

reported by Eigen.<sup>10</sup> This agrees with our experimental observation that the rate of formation of  $\text{NiY}^{-2}$  from  $\text{Ni}^{+2}$  and EDTA is much slower than the corresponding formation of  $\text{CuY}^{-2}$ . The failure of a  $\text{NiY}^*\text{Ni}$  intermediate to proceed readily with dentate transfer after a dentate cleavage from the initially bonded  $\text{Ni}^{+2}$  explains both the diminished effectiveness of  $\text{Ni}^{+2}$  and the increased importance of  $\text{H}^+$  in this reaction compared to the  $\text{Cu}^{+2}$  reaction.

The fact that  $\Delta S^*$  is  $-8$  e.u. for  $\text{Cu}^{+2}$  attack of  $\text{NiY}^{-2}$  despite the charge reduction of the transition state indicates a highly oriented transition state which still has a high coordination number for both metals. The total number of free particles cannot be increasing in the transition state which means that a  $\text{NiYCu}$  intermediate must still have six  $\text{H}_2\text{O}$  molecules coordinated to it and fair polar properties. One way this would be possible would be if the metal ions were at opposite ends of an open EDTA molecule.

A comparison of the direct reaction of  $\text{Cu}^{+2}$  with  $\text{NiY}^{-2}$ ,  $\text{CdY}^{-2}$  and  $\text{PbY}^{-2}$  would be valuable, but unfortunately strong acetate buffer was used for the

(10) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960). NOTE ADDED IN PROOF.—Since this paper was submitted Eigen has reported a second rate constant for water loss from  $\text{Cu}^{+2}$  which is 1000 times that for  $\text{Ni}^{+2}$ . M. Eigen, pp. 371-378, in S. Kirschner (Ed.), "Advances in the Chemistry of Coordination Compounds," the Macmillan Co., New York, N. Y., 1961.

other systems. The  $\text{PbY}^{-2}$  system later was corrected for acetate complexes and some comparison is possible but the corrected results are not completely satisfactory. Acetate buffer also was used in the radionickel system but apparently at sufficiently low concentrations not to interfere. If the same acetate and temperature correction used for the  $\text{PbY}^{-2} + \text{Cu}^{+2}$  reaction is applied to the  $\text{CdY}^{-2} + \text{Cu}^{+2}$  reaction, the value of  $k_1$  for  $\text{CdY}^{-2}$  is slightly greater than the  $k_1$  value for  $\text{PbY}^{-2}$ , and both are much greater than the  $k_1$  value for  $\text{NiY}^{-2}$ . Table V shows that the frequency factor ( $pZ$ ) is much

TABLE V

	$k_1$ , l. mole <sup>-1</sup> sec. <sup>-1</sup> at 25°	$pZ$	$E_a$ , kcal.	$\Delta H^*$ , kcal.	$\Delta S^*$ , e.u.
$\text{Cu}^{+2} + \text{PbY}^{-2}$	5.1	$2.7 \times 10^{16}$	20	19	10
$\text{Cu}^{+2} + \text{NiY}^{-2}$	0.016	$2.2 \times 10^{11}$	18.0	17.4	-8.0

greater for the  $\text{PbY}^{-2}$  system than for the  $\text{NiY}^{-2}$  system. In terms of the transition state theory the higher  $\Delta S^*$  indicates a more probable activated complex for  $\text{PbYCu}$  than for  $\text{NiYCu}$ . This can be interpreted as less unwrapping of EDTA from  $\text{Pb}^{+2}$  than from  $\text{Ni}^{+2}$  or more release of solvent from  $\text{PbYCu}$  than from  $\text{NiYCu}$ .

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## Iodine Complexes of Ethyl Mercaptan, Diethyl Sulfide and Diethyl Disulfide<sup>1,2</sup>

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The iodine complexes of ethyl mercaptan, diethyl sulfide and diethyl disulfide were studied in *n*-heptane and carbon tetrachloride. The results of the study have not been too surprising: diethyl sulfide is less basic than triethylamine and more basic than ethyl alcohol; it is more basic than diethyl disulfide. Reaction occurs in the system mercaptan-iodine. The results are further discussed in terms of dipole moments of the donors and the DA overlap integrals of the iodine complexes, and some arguments in favor of a geometry of the disulfide-iodine complex in which the iodine sits on the center of the  $-\text{S}-\text{S}-$  bond with the  $\text{I}-\text{I}$  axis perpendicular to the  $\text{S}-\text{S}$  axis are elaborated.

