

# Studies of the Association of Chlorine with Bis(*p*-fluorophenyl) Sulfide in Solution

G. Edwin Wilson, Jr.,\* and Ming May Y. Chang<sup>1</sup>

Contribution from the Polytechnic Institute of New York, Brooklyn, New York 11201.  
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**Abstract:** The complexation of chlorine by bis(*p*-fluorophenyl) sulfide in methylene chloride and acetonitrile has been studied by <sup>19</sup>F nmr and uv spectroscopy. Rapid equilibria involving only one covalent species with formation constants of *ca.*  $5 \times 10^5 M^{-1}$  are observed in both methylene chloride and acetonitrile. The fluorine chemical shift of the bis(*p*-fluorophenyl)chlorosulfonium cation was found to be 64.1 ppm downfield from internal hexafluorobenzene.

The 1:1 complexes of organic sulfides with halogens, commonly known as halosulfonium salts, have been considered to be involved as intermediates in a number of reactions which result in  $\alpha$ -halogenation of sulfides<sup>2,3</sup> or cleavage<sup>3,4</sup> of a carbon-sulfur bond. Recently the crystal structures of the chlorine complex of bis(*p*-chlorophenyl) sulfide<sup>5</sup> and the bromine adduct of thiophane<sup>6</sup> have been determined by single-crystal X-ray diffraction. A distorted tetracoordinate trigonal-bipyramidal geometry about sulfur was found in the former, and a tricoordinate pyramidal sulfur was found in the latter. Knowledge of the nature of the adduct of organic sulfides with halogens in solution is highly speculative, resting largely on interpretations of conductometric data<sup>7</sup> and deductions from stereomutation<sup>8</sup> and product<sup>2e</sup> studies.

In order to obtain additional rudimentary structural information regarding the chlorine-sulfide adducts in solution, the association of bis(*p*-fluorophenyl) sulfide and chlorine has been investigated by uv and <sup>19</sup>F nmr spectroscopy. The choice of bis(*p*-fluorophenyl) sulfide was made because of the absence of  $\alpha$ - and  $\beta$ -aliphatic protons to minimize those reactions which would destroy the halosulfonium salt and the presence of the fluorine atom to provide an nmr probe highly sensitive to the electronic environment of the sulfur atom.<sup>9</sup>

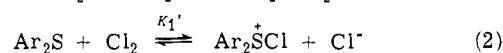
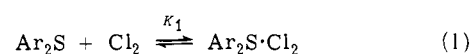
## Results

**Ultraviolet Spectral Data.** The spectroscopic behavior of a solution of bis(*p*-fluorophenyl) sulfide in methylene chloride upon incremental addition of chlorine is shown in Figure 1. The intensities of the characteristic absorption bands of the sulfide at 248.5 and 272.5 nm decrease gradually, and a peak below 230 nm, which is below the solvent cutoff wavelength, develops. A distinct isosbestic point at 243.5 nm is observed. After a few drops of concentrated chlorine solution are added, the curve below 300 nm becomes constant and a peak at 330 nm due to chlorine develops.

The optical densities at the isosbestic point and another wavelength were used to determine the concentrations of two components in the mixture. In the present system 272.5 nm was chosen as the second wavelength because it is a wavelength of maximum absorption of pure sulfide, the optical density at this wavelength always lies in the convenient range for the measurement, and the position of the peak is remote from the regions of interference by the chlorine peak and the peak of the adduct. The molar extinction coefficient of the sulfide-chlorine adduct at 272.5 nm was calculated from eq 7 and 8 (as shown in the Experimental Section) to be  $1.66 \times 10^3$  on the assumption that the sulfide can be entirely converted into its chlorine adduct with excess chlorine.

Although the primary equilibrium must involve only one

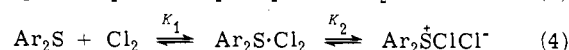
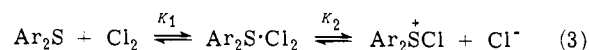
adduct, no restriction is imposed by the uv data on the nature of the adduct. The equilibrium constants for the formation of both covalent,<sup>10</sup>  $K_1$ , and ionic adduct,  $K_1'$ , at room temperature were calculated on the basis of eq 1 and 2. The



average values of seven measurements of  $K_1$  and  $K_1'$ , all of which lie within two standard deviations of the mean, were  $4.04 \times 10^5 M^{-1}$  and 17.46 respectively.

**Nmr Data.** Only one fluorine multiplet was observed for methylene chloride and acetonitrile solutions of bis(*p*-fluorophenyl) sulfide and chlorine over a wide range of molar ratios of chlorine to sulfide at  $-39$  and  $-5^\circ$ , and the position of the multiplet moved to lower field as the proportion of chlorine was increased (Tables I and II). These observations reflect the result of equilibria which are rapid on the nmr time scale, the observed single <sup>19</sup>F chemical shift in each case being a weighted average of the chemical shifts of sulfide and all of the complexed species, weighted according to their relative mole fractions in the solution. There is only a small effect on the <sup>19</sup>F chemical shift of the sulfide-chlorine solution when the solvent is changed from methylene chloride to acetonitrile. The possibility of equilibria involving nonionic species was indicated by the fact that the maximum <sup>19</sup>F chemical shift of the sulfide-chlorine system is much smaller than that of tris(*p*-fluorophenyl)sulfonium perchlorate in methylene chloride as shown in Tables I and III. The disparity between the maximum <sup>19</sup>F chemical shift for the sulfide-chlorine adduct and the single fluorine multiplet of the trichloromercurate of the bis(*p*-fluorophenyl)chlorosulfonium cation in acetonitrile,<sup>11</sup> 3617 Hz (64.1 ppm) downfield from C<sub>6</sub>F<sub>6</sub> (Table II), provides evidence that the sulfide-chlorine adduct exists as a nonionic species in the equilibrium.

