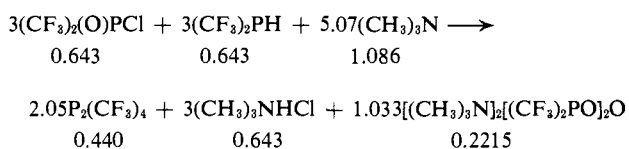


plex  $(\text{CF}_3)_2(\text{O})\text{P}(\text{Cl})\cdot(\text{CH}_3)_3\text{N}$  in the solid  $(\text{CH}_3)_3\text{NHCl}$ . On this basis the main reaction balance would be given in millimoles as



Thus the stoppage when only 60% of the phosphorus reactants had been consumed was due to removal of some 40% of the amine to form the double-amine complex of the phosphinic anhydride.

### Infrared Spectra

The infrared spectra of the three compounds shown in Table III were recorded by the Beckman IR7 instrument, using NaCl or CsI optics and windows of KBr or high-density polyethylene, as appropriate. Calibration by well-known bands limited the probable error to  $1\text{ cm}^{-1}$  for frequencies below  $2000\text{ cm}^{-1}$ . The relative intensity of each feature (peak or shoulder) is shown in parentheses after the frequency ( $\text{cm}^{-1}$ ) and was calculated by the arbitrary definition  $k = (100/PL) \log I_0/I$  for pressure  $P$  and path  $L$ , both in cm. For this purpose the  $I$  values were taken quite

literally, so that overlapping bands are overestimated in relation to true intensities.

The assignments are based primarily upon comparisons with phosphorus compounds, assuming that the bonds to arsenic are considerably weaker and vibrate with slightly higher reduced masses. For example, the  $\text{CF}_3$  deformation modes generally run about  $30\text{ cm}^{-1}$  lower than those for phosphorus compounds, while the As-CF<sub>3</sub> and As-O stretching modes appear about  $100\text{ cm}^{-1}$  lower than those for P-CF<sub>3</sub> and P-O.

Not listed in Table III were numerous overtones and combinations for which assignment would be difficult. Very similar for the three compounds were bands at  $1266$  (1.9),  $1263$  (1.7), and  $1252$  (2.6)  $\text{cm}^{-1}$ , respectively, all probably enhanced by proximity to the very strong C-F stretching bands. The following list of other minor peaks is not necessarily complete: for  $(\text{CF}_3)_2\text{AsF}$ ,  $1060$  (0.7),  $1036$  sh (0.4), and  $1030$  (0.6); for  $\text{CH}_3\text{OAs}(\text{CF}_3)_2$ ,  $2237$  (0.4),  $2050$  (0.2),  $1890$  (0.03),  $1850$  (0.05),  $1666$  (0.25),  $614$  sh (0.7),  $475$  sh (0.02), and  $447$  (0.02); for *t*-C<sub>4</sub>H<sub>9</sub>OAs(CF<sub>3</sub>)<sub>2</sub>,  $2317$  (0.2),  $2231$  (0.4),  $1660$  (0.2), and  $1563$  (0.34)—all in  $\text{cm}^{-1}$  with relative intensities in parentheses as usual.

The absence of some methyl-group modes is not unusual in compounds having high polarity elsewhere in the molecule; comparison with Table XII of ref. 3 is pertinent.

## Halogen Complexes. I. An Investigation by Nuclear Magnetic Resonance of Complexes Formed by Iodine and Some *para*-Substituted Phenyl Methyl Sulfides

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Contribution from the Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois. Received September 23, 1964

According to n.m.r. measurements, the enthalpy of association of iodine and *p*-methoxyphenyl methyl sulfide in carbon tetrachloride is  $-6.2 \pm 0.7\text{ kcal./mole}$ . The mean lifetime of the complex was measured for several concentrations at  $-27^\circ$ . Inductive effects appear to control the association of iodine with various *para*-substituted phenyl methyl sulfides.

### Introduction

In the present research, nuclear magnetic resonance spectroscopy provides several types of information about halogen complexes. The mean lifetimes of many halogen complexes in solution have magnitudes in the range where measurement of lifetimes by n.m.r. is feasible. Also, inductive effects and thermodynamic constants may be measured and the results compared with those from other techniques.

Iodine-sulfide systems have<sup>2-8</sup> been investigated previously by cryoscopy, measurements of dipole

moments, and spectrophotometric studies in the visible and ultraviolet regions. For the association of iodine and simple sulfides such as dimethyl, diethyl, and dibenzylsulfides in inert solvents, the equilibrium constants tend to be in the range 30 to 250 l. mole<sup>-1</sup> at room temperature and  $\Delta H$  is usually in the range  $-6$  to  $-9\text{ kcal./mole}$ .