### Introduction

The interaction of the iodine molecule with various organic solvents which can behave as electron donors has been the subject of a number of research studies involved in the elucidation of the structure of molecular complexes. In particular, the complexes of iodine with several oxygen containing solvents and some nitrogen containing solvents have been studied extensively and the results obtained have agreed very well with the concept of charge transfer.<sup>3-8</sup> The organic sulfur com-

pounds have a basic character intermediate between the organic oxygen and organic nitrogen compounds and should, therefore, be of interest both experimentally and theoretically with respect to the properties of their molecular iodine complexes. This paper describes the results obtained from a comprehensive spectrophotometric study of the complexes formed between three such sulfur compounds (ethyl mercaptan, diethyl sulfide and diethyl disulfide) and molecular iodine.

### Experimental

**A. Purification of Materials.** 1. **Iodine.**—Baker and Adamson reagent grade iodine was sublimed under partial vacuum of dry nitrogen and stored in a desiccator until used.

2. **Carbon Tetrachloride.**—Merck reagent grade material was shaken for several hours with saturated potassium hydroxide solution, separated, washed with distilled water, then shaken with concentrated sulfuric acid and again separated and washed. This treatment was repeated three times. This carbon tetrachloride was washed free of acid with distilled water, shaken with anhydrous U.S.P. grade calcium chloride and stored over fresh calcium chloride in brown bottles. Immediately before use the carbon tetra-

(1) This work was supported by a Research Corporation Grant and a National Science Foundation Grant G-7390 to the Louisiana State University.

(2) Abstracted from M.S. Thesis, Antoine Major, The Louisiana State University, 1956.

(3) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **75**, 3561 (1957).

(4) P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1192 (1957).

(5) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).

(6) R. S. Mulliken and C. Reid, *ibid.*, **76**, 3869 (1954).

(7) S. Nagakura, *ibid.*, **80**, 520 (1958).

(8) A. I. Popov and W. A. Deskin, *ibid.*, **80**, 2076 (1958).

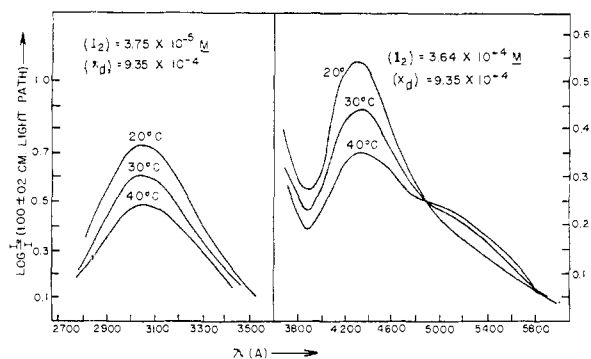


Fig. 1.—Temperature dependence of the visible and ultraviolet absorption spectra of diethyl sulfide-iodine solutions in carbon tetrachloride.

chloride was distilled from calcium chloride. The fraction distilling at 76.8 to 76.9 was used.

3. *n*-Heptane.—Matheson, Coleman and Bell reagent grade material was shaken three times with concentrated sulfuric acid, washed with distilled water and stored over anhydrous U.S.P. grade calcium chloride and distilled prior to use. The fraction distilling at 99° was used.

4. Ethyl Mercaptan.—Eastman Kodak Company Organic Chemicals white label grade was stored over magnesium sulfate and distilled immediately prior to use from anhydrous U.S.P. grade calcium chloride in a system protected from the atmosphere. The fraction distilling at 34.5 to 34.7° was used.

5. Diethyl Sulfide.—Eastman Kodak Company Organic Chemicals white label grade was stored over magnesium sulfate and distilled from clean sodium metal prior to use. The fraction distilling at 90.0 to 90.2° was used.

6. Diethyl Disulfide.—Eastman Kodak Company Organic Chemicals white label grade was stored over magnesium sulfate and distilled from anhydrous U.S.P. grade calcium chloride prior to use. The fraction distilling at 154.0 to 155.0° was used.

B. Procedure.—Solutions of the donor-iodine-solvent system were studied by measuring the optical densities of the peak maxima in both the visible and ultraviolet regions of the spectrum. Measurements were made at several different temperatures on solutions of various iodine and donor concentrations.

Stock solutions of the donor in a suitable inert solvent were prepared by measuring known volumes of the donor and diluting these with known weights of solvent. Iodine solutions were prepared by dissolving known weights of iodine in known volumes of the donor-solvent stock solutions.