Equilibrium constants were obtained from the <sup>19</sup>F nmr data by nonlinear least-squares methods for the equilibria shown in eq 1-4 and using the uv-determined values as ini-



tial guesses for  $K_1$ . The sole restraint imposed was that acceptable solutions must show a larger chemical shift for the ionic form than for the covalent form. Equations 1 and 2 provided the best fits to the experimental points. The derived equilibrium constants and chemical shifts are given in Table IV.

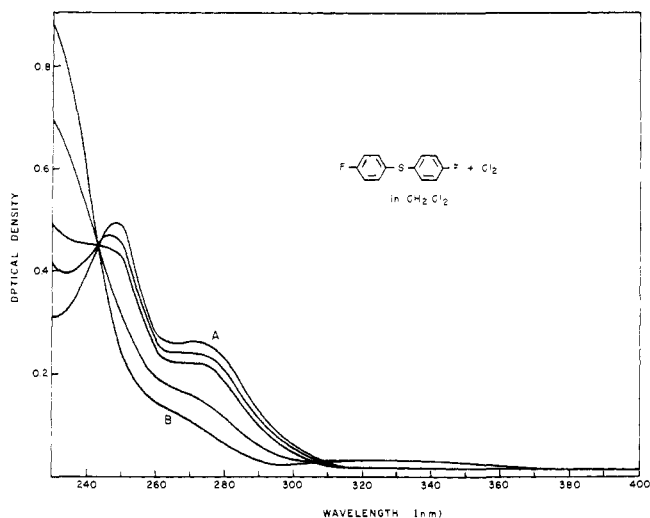


Figure 1. The ultraviolet spectrum of bis(*p*-fluorophenyl) sulfide  $5.2 \times 10^{-5} M$  in methylene chloride upon incremental addition of chlorine (A to B). The broad maximum at 330 nm is due to free chlorine.

### Discussion

Both the recovery of bis(*p*-fluorophenyl) sulfide from the low temperature anhydrous chlorination mixture of bis(*p*-fluorophenyl) sulfide in methylene chloride and the observation of only one fluorine multiplet for methylene chloride or acetonitrile solutions containing various molar ratios of bis(*p*-fluorophenyl) sulfide and chlorine at low temperature establish that an equilibrium fast on the nmr time scale exists between the starting materials and adducts. The formation of the sulfoxide upon water quenching of the reaction mixture of the sulfide and chlorine, which is consistent with the known oxidation of organic sulfides to sulfoxides by halogens in aqueous solution,<sup>12</sup> suggests that the complex of the sulfide and chlorine possesses a true chemical bond.

The uv data which show an isosbestic point for solutions of chlorine and sulfide in methylene chloride indicate that there is only one major sulfide-chlorine adduct and provide a convenient way for calculation of the equilibrium constants for the formation of both covalent,  $K_1$ , and ionic adduct,  $K_1'$ .

This conclusion is borne out by analysis of the  $^{19}\text{F}$  nmr data to provide equilibrium constants based on several models. Thus, the equilibrium involving a tight ion pair (eq 4) can be excluded on the basis of a much poorer fit of the experimental data than the other models. The equilibrium constants derived for eq 3 show a domination by one equilibrium. The facts that the concentrations used for ultraviolet measurement *ca.*  $10^{-4} M$  and  $^{19}\text{F}$  nmr studies (*ca.*  $1 M$ ) lie at two extreme positions and that the  $K_1$  has been calculated from both the ultraviolet spectral data taken at  $25^\circ$  and  $^{19}\text{F}$  nmr data obtained at low temperature provided increased confidence in the validity of the calculated values of the equilibrium constants.

A determination between the ionic or covalent equilibria was made on the basis of chemical shift comparison among the calculated values, the experimental value for the  $^{19}\text{F}$  chemical shift of the chlorine-bis(*p*-fluorophenyl) sulfide adduct, and the shift of bis(*p*-fluorophenyl)chlorosulfonium trichloromercurate generated by the action of mercuric chloride on a mixture of chlorine and sulfide.

In view of numerous successful attempts to trap the carbonium ion,<sup>13</sup> phosphonium,<sup>14</sup> and sulfonium salts<sup>15,16</sup> with metal halides or silver salt, we considered that by introduction of a Lewis acid capable of binding chloride ion but not sulfide sulfur into our sulfide-chlorine solution the adduct

Table I. Fluorine Chemical Shifts of Solutions of Chlorine and Bis(*p*-fluorophenyl) Sulfide in Methylene Chloride

| [Sulfide], <i>M</i> | [Cl <sub>2</sub> ]/[sulfide] | $\delta$ (Hz) <sup>a</sup> |
|---------------------|------------------------------|----------------------------|
| 0.798               | 0                            | 2684                       |
| 1.187               | 0.19                         | 2740                       |
| 2.245               | 0.24                         | 2749                       |
| 0.798               | 0.35                         | 2793                       |
| 1.570               | 0.31                         | 2825                       |
| 0.640               | 0.76                         | 2942                       |
| 0.600               | 0.71                         | 2952                       |
| 0.988               | 0.68                         | 3037                       |
| 0.980               | 0.82                         | 3067                       |
| 0.839               | 1.02                         | 3138                       |
| 0.449               | 1.99                         | 3195                       |
| 0.559               | 3.07                         | 3202                       |
| 0.495               | 3.22                         | 3202                       |

<sup>a</sup> Chemical shift downfield from internal  $\text{C}_6\text{F}_6$ ;  $T = -39^\circ$ .

