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CHLORINE-SULFIDE EQUILIBRIA IN SOLUTION

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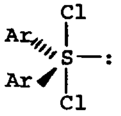
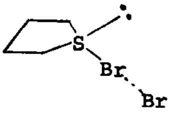
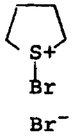
Structural questions regarding the metastable complexes between halogens and organic sulfides are at last being approached and answered. The sulfur atom exists as a tetracoordinate distorted trigonal bipyramid in the crystalline 1:1 adduct (I) of bis(p-chlorophenyl)sulfide with chlorine (1). By contrast, a tricoordinate pyramidal sulfur was found in the 1:1 charge transfer type adduct (II) of thiophane with bromine (2). In the latter case, in which the bromine-bromine distance is large compared to the normal bond length and the sulfur-bromine separation approaches the covalent bond length, we have concluded that the greatest contributor to the electronic representation is the ionic one (III) (2). We have investigated the nature of the adduct of chlorine with bis(p-fluorophenyl)sulfide in methylene chloride solution, and we have found that a rapid equilibrium exists between adduct and starting materials.



I



II



III

Low temperature (-39°) fluorine nmr spectra on methylene chloride solutions containing differing molar ratios of chlorine to sulfide (Table I) showed only one symmetric fluorine multiplet, and the multiplet moved to lower field with an increasing ratio of chlorine to sulfide. A similar effect obtains in acetonitrile. These results clearly require that any equilibria which are pertinent, such as those shown in equations 1-3 (3), be rapid on the nmr time scale.

$$Ar_2S + Cl_2 \rightleftharpoons Ar_2S\cdot Cl_2 \qquad (1)$$

$$Ar_2S + Cl_2 \rightleftharpoons Ar_2\overset{+}{S}\text{-}Cl + Cl^- \qquad (2)$$

$$Ar_2S + Cl_2 \rightleftharpoons Ar_2S\cdot Cl_2 \rightleftharpoons Ar_2\overset{+}{S}Cl + Cl^- \qquad (3)$$

The trichloromercurate of the *bis*(*p*-fluorophenyl)chlorosulfonium cation (4) could be generated by addition of mercuric chloride to an acetonitrile solution of the complex of chlorine with sulfide. This sulfonium salt shows one fluorine multiplet 3617 Hz downfield from C_6F_6. The disparity between the shift of this chlorosulfonium salt and the maximum shift for chlorine-sulfide systems (Table II) seems too large to be accounted for by differences in charge dislocations in contact ions. Thus, we favor equilibrium 1 as the best description of the processes in solution. This conclusion is also supported by uv data which show an isosbestic point for solutions of chlorine and sulfide in methylene chloride.

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TABLE I

Fluorine Chemical Shifts of Solutions of Chlorine and Bis(p-fluorophenyl) sulfide in Methylene Chloride.

[Sulfide] (M/ℓ)	$[Cl_2]/[\text{Sulfide}]$	δ (Hz)[a]
0.798	0	2684
0.600	0.71	2951
0.839	1.02	3138
0.449	1.99	3195
0.495	3.22	3202

(a) Chemical shift downfield from internal C_6F_6.

TABLE II

Fluorine Chemical Shifts of Solutions of Chlorine, Mercuric Chloride and Bis(p-fluorophenyl)sulfide in Acetonitrile.

[Sulfide] (M/ℓ)	$[Cl_2]/[\text{Sulfide}]$	$[HgCl_2]/[\text{Sulfide}]$	δ (Hz)[a]
0.94	0	0	2733
1.04	0	2.06	2730
.95	1.11	0	3054
1.07	3.00	0	3217
0.28	1.86	1.86	3683
0.36	1.97	1.00	3628
0.53	1.22	0.99	3617

(a) Chemical shift downfield from internal C_6F_6.

REFERENCES

1. N. C. Baenziger, R. E. Buckles, R. J. Maner and T. D. Simpson, J. Am. Chem. Soc., **91**, 5749 (1969).

2. G. Allegra, G. E. Wilson, Jr., E. Benedetti, C. Pedone and R. Albert, J. Am. Chem. Soc., **92**, 4002 (1970).

3. We mean to imply a molecular composition but no structural preference in the complexes described by a dot bond.

4. The hexachloroantimonate of the chloro dimethylsulfonium cation synthesized in this manner has been isolated. See, H. Meerwein, K. F. Zenner and R. Gipp, Ann. **688**, 67 (1965).