Two samples of different iodine concentrations in the same donor-solvent system were placed in a constant temperature bath, the water from which, by circulation through the cell block, was also used to maintain a constant temperature for the Beckmann DU Spectrophotometer. After fifteen minutes, the samples were transferred to glass-stoppered cells of  $1.00 \pm 0.02$  cm. light path and were examined using the same donor-solvent system as blank. The optical densities were measured at a series of wave lengths at and near the complex peak absorption maxima (both visible and ultraviolet) within the close vicinity ( $\pm 0.1^\circ$ ) of each of the three temperatures, 20.0, 30.0 and 40.0°. The cells were allowed to equilibrate to block temperature until constancy of optical density readings were obtained. After readings at 40°, the optical densities were again checked at 20° and were found to be in close agreement within the limits of experimental error. Thus, it was assumed that any changes in composition of the solution due to evaporation or hydration were negligible. It was also found that spectra of various solutions of the donors (with the exception of ethyl mercaptan) were reproducible even after a day of standing.

However, due to excessive donor absorption in the ultraviolet region of the spectrum for the diethyl disulfide-iodine complex, it was not possible to obtain the ultraviolet charge-transfer spectrum at different temperatures.<sup>9</sup> The Beck-

(9) See, however, J. Nag-Chaudhuri, M. Good and S. P. McGlynn, *J. Am. Chem. Soc.*, submitted for publication, for an extensive investi-

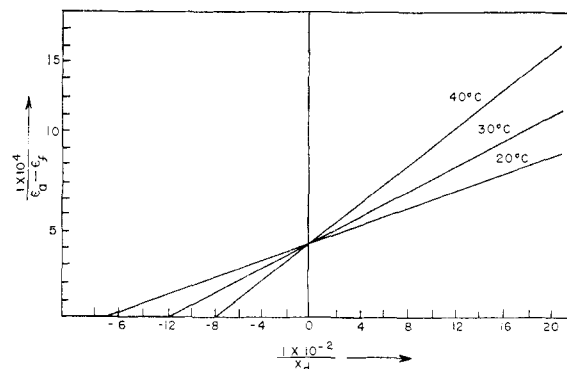


Fig. 2.—A graphical determination of the stability constants and extinction coefficients for the diethyl sulfide-iodine complex in carbon tetrachloride from absorption measurements at 4300 Å

mann DU Spectrophotometer used did not have sufficient sensitivity to allow detection of the complex peak. Therefore, the ultraviolet absorption of this complex was studied on a Beckmann DK Recording Spectrophotometer which, unfortunately, was not equipped with a constant temperature control.

## Results

A 1:1 complexation represented by the equilibrium  $d + I_2 \rightleftharpoons dI_2$ , where  $d$  is the sulfur containing donor, is assumed to occur; the Benesi-Hildebrand<sup>10</sup> equation is assumed to apply in the form

$$1/\epsilon_a = (1/K_x \epsilon_c) 1/x_d + 1/\epsilon_c$$

where  $1/\epsilon_a = (I_2)/(\log I_0/I)$  and  $1/\epsilon_c = (dI_2)/(\log I_0/I)$  for a 1 cm. path, where  $(I_2)$  is the molar concentration of iodine both free and complexed, where  $(dI_2)$  is the molar concentration of complex, where  $x_d$  is the mole fraction of donor and where  $K_x$  is a dimensionless stability constant for the equilibrium specified above. The B-H equation may be applied without modification to the intense ultraviolet charge-transfer band (depicted in Fig. 1 for  $(C_2H_5)_2S \cdot I_2$ ) but is modified according to Van de Stolpe<sup>11</sup> for investigations in the visible region of the blue-shifted  $^1\Sigma_g^+ \rightarrow ^3\Pi_{0+u}$  transition of  $I_2$  (also depicted in Fig. 1 for  $(C_2H_5)_2S \cdot I_2$ ). The resulting equation is

$$1/(\epsilon_a - \epsilon_f) = 1/(\epsilon_c - \epsilon_f)x_d K_x + 1/(\epsilon_c - \epsilon_f)$$

and differs only from the former in that  $\epsilon_c$  is corrected by subtracting off the molar extinction coefficient of the uncombined iodine species,  $\epsilon_f$ . Plots of the spectral results illustrating typical data of the present work and using the former of these two equations are given in Fig. 2. Thermodynamic data were obtained in the usual manner<sup>12</sup> and are tabulated in Table I.