Table II. Fluorine Chemical Shifts of Solutions of Chlorine, Mercuric Chloride, and Bis(*p*-fluorophenyl) Sulfide in Acetonitrile

| [Sulfide], <i>M</i> | [Cl <sub>2</sub> ]/[sulfide] | [HgCl <sub>2</sub> ]/[sulfide] | $\delta$ (Hz) <sup>a</sup> |
|---------------------|------------------------------|--------------------------------|----------------------------|
| 0.940               | 0                            | 0                              | 2733 <sup>b</sup>          |
| 0.885               | 0.47                         | 0                              | 2862 <sup>b</sup>          |
| 0.681               | 0.68                         | 0                              | 2941 <sup>b</sup>          |
| 0.536               | 0.80                         | 0                              | 3039 <sup>b</sup>          |
| 0.946               | 1.11                         | 0                              | 3054 <sup>b</sup>          |
| 0.553               | 1.76                         | 0                              | 3198 <sup>b</sup>          |
| 1.072               | 2.98                         | 0                              | 3217 <sup>b</sup>          |
| 0.231               | 4.44                         | 0                              | 3269 <sup>b</sup>          |
| 1.04                | 0                            | 2.06                           | 2730 <sup>b</sup>          |
| 0.53                | 1.22                         | 0.99                           | 3617 <sup>c</sup>          |
| 0.36                | 1.97                         | 1.00                           | 3628 <sup>c</sup>          |
| 0.28                | 1.86                         | 1.86                           | 3683 <sup>c</sup>          |
|                     |                              |                                | 3662 <sup>b</sup>          |

<sup>a</sup> Chemical shift downfield from internal  $\text{C}_6\text{F}_6$ . <sup>b</sup> At  $-5^\circ$ . <sup>c</sup> Ambient probe temperature.

might be converted completely to sulfonium salt associated with a nonnucleophilic anion. Alternatively, the chloride ion could be substituted by a nonnucleophilic counterion by other means. The  $^{19}\text{F}$  chemical shift of such a sulfonium salt would be expected to be as large as that of tris(*p*-fluorophenyl)sulfonium salts. Silver fluoroborate was found to be unsuitable for our purpose as indicated by the tremendous  $^{19}\text{F}$  chemical shift of the mixture of the sulfide and the silver salt as compared with that of pure sulfide. This in no way implies that the cation is not generated but only that we would have no way of detecting it. The  $^{19}\text{F}$  chemical shift of a 1:1 mixture of antimony pentachloride and bis(*p*-fluorophenyl) sulfide in liquid sulfur dioxide was found to be almost the same as that of the mixture of the sulfide-chlorine adduct and the Lewis acid (Table V). Although it is possible that the complex formation between the phenyl ring of the sulfide and the Lewis acid provides the large shift, the result does not allow the conclusion that antimony pentachloride promotes ionization of the sulfide-chlorine complex.

By contrast to the above attempts, the action of mercuric chloride was found remarkable. One fluorine multiplet (3617 Hz) was observed for the chlorine-bis(*p*-fluorophenyl) sulfide adduct with mercuric chloride in acetonitrile (Table II). Addition of mercuric chloride to the sulfide, on the other hand, led to a single multiplet at 2730 Hz, a position almost the same as that of the sulfide multiplet. By analogy to the reported examples in the literature, the ready formation of complexes of mercuric halides with halide ion as indicated from the equilibrium constants<sup>17</sup> has led us to the conclusion that we have observed the forma-

Table III. Nmr Spectra<sup>a</sup> of

|                              | -S-                       |                           |                           |                           |                           |
|------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| $\delta_{H_A}^b$ (Hz)        | 410.80 (m)                | 429.46 (m)                | 431.98 (m)                | 446.60 (m)                | 447.75 (m)                |
| $\delta_{H_B}^b$ (Hz)        | 432.95 (m)                | 459.07 (m)                | 479.70 (m)                | 477.35 (m)                | 489.55 (m)                |
| $J_{H_A F}$                  | 8.23                      | 8.41                      | 8.30                      | 7.73                      | 7.65                      |
| $J_{H_B F}$                  | 5.28                      | 5.17                      | 5.08                      | 4.65                      | 4.85                      |
| $J_{H_A H_B}$                | 9.03                      | 8.92                      | 8.88                      | 9.11                      | 8.95                      |
| $\delta_F$ (Hz) <sup>e</sup> | 2684 ± 1 <sup>c</sup> (m) | 3017 ± 5 <sup>c</sup> (m) | 3257 ± 2 <sup>c</sup> (m) | 3503 ± 2 <sup>d</sup> (m) | 3447 ± 2 <sup>d</sup> (m) |

<sup>a</sup> Chemical shifts are in hertz downfield from either TMS (for protons) or hexafluorobenzene (for fluorines). <sup>b</sup> In CDCl<sub>3</sub> with TMS as internal standard. <sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub> and at -39°. <sup>d</sup> In CDCl<sub>3</sub> and at ambient temperature. <sup>e</sup> At 56.4 MHz.