### Experimental

**Reagents and Solutions.** Methyl phenyl sulfide, *p*-bromophenyl methyl sulfide, *p*-nitrophenyl methyl sulfide, and *p*-methoxyphenyl methyl sulfide were kindly supplied by Dr. W. Brannen of this department. The preparation and purification are described elsewhere.<sup>9</sup>

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(4) M. Good, A. Major, J. Nag-Chaudhuri, and S. P. McGlynn, *ibid.*, **83**, 4329 (1961).

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(8) K. A. Jensen, *Z. anorg. allgem. Chem.*, **250**, 245 (1943).

(9) W. Brannen, Thesis, Northwestern University, 1962.

(1) Alfred P. Sloan Research Fellow.

(2) N. W. Tideswell and J. D. McCullough, *J. Am. Chem. Soc.*, **79**, 1031 (1957).

**Table I.** Observed Proton Chemical Shifts and Values of  $1/T_2'$  for the  $-\text{SCH}_3$  Group in the *p*-Methoxyphenyl Methyl Sulfide-Iodine-Carbon Tetrachloride System

Soln. no.	$I_2$ , m.f.	$\text{CH}_3\text{SC}_6\text{H}_4\text{-OCH}_3$ , m.f.	$1/T_2'$ , radians/sec. at $-22^\circ$	$\nu$ , c.p.s.				
				$-22^\circ$	$25^\circ$	$35^\circ$	$45^\circ$	$55^\circ$
1	0.0000	0.0197	0.67	-143.0	-142.7	-142.7	-142.7	-142.7
2	0.0021	0.0196	0.83	-145.3	-143.8	-143.7	-143.1	-143.0
3	0.0053	0.0195	1.00	-148.2	-146.4	-145.8	-145.4	-144.6
4	0.0114	0.0194	1.33	-155.0	-150.6	-148.8	-148.2	-146.8
5	0.0244	0.0191	1.80	-162.2	-156.4	-155.0	-153.0	-151.8

Carbon tetrachloride (Eastman Organic Chemicals Spectro grade) was used without purification. Iodine (Mallinckrodt) was resublimed and stored in a desiccator over magnesium perchlorate. Tetramethylsilane (Anderson Chemical Co.) was used without further purification since the concentration never exceeded 0.01 mole fraction.

**Solutions and N.m.r. Measurements.** The solutions, in 5-mm. o.d. Pyrex tubes, were degassed, sealed, and stored under Dry Ice until shortly before use. The p.m.r. spectra were obtained with a Varian Associates, Inc., HR spectrometer, operating at 60 Mc./sec. Relaxation times were measured by calibrating the sweep of the field, as displayed on the oscilloscope, and matching the observed exponential decay envelope of the signal with an appropriate template. Chemical shifts were measured by the side-band technique and are reported in c.p.s. with negative numbers corresponding to resonance at lower fields than that required for the internal reference, tetramethylsilane.

## Results and Discussion

**N.m.r. Spectra and Thermodynamic Constants for the Iodine-*p*-Methoxyphenyl Methyl Sulfide Equilibrium.** Chemical shifts and line widths were measured for solutions of approximately 0.02 mole fraction (m.f.) of *p*-methoxyphenyl methyl sulfide, 0.01 m.f. of tetramethylsilane and carbon tetrachloride, and from 0 to 0.0244 m.f. of iodine. Measurements were made at temperatures in the range  $-22$  to  $55^\circ$ , as shown in Table I, where  $\nu$  refers to the chemical shift of the  $-\text{SCH}_3$  protons relative to the internal reference, tetramethylsilane.

The equilibrium constant, in m.f. units, for the reaction



may be written

$$K_N = \frac{C(A + B + S - C)}{(A - C)(B - C)} \quad (2)$$

where  $A$ ,  $B$ ,  $C$ , and  $S$  refer to the number of moles of acid present initially, base present initially, complex formed when equilibrium has been established, and solvent, respectively. The  $-\text{SCH}_3$  group of *p*-methoxyphenyl methyl sulfide exhibits only one n.m.r. absorption peak and is therefore rapidly exchanging between free and complexed sites. The observed frequency,  $\delta_{\text{obsd}}$ , is given by the expression<sup>10,11</sup>