Approximate values for the oscillator strength, "f," of the charge-transfer transitions for the complexes were calculated using the relation

$$"f" = 4.32 \times 10^{-9} \int \epsilon_c d\bar{\nu}$$

The quantity  $\int \epsilon_c d\bar{\nu}$  represents the area under the curve where  $\epsilon_c$ , the molar extinction coefficient, is

gation of the ultraviolet absorption spectrum of diethyl disulfide-iodine and diamyl disulfide-iodine solutions in heptane.

(10) H. B. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(11) C. Van de Stolpe, Thesis, University of Amsterdam, Holland, 1954.

(12) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 2164 (1955).

TABLE I  
SPECTROPHOTOMETRIC AND THERMODYNAMIC VALUES FOR SULFUR-IODINE COMPLEXES

Donor	Solvent	Temp., °C.	$\lambda$ , Å	$\epsilon$	$K_x^a$	$-\Delta F$ , kcal./mole	$-\Delta H$ , kcal./mole	$-\Delta S$ , e.u.
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S	CCl <sub>4</sub> ultraviolet region	20	3050	29400	2410	4.55		
		30	3050	27800	1630	4.48	8.05	11.7
		40	3050	26300	1060	4.45		
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S	CCl <sub>4</sub> visible region	20	4300	2330	1880	4.40		
		30	4300	2320	1160	4.25	8.51	14.0
		40	4300	2310	771	4.16		
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S	<i>n</i> -Heptane ultraviolet region	20	3050	23800	2160	4.50		
		30	3050	22800	1440	4.40	8.05	12.0
		40	3050	20800	937	4.28		
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S	<i>n</i> -Heptane visible region	20	4300	1910	1540	4.30		
		30	4300	1890	915	4.14	8.98	15.95
		40	4300	1840	592	4.00		
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>2</sub>	CCl <sub>4</sub> ultraviolet region	20	3020	8200	47.0	..	..	..
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>2</sub>	CCl <sub>4</sub> visible region	20	4500	1700	47.5	2.26		
		30	4500	1630	36.2	2.18	5.75	11.8
		40	4500	1610	26.3	2.04		
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>2</sub>	<i>n</i> -Heptane visible region	20	4600	1420	38.7	2.14		
		30	4600	1400	26.0	1.97	7.13	17.0
		40	4600	1360	18.2	1.82		

<sup>a</sup> These values of  $K_x$  are calculated from the average results of data taken at three different wave lengths precise to within 3%.

plotted *versus* the frequency,  $\bar{\nu}$ . The maximum  $\epsilon_c$  was calculated from spectrophotometric data. Using this value, the peak frequency and the absorption curves for the complex, a plot of  $\epsilon_c$  *versus*  $\bar{\nu}$  was constructed. The area under the curve was obtained and the " $f$ " values approximated. By this method the " $f$ " value for the diethyl sulfide-iodine complex was found  $\sim 0.67$  and that for the diethyl disulfide-iodine complex was  $\sim 0.3$ .

Stability constants and other thermodynamic data could not be calculated for the ethyl mercaptan-iodine complex because of a rapid decrease of intensity with time of both the blue shifted iodine absorption and the charge transfer absorption. Although the charge-transfer complex peak decreased more rapidly than the blue shifted iodine peak there was no subsequent growth of tri-iodide bands or any other absorption bands. The positions of the wave length maxima were found to be independent of temperature and donor concentrations. From the position of the blue shifted iodine peak for the ethyl mercaptan-iodine complex ( $\lambda_{\max} = 4600$  Å.), one might expect the heat of formation and stability constant for this complex to be greater than for the corresponding ethanol-iodine complex ( $\lambda_{\max} = 4680$  Å.).<sup>4</sup>

#### Discussion

It will be noted from Table II that the diethyl sulfide-iodine complex is a stronger complex than the corresponding ethyl ether-iodine complex but that it is not as strong as the triethylamine-iodine complex. This sequence is what one would expect from the relative base strengths of the donors involved. Investigation shows that the molar extinction coefficient at the wave length maxima for the triethylamine-iodine complex and the diethyl sulfide-iodine complex are 25,600 and 29,400, respectively. However, the oscillator strength for the transition is larger for the triethylamine-iodine complex (approximately  $0.85^{13}$ ) than

for the diethyl sulfide-iodine complex (approximately 0.67). This emphasizes that " $f$ " values rather than extinction coefficients should be used when comparing the intensities of absorption bands of different strong complexes, where contact effects are negligible.

