. Since BCl_3 is as least as good a Lewis acid as BF_3 the observed fluorination reaction rather than the formation of any isolable adduct is evidence against SF_4 behaving as a Lewis base. The observed reactions can however be readily explained by assuming that SF_4 functions as an F^- donor, as illustrated in the following reactions:

$$SF_4 + BCl_3 = [SF_3^+BFCl_3^-] = SF_3Cl + BFCl_2$$

$$2BFCl_2 = BF_2Cl + BCl_3$$

$$SF_4 + BFCl_2 = [SF_3^+BF_2Cl_2^-] = SF_3Cl + BF_2Cl$$

$$SF_3Cl + BCl_3 = [SF_2Cl^+BFCl_3^-] = SF_2Cl_2 + BF_2Cl \text{ etc}$$

It is of course well known that a gaseous system of boron halides containing two

(8) D. P. STEVENSON, J. Chem. Phys. 9, 403 (1941).

⁽⁸⁾ Selected Values of Chemical Thermodynamic Properties. National Bureau of Standards Circular 500, Washington, D.C. (1952).

⁽¹⁰⁾ I. SHEFT, A. F. MARTIN and J. J. KATZ, J. Amer. Chem. Soc. 78, 1557 (1956).

kinds of halogen rapidly equilibrates to produce all possible mixed halide molecules. It is possible that sulphur(IV) halides also do this. In that case reactions like the last one above need not be postulated. In any event a fluoride ion transfer process like that shown in the first reaction provides a plausible explanation of the over-all fluorination.

EXPERIMENTAL

The apparatus shown in Fig. 1 was used to prepare sulphur tetrafluoride according to the method of BROWN and ROBINSON.⁽¹⁾ Particular attention was given to the



FIG. 1.-Fluorination apparatus

exclusion of moisture and oxygen, the preparation of a thin sulphur sublimate to be treated with fluorine, and the maintenance of low temperature $(-75^{\circ}C)$ during reaction.

Fluorine from a cylinder (Pennsalt Chemical Co.) was passed through a trap containing NaF pellets to remove HF then bubbled through bubble-counter A for flow rate estimation prior to cooling and mixing with dried, deoxygenated nitrogen in U-tube C. The gases were further cooled in D before reaction with the sulphur sublimate in E. The products were trapped in F, and non-condensable gases vented through soda-lime traps as indicated. The products were transferred to a vacuum line and a portion of the most volatile part of the sample (SiF₄, SF₆) removed by fractionation. SF₄, together with SOF₂ and other impurities, was present in substantial amount in the middle fraction, with S₂F₁₀ concentrating in the lower. For most experiments, samples of the middle fraction were used directly without any attempt at further purification.

Infra-red spectroscopic analysis was employed to analyse gas mixtures throughout this work. Spectra for essentially all likely components of our reaction systems are in the literature. A Baird model AB spectrophotometer was used with an NaCl prism to cover the frequency range 5000 to 700 cm⁻¹, and with a KBr prism between 700 and 400 cm⁻¹.

The SF_4 -BF₃ adduct was prepared by condensing impure SF_4 with excess BF_3 (Matheson Co., Inc.) at -195°C. The mixture was warmed to --75°C and impurities in the SF_4 plus excess BF_3 removed by application of vacuum. Attempts were made to prepare Nujol mulls and KBr pellets of the adduct for spectroscopic examination

but, even using drybox techniques, decomposition and/or reaction of the material was always encountered. Presumably this difficulty is related to the moderate vapour pressure of SF_4BF_3 at room temperature, and the extreme sensitivity of SF_4 to traces of moisture. Consequently, the spectra obtained were not necessarily representative of the SF_4BF_3 species. While indication of the BF_4^- ion was obtained from these spectra this must not be taken as structural proof since hydrolysis involving SF_4 and BF_3 would almost certainly give rise to the BF_4^- ion.

Failure to obtain definitive results with the above technique prompted us to try condensing the adduct on a silver chloride disk maintained in a vacuum cell at liquid nitrogen temperature. The spectra obtained using this procedure were either blank or of the gases SF_4 , BF_3 , SOF_2 and SiF_4 . The inability to obtain any new lines in the spectra is ascribed to large particle size of the solid SF_4BF_3 which did condense on the disk, while volatilization of the sample and reaction with moisture and/or Pyrex leads to the presence of the gaseous species.

That SF_4BF_3 is fully dissociated in the gas phase was established by infra-red examination in a gas cell of 10 cm path length, and by measurement of vapour density in a Pyrex bulb of approximately 0.51. volume. Only lines ascribed to SF_4 and BF_3 were observed in the spectrum, and the molecular weight values obtained from vapour density data from different trials were 85 and 86. [SF₄, 108; BF₃, 68; average, 88.] The low values may be due to reaction of SF₄ with glass, mercury and moisture producing volatile lower molecular weight species.

The vapour pressure of the compound was measured using an ordinary mercury manometer attached directly to the sample and a vacuum manifold. Suitable baths of ice-water, benzene slush and water at temperatures up to room temperature were used to maintain temperatures in the 0 to 25°C range. Temperatures were determined with a mercury thermometer checked at the ice point. The plot of log p vs. 1/T obeys the relation $\log_{10} p \text{ (mm Hg)} = 12.84 - 3230/T$, and gives an enthalpy of $14.8 \pm 1 \text{ kcal/mole.}$

The reaction of SF_4 with chlorine was studied in two ways. Firstly, known pressures of the two gases (chlorine was purified and dried by passage through $KMnO_4$ solution, conc. H_2SO_4 and P_2O_5) were condensed in a 1 l. Pyrex bulb attached to the vacuum line and to a glass spiral pressure gauge. On warming to room temperature the total pressure was measured. Although such mixtures were heated to 75°C via an infra-red bulb, and also exposed to a strong ultra-violet source for as long as 7 hr, no pressure variations indicative of reaction were observed. Spectroscopic examination of the gases before and after these experiments gave no evidence of new species.

The behaviour of SF_4 and Cl_2 was also studied by passing the gases slowly through a monel metal tube wrapped in heating tape. At temperatures up to 300°C no change in the spectrum of the SF_4 was noted. In contrast, the flow reaction of SF_4 with excess F_2 gave complete conversion to SF_6 even at room temperature.

Using this same apparatus an attempt was made to react BrF_3 with SF_4 by bubbling the latter through the former at room temperature, and subsequently heating the gases passing through the monel tube. Again no significant alteration in the SF_6/SF_4 ratio was shown by infra-red examination, although the slight decrease in the total volume of the SF_4 sample passed through the BrF_3 is suggestive of a small solubility of SF_4 in BrF_3 . The reactions of SF₄ with BCl₃ were studied by condensing the volatile reactants together in a Pyrex tube at -195° C and allowing them to warm to -75° C. At the latter temperature the reaction mixture was liquid except for solid SF₄BF₃ and yellow and the colour grew steadily more intense, due presumably to the formation of SCl₄ and/or SCl₂. Successive fractions of the products were examined spectroscopically in a 10 cm gas cell in the NaCl and KBr regions. The spectra of BCl₃, BF₃ and the mixed halides have been reported in detail by LINDEMAN and WILSON,⁽¹¹⁾ and the Raman spectrum of SCl₂ by STAMMREICH *et al.*⁽¹²⁾

⁽¹¹⁾ L. LINDEMAN and M. K. WILSON, J. Chem. Phys. 24, 242 (1956).

⁽¹²⁾ H. STAMMREICH, R. FORNERIS and K. SONE, J. Chem. Phys. 23, 972 (1955).