$$\delta_{\text{obsd}} = P_c \Delta + \delta_{\text{free}} \quad (3)$$

where  $\delta_{\text{free}}$  is the chemical shift of the free base in the absence of exchange,  $\Delta$  (or the "association shift") is  $\delta_{\text{complex}} - \delta_{\text{free}}$ ,  $\delta_{\text{complex}}$  is the chemical shift of the complexed base in the absence of exchange, and  $P_c$  is  $C/B$  or the ratio of the number of moles of complexed base to the total number of moles of base present. The value of  $\Delta$  is equal to the slope of the line in a plot of  $\delta_{\text{obsd}}$  as a function of  $C/B$ . Values of  $C$  required for the plot may be calculated from eq. 1 provided that  $K_N$  is known. If  $K_N$  is not known, both  $C$  and  $K_N$  can be determined by plotting  $\delta_{\text{obsd}}$  vs.  $C/B$  employing  $K_N$  as a parameter in eq. 1. Only use of the correct  $K_N$  will allow the plot to be a straight line, and  $\Delta$  is determined as the slope of the line.<sup>12</sup>

From the data in Table I and with the aid of an IBM 709 computer, values of  $K_N$  and  $\Delta$  were obtained and are presented in Table II. The least-squares plot of

**Table II.** Equilibrium Constants and Association Shifts for the Reaction of Iodine and *p*-Methoxyphenyl Methyl Sulfide

Temp., $^\circ\text{C}$ .	$K_N$ , (m.f.) <sup>-1</sup>	$-\Delta$ , c.p.s.
25	$218 \pm 25^a$	20.5
35	$175 \pm 41$	18.5
45	$136 \pm 6$	16.7
55	$82 \pm 7$	17.4

<sup>a</sup> Probable error.

$\log K_N$  vs.  $1/T$  gives  $-6.2 \pm 0.7$  kcal./mole for the enthalpy of association and  $-7.8 \pm 2.3$  e.u. for the entropy of association.

The enthalpy of association and the equilibrium constants in Table II are less than most of those for several previously studied iodine-sulfide systems which are discussed in ref. 2-8. The replacement of an alkyl group by a *p*-methoxyphenyl group appears to lower the basicity of sulfur as well as selenium. For the association of iodine and dimethyl selenide in carbon tetrachloride,  $K$  is  $495$  l. mole<sup>-1</sup> at  $25^\circ$ ,<sup>13</sup> and  $315$  l. mole<sup>-1</sup> at  $35.8^\circ$ <sup>14</sup>; for the association of iodine and diphenyl selenide,  $K$  is  $28$  l. mole<sup>-1</sup> at  $25^\circ$ .<sup>2</sup>

The association presumably occurs through sulfur since the base strength of sulfur is greater than that of oxygen or of the aromatic rings and since the associa-

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tion shifts of the methoxy group and of the ring hydrogen atoms are relatively small. The association shift of the *p*-methoxy group is less than 3 c.p.s. Analysis of the absorption by the ring hydrogens gives chemical shifts of  $-405.0$  and  $-430.2$  c.p.s. and  $J_{AB} = 8.5$  c.p.s.<sup>15</sup> for dilute *p*-methoxyphenyl methyl sulfide in carbon tetrachloride and, when enough iodine is added to complex 90% of the sulfide, chemical shifts of 411.0 and 441.00 c.p.s. and  $J_{AB} = 8.4$  c.p.s.<sup>16</sup> Thus, association shifts of  $-6.7$  and  $-12.0$  c.p.s. are calculated for the two types of ring protons.

**Table III.** Chemical Shifts and Values of  $1/T_2'$  at  $-27^\circ$  for the  $-SCH_3$  Group in the *p*-Methoxyphenyl Methyl Sulfide-Iodine-Carbon Tetrachloride System

$I_2$ , m.f.	$CH_3SC_6H_4-$ $OCH_3$ , m.f.	$1/T_2'$ , radians/ sec.	$\nu$ , c.p.s.	$\tau_C$ , sec. $\times$ $10^4$
0.0000	0.0343	2.5	-142.7	...
0.0010	0.0343	2.6	-143.1	...
0.0042	0.0342	3.0	-144.4	2.3
0.0061	0.0340	3.0	-146.4	1.4
0.0095	0.0340	3.1	-148.4	1.1
0.0111	0.0339	3.3	-149.5	1.7
0.0257	0.0335	3.6	-158.0	2.6
0.0396	0.0358	3.7	-162.9	...

*Mean Lifetimes of the Iodine-p-Methoxyphenyl Methyl Sulfide Complex at  $-22$  and  $-27^\circ$ .* At  $-22$  and  $-27^\circ$ , only one n.m.r. absorption peak was observed for the  $-SCH_3$  group in the iodine-*p*-methoxyphenyl methyl sulfide-carbon tetrachloride system owing to rapid exchange of sulfide between free and complexed sites.