TABLE II

ILLUSTRATING RELATIVE BASICITY OF DIETHYL ETHER DIETHYL SULFIDE AND TRIETHYLAMINE AS DETERMINED FROM THEIR IODINE COMPLEXES

Donor	$\lambda_{\max}$ (CT), Å. <sup>a</sup>	$\epsilon_{CT}$	" $f$ " <sub>CT</sub>	$K_x$	$\frac{\Delta H}{\text{mole}}$ (kcal./mole)	$\lambda_{I_2}$ , Å. <sup>a</sup>	$I_d$ (e.v.)
Diethyl ether <sup>b</sup>	2500	6000	0.35	10.1	-4.3 <sup>c</sup>	4680	10.21
Diethyl sulfide	3030	29400 <sup>e</sup>	.67 <sup>e</sup>	2410	-8.05	4300	9.30
Triethylamine <sup>d</sup>	2780	25600	.85 <sup>e</sup>	6530	-12.00	4140	7.56

<sup>a</sup>  $\lambda_{\max}$  (CT) is the absorption maximum of the CT band with  $\epsilon = \epsilon_{CT}$ . " $f$ "<sub>CT</sub> is the oscillator strength of this band.  $\lambda_{I_2}$ , Å. is the position of the 5200 Å. band of I<sub>2</sub> in the spectrum of the complex. <sup>b</sup> These data are from ref. 4 as well as from J. S. Ham, *J. Chem. Phys.*, **20**, 1170 (1952), and K. Hartley and J. A. Skinner, *Trans. Faraday Soc.*, **46**, 621 (1950). <sup>c</sup> All of these data are at 25° in heptane. <sup>d</sup> These data are from ref. 7. <sup>e</sup> Note that  $\epsilon$  (diethyl sulfide)/ $\epsilon$  (triethylamine) is greater than unity and thus contrary to theory but that a similar ratio of oscillator strengths is less than unity.

It is known that the position of the charge-transfer absorption peak may in many cases be predicted from the ionization potentials of the donors using semi-empirical relationships given by McConnell, Ham and Platt.<sup>14</sup> The observed ionization potentials<sup>15,16</sup> and the predicted and observed wave length maxima for the charge transfer bands are

(13) This approximate " $f$ " value was obtained from an article by Nagakura<sup>7</sup>; see Fig. 6 in that article.

(14) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

(15) W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

(16) J. L. Franklin and H. E. Lumpkin, *J. Am. Chem. Soc.*, **74**, 1023 (1952).

compared in Table III. It will be noted that in no case does a good absolute agreement obtain but that the relative positions are predicted correctly. It will be noted further that the data of Price<sup>15</sup> fit better; this is entirely reasonable because the results of Franklin and Lumpkin<sup>16</sup> are actually appearance potentials of the positive ions and undoubtedly much too large.

Some additional data on various sulfide compounds are tabulated in Table IV. The large difference between the inductive (+I) effects of methyl and ethyl groups is shown by the increased stability of diethyl disulfide-iodine over dimethyl disulfide-iodine. This increased stability is evidenced by the greater blue shift of  $\lambda_1$  for the diethyl sulfide complex (4500 as opposed to 4550 Å.). The marked stability of isopropyl mercaptan-I<sub>2</sub> and isoamyl sulfide-I<sub>2</sub> is presumably to be attributed to the +I effect of additional methyl groups. It is also possible to induce from the results of Table IV an increase of basic strength of a given type of sulfide with increase in size of the alkyl attachments.

Stability constants usually have been determined from both the visible and ultraviolet absorption whenever possible. Values usually agree to within 3%.<sup>4,12</sup> However, for the diethyl sulfide-iodine complex,  $K_x$  calculated in the visible region varies from  $K_x$  calculated in the ultraviolet region by 20%. This discrepancy could be caused by many factors. It is assumed in these calculations that the molar extinction coefficient of the uncombined iodine species does not change (or changes regularly) in passing from carbon tetrachloride or *n*-heptane to the diethyl sulfide-carbon tetrachloride or diethyl sulfide-*n*-heptane solvents. If this is not true, the discrepancy will appear as incorrect values of stability constants in the visible region. Likewise, if any tri-iodide ion is present, the superposition of its shorter wave length absorption (peak maxima at 2950 and 3650 Å.) on the ultraviolet charge-transfer absorption should cause an error in quantitative consideration of this region. However, under the conditions used, no absorption maximum near 3650 Å. was observed. This seems to indicate that the tri-iodide concentration in the mixed solution is very small and that the effect of this ion is not appreciable; the discrepancy is then to be attributed to the former reason, as well as to the effect of variations in the I<sub>2</sub>-I<sub>3</sub> equilibrium.