Table IV. Equilibrium Constants and <sup>19</sup>F Chemical Shifts for Chlorine-Sulfide Equilibria

| Solvent                                      | T, °C | 10 <sup>5</sup> K <sub>1</sub> , M <sup>-1</sup> | $\delta(\text{Ar}_2\text{SX}_2)^c$ | K <sub>1</sub> ' <sup>c</sup> | $\delta(\text{Ar}_2\text{SX})^c$ | K <sub>2</sub> | $\delta(\text{Ar}_2\text{SX})^c$ | $\delta(\text{Ar}_2\text{SXX})^c$ |
|--|-------|--|------------------------------------|-------------------------------|----------------------------------|----------------|----------------------------------|-----------------------------------|
| CH <sub>2</sub> Cl <sub>2</sub> <sup>a</sup> | -39   | 4.47 ± 0.4                                       | 3172 ± 16                          |                               |                                  |                |                                  |                                   |
| CH <sub>2</sub> Cl <sub>2</sub>              | -39   |  |                                    | 17.45 ± 0.0                   | 3186 ± 31                        |                |                                  |                                   |
| CH <sub>2</sub> Cl <sub>2</sub>              | -39   | 3.63 ± 0.2                                       | 3135 ± 172                         |                               |                                  | 0.11 ± 0.0     | 3254 ± 330                       |                                   |
| CH <sub>2</sub> Cl <sub>2</sub>              | -39   | 4.04 ± 0.0                                       | 2964 ± 6.9 × 10 <sup>5</sup>       |                               |                                  | 16.93 ± 0.0    |                                  | 3190 ± 4.08 × 10 <sup>4</sup>     |
| CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup> | 25    | 4.04 ± 0.4                                       |                                    |                               |                                  |                |                                  |                                   |
| CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup> | 25    |  |                                    | 17.46 ± 1                     |                                  |                |                                  |                                   |
| CH <sub>3</sub> CN <sup>a</sup>              | -5    | 4.43 ± 7   | 3124 ± 38                          |                               |                                  |                |                                  |                                   |
| CH <sub>3</sub> CN                           | -5    |  |                                    | 17.45 ± 0                     | 3173 ± 71                        |                |                                  |                                   |
| CH <sub>3</sub> CN                           | -5    | 19.1 ± 3   | 3085 ± 394                         |                               |                                  | 0.11 ± 0.0     | 3102 ± 741                       |                                   |
| CH <sub>3</sub> CN                           | -5    | 3.93 ± 1.30                                      | 2795 ± 1.56 × 10 <sup>6</sup>      |                               |                                  | 16.93 ± 0.0    |                                  | 3152 ± 9.2 × 10 <sup>4</sup>      |

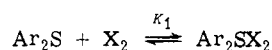
<sup>a</sup> Calculated according to eq 1 which gave the best description of chlorine-sulfide equilibria. <sup>b</sup> Obtained from uv data. <sup>c</sup> H<sub>2</sub> downfield from C<sub>6</sub>F<sub>6</sub>.

Table V. <sup>19</sup>F Nmr Chemical Shifts at -15° of SO<sub>2</sub> Solutions of Chlorine, Bis(*p*-fluorophenyl) Sulfide, and Antimony Pentachloride

| [Sulfide], M | [Cl <sub>2</sub> ]/[sulfide] | [SbCl <sub>5</sub> ]/[sulfide] | $\delta$ (Hz) |
|--------------|------------------------------|--------------------------------|---------------|
| 1.115        | 0                            | 0                              | 2793          |
| 1.539        | 0                            | 1.5                            | 3850          |
| 0.564        | 1.12                         | 1.35                           | 3799          |

tion of bis(*p*-fluorophenyl)chlorosulfonium trichloromercurate. It is noted that the <sup>19</sup>F chemical shift of this trichloromercurate is comparable to that of tris(*p*-fluorophenyl)sulfonium salt as expected. The observed disparity between the calculated (3124 Hz) and experimental (~3200 Hz) maximum <sup>19</sup>F chemical shift for the chlorine-bis(*p*-fluorophenyl) sulfide adduct and the <sup>19</sup>F chemical shift of the trichloromercurate of the bis(*p*-fluorophenyl)chlorosulfonium cation provides convincing evidence that the sulfide-chlorine adduct exists as a nonionic species in the equilibrium, and this disparity seems too large to be accounted for by a difference in charge dislocations in contact ions.

Therefore, our observations lead us to the conclusion that the following equilibrium involving a covalent or charge



transfer type adduct is the best description of the process in solution containing bis(*p*-fluorophenyl) sulfide and chlorine in aprotic solvents such as methylene chloride or acetonitrile. The equilibrium constants (4.47 × 10<sup>5</sup> and 4.43 × 10<sup>5</sup> M<sup>-1</sup>) in Table IV are of comparable magnitude to the

values indirectly obtained by Modena, *et al.*,<sup>18</sup> in their studies of the oxidation of the alkyl aryl sulfides to sulfoxide by bromine in methanol-water. Solvent independence of the equilibrium constant and the chemical shift of the sulfide-chlorine adduct emphasizes the nonionic nature of the adduct. The difference between the maximum <sup>19</sup>F chemical shift of the methylene chloride solution of sulfide and chlorine (3202 Hz) at high chlorine concentration and the calculated <sup>19</sup>F chemical shift (3172 Hz) of the sulfide-chlorine complex in the same solvent could be due to a medium effect arising from the high molar ratio of chlorine to sulfide or the modification of the solvent by chlorine.