**Table IV.** Observed Chemical Shifts for  $CH_3SC_6H_4Y$  with Iodine in Carbon Tetrachloride at  $25^\circ$

Sulfide	$\delta_{free}$	$\delta_{2\%I}$	$\delta_{free} - \delta_{2\%I_2}$	$K_N$ , (m.f.) <sup>-1</sup>	$\Delta$ , c.p.s.
Methyl <i>p</i> -nitrophenyl sulfide	-152.5	-153.2	-0.7	0.2	<i>a</i>
<i>p</i> -Bromophenyl methyl sulfide	-145.6	-149.9	-4.3	10	$-4 \times 10$
Methyl phenyl sulfide	-145.0	-150.3	-5.3	$4 \times 10$	$-2 \times 10$
<i>p</i> -Methoxyphenyl methyl sulfide	-142.7	-153.4	-10.7	218	$-2 \times 10$

<sup>a</sup> The magnitude of  $\delta_{free} - \delta_{2\%I}$  is too small to permit the estimation of  $\Delta$ .

An expression<sup>16,17</sup> for the width of an n.m.r. absorption peak, owing to nuclei rapidly exchanging between two magnetically different sites, is

$$\frac{1}{T_2'} = \frac{P_B}{T_{2B}} + \frac{P_C}{T_{2C}} + P_B^2 P_C^2 (\omega_B - \omega_C)^2 (\tau_B + \tau_C) \quad (4)$$

where  $1/T_2'$  is half the observed line width and  $\omega_B$ ,  $\omega_C$ ,  $T_{2B}$ ,  $T_{2C}$ ,  $\tau_B$ ,  $\tau_C$ ,  $P_B$ , and  $P_C$  are the chemical shifts in radians/sec., transverse relaxation times, average lifetimes, and fractions of protons in sites B and C, respectively. Using the relationships

(15) Also, low intensity peaks were present owing to additional spin-spin coupling in the ring.

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$$\frac{P_B}{\tau_B} = \frac{P_C}{\tau_C} \quad P_B = (1 - P_C) \quad (5)$$

to eliminate  $\tau_B$  and  $P_B$  from eq. 4, one obtains

$$\frac{1}{T_2'} = \frac{1}{T_{2B}} + P_C \left[ \frac{1}{T_{2C}} - \frac{1}{T_{2B}} \right] + P_C (1 - P_C)^2 (\omega_B - \omega_C)^2 \tau_C \quad (6)$$

The value of  $(\omega_B - \omega_C)$  is the "association shift,"  $\Delta$ , which was previously determined. The transverse relaxation time,  $T_{2B}$ , of the free base can be measured in a sample containing only sulfide and solvent, and  $T_{2C}$  can be measured in a sample in which there is enough excess iodine to complex essentially all the sulfide. An estimate of  $\tau_C$  may be obtained for a given sample of iodine, sulfide, and solvent from eq. 6.

The concentrations at equilibrium and the association shift are estimated by assuming that essentially all of the iodine is complexed if excess *p*-methoxyphenyl methyl sulfide is present at either  $-22$  or  $-27^\circ$ . This assumption appears to be valid since: (1) the above values of  $K_N$  at higher temperatures and  $\Delta H$  indicate that  $K_N$  is large at  $-22^\circ$ ; (2) a plot of the chemical shift at  $-22^\circ$ , Table I, vs. the fraction of sulfide complexed assuming all of the iodine to be complexed is linear; the value of the association shift obtained from this plot is  $-20.7$  c.p.s.; (3) two samples in which the iodine was in excess with respect to the sulfide, but to different extents, were observed to have the same line width and chemical shift within experimental error.

The mean lifetime of the complex at  $-22^\circ$  was estimated from eq. 4 and the data in Table I. For the

solutions numbered 2, 3, and 4 in Table I,  $\tau_C$  is approximately  $10^{-4}$  sec. The value of  $\tau_C$  determined at  $-22^\circ$  must be considered an upper limit to the mean lifetime of the complex since the plot of  $1/T_2'$  vs.  $P_C$  is almost a straight line.

Chemical shifts and line widths were measured on a separate series of samples at  $-27^\circ$  and are presented in Table III. The association shift determined from a plot of  $\delta_{obsd}$  vs.  $P_C$  at  $-27^\circ$  is  $-20.4$  c.p.s. The values of  $\tau_C$ , as estimated from eq. 4, are also presented in Table III. The largest source of error in the determination of the lifetime of the complex is the uncertainty of the line width. The error is estimated to be  $\pm 1 \times 10^{-4}$  sec.