### Experimental Section

**General.** Melting points and boiling points are uncorrected. Infrared spectra were determined using a Perkin-Elmer spectrophotometer. Vpc analyses were carried out on an Aerograph Model 200B vapor phase chromatograph using helium as the carrier gas and columns containing 20% of either FFAP or SE-30 on 60-80 mesh acid-washed Chromosorb-W. Optical densities were measured in 1-cm matched quartz cells with a Cary 14 spectrophotometer using a thermostated cell compartment with the sample temperature maintained at 25 ± 0.1°. All sample solutions were prepared with freshly distilled spectrograde methylene chloride just prior to use. Four scans were obtained for each determination, and an average value was taken.

The <sup>19</sup>F nmr measurements were carried out with a Varian Model V-4311 spectrometer, operating at 56.4 MHz, equipped with a variable temperature probe. Frequency measurements were made by the usual audio side band interpolation technique using hexafluorobenzene as an internal reference. A Hewlett-Packard Model 200 CD wide range oscillator was used to produce a side band of the reference signal, and the frequency of the output signal was monitored with a Monsanto Model 100A frequency counter.

All side band frequencies are accurate to  $\pm 1$  Hz. Spectra were recorded with a Varian Model G-10 graphic recorder. Temperature measurements were made with an external thermocouple calibrated against a thermocouple in the sample position and are considered accurate to  $\pm 1^\circ$ . Spectrograde methylene chloride or acetonitrile was used as solvent.

**Bis(*p*-fluorophenyl) Sulfoxide by the Friedel-Crafts Method.** The method used by Leonard, *et al.*,<sup>19</sup> was adopted to prepare bis(*p*-fluorophenyl) sulfoxide. Several recrystallizations of the crude sulfoxide from pentane or sublimation at  $35\text{--}40^\circ$  (13 mm) gave fine white needles: mp  $50\text{--}51^\circ$  (lit. mp  $50.5^\circ$ ,<sup>19</sup>  $70^\circ$ <sup>20</sup>);  $\lambda_{\text{inf}}^{\text{CH}_2\text{Cl}_2}$  250 nm ( $\epsilon$  220);  $\nu_{\text{max}}^{\text{KBr}}$  3090, 3060, 1583, 1484, 1396, 1290, 1213, 1154, 1148, 1088, 1072, 1045, 1003, 959, 940, 835, 810, 526, 513, 447  $\text{cm}^{-1}$ . Nmr data are shown in Table III.

**Bis(*p*-fluorophenyl) Sulfide.** A solution of bis(*p*-fluorophenyl) sulfoxide (6.27 g, 0.024 mol) in 35 ml of anhydrous tetrahydrofuran was added dropwise into a stirred solution of lithium aluminum hydride (1.52 g, 0.040 mol) in 50 ml of anhydrous THF under a stream of nitrogen. When the addition was complete, the mixture was heated under reflux for 10 hr, then it was cooled to room temperature. Unreacted lithium aluminum hydride was destroyed by slow addition of 4 ml of water and 2.4 ml of 10% aqueous sodium hydroxide solution. The liquid phase of the clarified mixture after 30 min of stirring was separated by filtration, and the solid was washed several times with THF. The original colorless filtrate and washings were combined, and the whole was evaporated to remove THF. Fractional distillation of the remaining viscous residue provided 2.40 g (43% yield) of bis(*p*-fluorophenyl) sulfide: bp  $102\text{--}103^\circ$  (1.3 mm) (lit. bp  $136\text{--}137^\circ$  (9 mm),<sup>19</sup>  $133\text{--}135^\circ$  (7 mm)<sup>21</sup>);  $n_{\text{D}}^{20}$  1.5853;  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  248.5, ( $\epsilon$  9750), 272.5 nm ( $\epsilon$  4970);  $\nu_{\text{max}}^{\text{KBr}}$  3063, 1485, 1393, 1227, 1152, 1088, 1080, 1010, 823, 640, 623, 522  $\text{cm}^{-1}$ . Nmr data are given in Table III.

**Bis(*p*-fluorophenyl) Sulfone from the Oxidation of Bis(*p*-fluorophenyl) Sulfoxide with *m*-Chloroperbenzoic Acid.** A solution of 7.85 g (0.033 mol) of bis(*p*-fluorophenyl) sulfoxide in 90 ml of chloroform was added dropwise into a stirred solution of 5.75 g (0.033 mol) of *m*-chloroperbenzoic acid in 160 ml of chloroform maintained between  $-5$  and  $-10^\circ$ . After the addition was completed, the mixture was allowed to warm to room temperature. The white precipitate of *m*-chlorobenzoic acid accumulated overnight was removed by filtration and washed with chloroform. The combined filtrate and washings were then extracted with 100 ml of 10% sodium carbonate solution in one portion. The chloroform layer was separated, dried, filtered, and concentrated under vacuum to afford 6.2 g (74% yield) of crude bis(*p*-fluorophenyl) sulfone, which was recrystallized from ethanol as colorless needles: mp  $98\text{--}99^\circ$  (lit.<sup>19</sup> mp  $98\text{--}98.5^\circ$ );  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  236.6 ( $\epsilon$  1650),  $\lambda_{\text{inf}}$  260 nm ( $\epsilon$  1480);  $\lambda_{\text{max}}^{\text{KBr}}$  3100, 3062, 3020, 1583, 1488, 1402, 1290, 1233, 1152, 1097, 1067, 1012, 832, 810, 710, 673, 627, 544, 490  $\text{cm}^{-1}$ . Nmr data are given in Table V.

**Tris(*p*-fluorophenyl)sulfonium Salts from the Reaction of Aryl Grignard Reagent with Bis(*p*-fluorophenyl) Sulfoxide.**<sup>22</sup> A solution of 10.98 g (0.04 mol) of bis(*p*-fluorophenyl) sulfoxide in 100 ml of dry benzene was added slowly to 200 ml of a clear, dark brown benzene solution of *p*-fluorophenylmagnesium bromide, prepared under nitrogen from 37.92 g (0.21 mol) of magnesium turnings and 200 ml of dry ether, which was then replaced with the dry benzene. After the addition was completed at room temperature, the mixture was heated under reflux under nitrogen for 24 hr. The resulting mixture, which contained a yellow precipitate, was cooled to  $0^\circ$  and hydrolyzed with a solution containing 14 ml of hydrobromic acid (specific gravity 1.38) and 14 ml of water. The benzene layer was separated and extracted three times with 150-ml portions of aqueous 5% hydrobromic acid. The aqueous layer from hydrolysis and the extracts were combined and extracted with three 200-ml portions of chloroform. The combined chloroform extracts were dried over anhydrous sodium sulfate, filtered, and concentrated to dryness to yield 2.16 g (13% yield) of a brown oil which solidified on standing at room temperature. Dissolution of the solid in methylene chloride and subsequent addition of ether resulted in the formation of crystals. Recrystallization from methylene chloride-ether gave pure tris(*p*-fluorophenyl)sulfonium bromide, colorless cubic crystals: mp  $215.5\text{--}216.5^\circ$ ;  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  237 ( $\epsilon$  26,830),  $\lambda_{\text{inf}}$  265 ( $\epsilon$  10,300),  $\lambda_{\text{sh}}$  273 nm ( $\epsilon$  6060);  $\lambda_{\text{max}}^{\text{KBr}}$  3085, 3019, 1580, 1490, 1404, 1297, 1235, 1160, 1100, 1069, 1007, 843, 813, 520, 453, 435  $\text{cm}^{-1}$ . Nmr data are shown in Table III. Upon the addi-

tion of silver nitrate solution to the aqueous solution of the sulfonium salt, silver bromide was formed immediately.

A solution of 0.21 g (1.50 mmol) of potassium perchlorate in 10 ml of water was added to a stirred solution of 0.5 g (1.26 mmol) of tris(*p*-fluorophenyl)sulfonium bromide in 10 ml of water. After warming and digesting the solution, 0.44 g (85% yield) of colorless crystals were obtained. Recrystallization from a mixture of acetone and ether gave colorless fine needles of tris(*p*-fluorophenyl)sulfonium perchlorate: mp  $175\text{--}176^\circ$ ;  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  238 ( $\epsilon$  14,800),  $\lambda_{\text{inf}}$  265 ( $\epsilon$  5920),  $\lambda_{\text{sh}}$  273 nm ( $\epsilon$  3120);  $\lambda_{\text{max}}^{\text{KBr}}$  3085, 3017, 2970, 1580, 1487, 1401, 1295, 1233, 1160, 1097, 1005, 840, 812, 520, 450  $\text{cm}^{-1}$ . Nmr data are given in Table III.

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{12}\text{F}_3\text{SClO}_4$ : C, 51.95; H, 2.90; F, 13.70; S, 7.69; Cl, 8.54. Found: C, 51.65; H, 2.83; F, 14.64; S, 7.86; Cl, 8.46.

The sulfonium salts gave blue, chloroform-soluble precipitates upon the addition of an acidic aqueous solution containing cobaltous ion and excess thiocyanate ion.

**Concentration Calibrations and Molar Extinction Coefficient of the Chlorine-Bis(*p*-fluorophenyl) Sulfide Adduct.** A methylene chloride solution which contained a known amount of bis(*p*-fluorophenyl) sulfide and gave a suitable absorbance reading was treated with a small drop of concentrated chlorine solution in the sample cell; the ultraviolet spectrum was taken. The optical densities at the isosbestic point ( $\lambda_i$  243.5 nm) plotted against the concentrations of the corresponding sulfide solution provided a calibration curve for total sulfide. The optical densities of chlorine solutions of known concentration in methylene chloride at 330 nm were used to prepare a calibration curve. Chlorine concentrations of the standards were established by titration against sodium thiosulfate solutions of known concentration.