No electron magnetic resonance absorption was observed in samples comparable to those studied by n.m.r. It is highly unlikely that the line broadening in the n.m.r. spectra is caused by paramagnetic species.

The question of paramagnetic species in complexes of iodine with certain amines has been discussed elsewhere.<sup>18, 19</sup>

*Inductive Effects in para-Substituted Phenyl Methyl Sulfides.* The chemical shifts of a series of sulfides of the type  $\text{CH}_3\text{SC}_6\text{H}_4\text{Y}$  in carbon tetrachloride at 25° are presented in Table IV. The chemical shift  $\delta_{\text{free}}$  refers to the proton shift of the  $-\text{SCH}_3$  group in carbon tetrachloride solution containing 2% sulfide (by weight), and  $\delta_{2\% \text{I}_2}$  refers to the methyl proton shift of the sulfide in a carbon tetrachloride solution containing 2% sulfide and 2% iodine (by weight).

The values of the equilibrium constants,  $K_N$ , for the sulfides other than *p*-methoxyphenyl methyl sulfide were obtained from a Hammett plot.<sup>20</sup> The value of  $\rho$ ,  $-2.6$ , was selected from a plot of  $\log(k/k_0)$  vs.  $\sigma$  for the hydrolysis of a series of *para*-substituted aryl chloromethyl sulfides in aqueous acetone,<sup>21</sup> where the dependence of the rate constant for hydrolysis upon electron density around the sulfur atom would be expected to be approximately the same as the dependence of the equilibrium constant for complex formation with iodine. The value of  $\rho$  for the acid dissociation of thiophenol and substituted thiophenols is  $+2.578$ .<sup>22</sup> The value of  $\sigma$  for the  $-\text{NO}_2$  group *para* to divalent sulfur was found<sup>22</sup> to be  $+1.00$ , and this value is used in the present study. The "association shifts" were

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obtained by calculating the fraction complexed using the values of  $K_N$  from the Hammett plot and extrapolating the chemical shift to a proton fraction of unity.

The Hammett plot would be expected to give only a rough correlation for the measured chemical shifts extrapolated to a mole fraction of unity since errors in measurements would result in large errors in the extrapolation. The agreement among the various substituted sulfides is good considering that  $K_N$  changes by a factor greater than 200 while the "association shifts" vary only by a factor of 2. This seems to indicate that the "association shifts" are the same or nearly the same for the sulfides studied and that the variation in the values of  $\delta_{\text{free}} - \delta_{2\% \text{I}_2}$  arise mainly from differences in the equilibrium constants.

A Hammett plot for the association of iodine and *para*-substituted aryl selenides was linear with a  $\rho$ -value of  $-0.7$ .<sup>23</sup>

From the variation in  $\delta_{\text{free}}$  for the sulfides, it is evident that  $\delta_{\text{free}}$  correlates well with the electron-withdrawing power of the substituted group; the strongest electron-withdrawing group causes the largest downfield shift for the methyl protons.

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## Halogen Complexes. II. The Types and Mean Lifetimes of Complexes Formed by Iodine and 2,4,6-Trimethylpyridine

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Contribution from the Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois. Received September 23, 1964

The system containing iodine and 2,4,6-trimethylpyridine in mixtures of nitrobenzene and carbon tetrachloride was studied by *n.m.r.* Evidence is presented for this system containing two types of complexes,  $\text{C}_8\text{H}_{11}\text{N}\cdot\text{I}_2$  and  $[(\text{C}_8\text{H}_{11}\text{N})_2\text{I}]^+\text{I}_3^-$ . The amount of the latter type of complex formed in solution was found to depend upon the dielectric constant of the solvent. The Bloch equations were modified to apply to a three-site case,  $A \rightleftharpoons B \rightleftharpoons C$ , in which there is no direct exchange between sites *A* and *C*, and were solved after assuming that the mean time of a nucleus in site *C* before exchange is much shorter than in site *A*. The resulting expression was used to measure

the rates of exchange of the ionic complex using the *n.m.r.* absorption line shapes and chemical shifts.

### Introduction

Complexes of iodine with amines have been studied<sup>2</sup> by spectroscopic methods and also by X-ray methods in the case of the more stable complexes. These methods make possible the determination of thermodynamic variables, equilibrium constants, and the

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(1) Alfred P. Sloan Research Fellow.