The optical densities at 272.5 nm,  $A^{272.5}$ , of three samples of the complex of bis(*p*-fluorophenyl) sulfide with chlorine in methylene chloride were used to calculate the molar extinction coefficient using the standard equation assuming that the sulfide can be

$$C_{\text{st}} = C_s + C_{\text{sc}} \quad (5)$$

$$A^{272.5} = [C_s \epsilon_s + C_{\text{sc}} \epsilon_{\text{sc}}] b \quad (6)$$

completely converted into its chlorine complex by addition of an excess of chlorine, *i.e.*,  $C_s = 0$ .  $C_s$  is the concentration of bis(*p*-fluorophenyl) sulfide,  $C_{\text{st}}$  is the sum of the concentrations of the sulfide and its chlorine complex,  $C_{\text{sc}}$  and  $\epsilon_s$  and  $\epsilon_{\text{sc}}$  are the corresponding molar extinction coefficients, and  $b$  is the cell path length in centimeters. The optical densities of the complex at various concentrations were obtained by treating sulfide solutions of known concentration repeatedly with extremely small amounts of concentrated chlorine solutions until the optical densities remained constant.

**Ultraviolet Measurement of the Reaction of Bis(*p*-fluorophenyl) Sulfide and Chlorine in Methylene Chloride.** A dilute chlorine solution in methylene chloride with optical density at 330 nm below 0.1 was prepared in a volumetric flask. From the calibration curve of chlorine concentration the concentration of chlorine in this solution was obtained. Then a known amount of bis(*p*-fluorophenyl) sulfide, obtained by weight differences, was added into the chlorine solution by microsyringe, and the solution was shaken thoroughly. The solution was diluted according to the amount of bis(*p*-fluorophenyl) sulfide added so that the optical density at the isosbestic point would be less than 1. The ultraviolet spectra of several diluted solutions were then taken. The concentration of initial bis(*p*-fluorophenyl) sulfide in each diluted solution was obtained from the calibration curve of total sulfide concentrations.

The concentration of the complex,  $C_{\text{sc}}$ , was evaluated by solving eq 5 and 6. Equilibrium constants were calculated using both of the following equations where  $C_{\text{Cl}_2}$  is the concentration of chlorine at equilibrium.

$$K_1 = \frac{C_{\text{sc}}}{C_s C_{\text{Cl}_2}} \quad (7)$$

$$K_1' = \frac{C_{\text{sc}}^2}{C_s C_{\text{Cl}_2}} \quad (8)$$

**Procedures for Preparing Bis(*p*-fluorophenyl) Sulfide-Chlorine Nmr Samples.** About 0.2 ml of spectrograde methylene chloride or spectrograde acetonitrile and a few drops of internal standard,

hexafluorobenzene, were weighed separately into an nmr tube containing a known amount of bis(*p*-fluorophenyl) sulfide. The chlorine solution was prepared by introducing chlorine into dry methylene chloride in a reservoir bottle which was cooled externally with a Dry Ice-acetone mixture and was equipped with an automatic buret with attached drying tube. The concentration of the chlorine solution was approximately determined by titration and the required volume of chlorine solution for the known amount of sulfide was calculated. The desired volume (*ca.* 0.2–1.5 ml) of chlorine solution was added into a cooled nmr tube, modified with a joint so that a small drying tube could be attached during sealing, and the very first and the last portions of chlorine solution from the same batch were withdrawn from the buret for obtaining the exact concentration of chlorine iodometrically. The volume was adjusted with methylene chloride or acetonitrile in a level corresponding to about 0.5 ml of liquid. The total weight of solvent was obtained gravimetrically. The nmr tube was then sealed and stored in Dry Ice-acetone mixture.

**Bis(*p*-fluorophenyl)chlorosulfonium Trichloromercurate.** After  $4.56 \times 10^{-2}$  g ( $6.44 \times 10^{-4}$  mol) of chlorine in spectrograde acetonitrile had been added to 0.0728 g ( $3.28 \times 10^{-4}$  mol) of bis(*p*-fluorophenyl) sulfide in an nmr tube below 0° as described above, 0.0884 g ( $3.25 \times 10^{-4}$  mol) of mercuric chloride in a known amount of acetonitrile was added to the solution in a glove bag. The nmr tube was then sealed and stored in a Dry Ice-acetone mixture until the nmr spectrum could be obtained.

**Attempted Use of Silver Fluoroborate and Antimony Pentachloride as Stabilizers of the Sulfide-Chlorine Adduct.** After 0.1 ml (0.23 g,  $7.6 \times 10^{-4}$  mol) of antimony pentachloride was added with a syringe into a solution of 0.125 g ( $5.64 \times 10^{-4}$  mol) of sulfide and a known amount of methylene chloride in an nmr tube below 0°, a chlorine solution (0.044 g,  $6.34 \times 10^{-4}$  mol) in methylene chloride was added into the solution. The nmr tube was then sealed and stored in the refrigerator. This <sup>19</sup>F nmr spectrum showed almost the same chemical shift, 3800 Hz, as that of the 1:1 mixture of sulfide and antimony pentachloride, 3850 Hz.

About 0.2 ml of spectrograde methylene chloride and a few drops of hexafluorobenzene were weighed separately into an nmr tube containing 0.0977 g ( $4.39 \times 10^{-4}$  mol) of bis(*p*-fluorophenyl) sulfide. A known amount of silver fluoroborate (0.0755 g,  $3.88 \times 10^{-4}$  mol) was added into the nmr tube in a glove bag. After the volume of the solution had been adjusted with methylene chloride, the nmr tube was sealed. The <sup>19</sup>F nmr spectrum of this sample solution showed a multiplet for the sulfide at 2885 Hz as well as a singlet for fluoroborate at 712 Hz downfield from the internal standard.

**Water Quenching of Reaction Mixture of the Sulfide and Chlorine.** After bis(*p*-fluorophenyl) sulfide (0.11 g,  $5.00 \times 10^{-4}$  mol) was treated over 30 min in 20 ml of methylene chloride with 0.11 g ( $1.53 \times 10^{-3}$  mol) of chlorine below 0°, water, 10 ml, was added to the mixture with resultant formation of a yellowish precipitate. The precipitate was collected by filtration, washed with water, filtered, and dried. The infrared spectrum of the white solid showed a strong band at 1040 cm<sup>-1</sup>, which was identical with that of bis(*p*-

fluorophenyl) sulfoxide.

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## References and Notes

- (1) Taken from the dissertation of Ming May Y. Chang, submitted in partial fulfillment of the requirements for the Ph.D. degree in chemistry at the Polytechnic Institute of New York.
- (2) (a) H. Böhme, H. Fischer, and R. Frank, *Justus Liebigs Ann. Chem.*, **563**, 54 (1949); (b) W. E. Lawson and T. P. Dawson, *J. Amer. Chem. Soc.*, **49**, 3119 (1927); (c) H. Böhme and H. Gran, *Justus Liebigs Ann. Chem.*, **581**, 133 (1953); (d) H. Richtzenhain and B. Alfredsson, *Chem. Ber.*, **86**, 142, (1953); (e) F. G. Bordwell and B. M. Plitt, *J. Amer. Chem. Soc.*, **77**, 572 (1955).
- (3) G. E. Wilson, Jr., and M. G. Huang, *J. Org. Chem.*, **35**, 3002 (1970).
- (4) (a) J. M. Stewart and H. P. Cordts, *J. Amer. Chem. Soc.*, **74**, 5880 (1952); (b) J. M. Stewart and C. H. Burnside, *ibid.*, **75**, 243 (1953); (c) D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 1 (1951); (d) H. Kwart and R. K. Miller, *J. Amer. Chem. Soc.*, **78**, 5008 (1956); (e) H. Kwart and L. J. Miller, *ibid.*, **80**, 884 (1958); (f) H. Kwart and R. W. Body, *J. Org. Chem.*, **30**, 1188 (1965); (g) H. Kwart, R. W. Body, and D. M. Hoffman, *Chem. Commun.*, **765** (1967); (h) H. Kwart and P. S. Strliko, *ibid.*, **767** (1967); (i) G. E. Wilson, Jr., *J. Amer. Chem. Soc.*, **87**, 3785 (1965).
- (5) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5749 (1969).
- (6) G. Allegra, G. E. Wilson, Jr., E. Benedetti, C. Pedone, and R. Albert, *J. Amer. Chem. Soc.*, **92**, 4002 (1970).
- (7) H. Böhme and E. Boll, *Z. Anorg. Allg. Chem.*, **290**, 17 (1957).
- (8) (a) K. Mislow, T. Simmons, J. T. Mellillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964); (b) K. Mislow, *Rec. Chem. Progr.*, **28**, 217 (1967).
- (9) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963), and references therein.
- (10) It should be noted that the treatment does not allow judgment on the nature of the adduct. Any equilibrium which supplies a one-particle adduct will satisfy the data. Thus the adduct might equally well be considered to be the charge transfer type or to consist of a tight ion pair on the basis of these data.
- (11) G. E. Wilson, Jr., and M. M. Y. Chang, *Tetrahedron Lett.*, 875 (1971).
- (12) (a) W. O. Ranky and D. C. Nelson in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N.Y., 1961, Chapter 17; (b) H. H. Szmant, *ibid.*, Chapter 16; (c) U. Miotti, G. Modena, and L. Seda, *J. Chem. Soc. B*, 802 (1970).
- (13) (a) D. Bethell and V. Gold, "Carbonium Ions, an Introduction," Academic Press, London, 1967, p 48; (b) J. W. Bayles, A. G. Evans, and J. R. Jones, *J. Chem. Soc.*, 1020 (1957); (c) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964); (d) G. A. Olah, "Friedel-Crafts and Related Reactions," Wiley, New York, N.Y., 1963.
- (14) (a) D. B. Denney, D. Z. Denney, and B. C. Chang, *J. Amer. Chem. Soc.*, **90**, 6332 (1968); (b) G. A. Wiley and W. R. Stine, *Tetrahedron Lett.*, 2321 (1967).
- (15) H. Meerwein, K. F. Zerner, and R. Gipr, *Justus Liebigs Ann. Chem.*, **688**, 67 (1965).
- (16) C. R. Johnson and J. J. Rigan, *J. Amer. Chem. Soc.*, **91**, 5398 (1969).
- (17) Y. Marcus, *Acta Chem. Scand.*, **11**, 599 (1957).
- (18) V. Miotti, G. Modena, and L. Seda, *J. Chem. Soc. B*, 802 (1970).
- (19) N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, **70**, 1564 (1948).
- (20) G. Olah and A. Pavlath, *Acta Chir. (Budapest)*, **4**, 111 (1954).
- (21) T. Osaka and K. Tottori, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **65**, 1199 (1962).
- (22) B. S. Wildi, S. W. Taylor, and H. A. Potratz, *J. Amer. Chem. Soc.*, **73**, 1965 (1951).