The stability constants for the diethyl sulfide-iodine complex in carbon tetrachloride were found to be larger, but of the same order of magnitude, as those for the complex in *n*-heptane at the same temperature. The heats of formation determined in the ultraviolet region for both solvents are the same, whereas heats of formation calculated using the visible region of the spectrum showed the heat of formation for the complex in *n*-heptane to be greater than that for the complex in carbon tetrachloride (Table I). Since the ultraviolet absorption is practically independent of any absorptions other than those of the complex, values obtained from data taken in this region are considered the better approximation to the true thermodynamic values of the complex.

The values of the stability constant for the complex formed between diethyl disulfide and molecular iodine in the inert solvent carbon tetrachloride were also calculated from data in both the visible and the ultraviolet region of the spectrum. Good agreement was found between the two values. The stability constants for the diethyl disulfide-iodine complex in carbon tetrachloride are again larger but of the same order of magnitude as those for the complex in *n*-heptane. However, the heat of formation, as for C<sub>2</sub>H<sub>6</sub>S-I<sub>2</sub>, is greater in *n*-heptane than in carbon tetrachloride.

From the data in Table I and Table III, as well as the fact that "*f*"<sub>CT</sub> (diethyl disulfide)  $\approx 0.3$ , it may be concluded that the disulfide forms a

TABLE III  
PREDICTED AND OBSERVED POSITIONS OF THE CHARGE  
TRANSFER ABSORPTION MAXIMUM

$\lambda_a$ (Price). ev. <sup>a</sup>	$\lambda_a$ (Franklin and Lumpkin). ev. <sup>b</sup>	Donor molecule	Obsd. CT peak, Å.	Predicted CT peak, Å.	
				Using col. 1	Us- ing col. 2
9.30	11.15	Diethyl sulfide	3050	2870	2230
..	11.18	Diethyl disulfide	3020 <sup>c</sup>	..	2220
9.70	11.69	Ethyl mercaptan	2860	2710	2095
(8.53) <sup>d</sup>	(10.01) <sup>d</sup>	1,2-Dithiolane	..	3230	2600
(8.95) <sup>e</sup>	(9.10) <sup>f</sup>	Thiophene	2980 <sup>g</sup>	3122	3009

<sup>a</sup> See ref. 15, <sup>b</sup> See ref. 16. <sup>c</sup> In actuality  $\lambda_{CT}$  for the disulfide varies somewhat with both donor concentration and temperature. The value 3020 Å. is that found in concentrated solution. <sup>d</sup> Calculated, using the simple M.O. theory of ref. 9. <sup>e</sup> W. C. Price and A. D. Walsh, *Proc. Roy. Soc. (London)*, 179A, 201 (1941). <sup>f</sup> J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, 20, 1021 (1952). <sup>g</sup> J. E. Collin, *Z. physik. Chem.*, 64, 936 (1940).

TABLE IV  
ABSORPTION MAXIMA OF VARIOUS SULFIDE-IODINE-CARBON  
TETRACHLORIDE SOLUTIONS<sup>a</sup>

Donor	$\lambda_1$ , Å.	$\lambda_{max}$ (CT), Å.
<i>n</i> -Amyl mercaptan	4580	2880
Benzyl mercaptan	..	3000
Butyl mercaptan	..	2860
Ethyl mercaptan	4600	2860
<i>n</i> -Hexyl mercaptan	4510	2820
Isopropyl mercaptan	4480	2920
Allyl sulfide	4350	3060
Benzyl sulfide	4400	3210, 3070 (?)
Diethyl sulfide	4300	3050
Isoamyl sulfide	4270	3090
<i>n</i> -Amyl disulfide	4320	..
Diethyl disulfide	4500	3020
Methyl disulfide	4550	..
Isoamyl disulfide	4510	..

<sup>a</sup> S. A. Shchukarev and L. S. Lilich, *Uchenye Zapiski Leningrad. Gosudarst. Univ. im A. A. Zhdanova No. 155; Ser. Khim. Nauk*, 11, 3 (1952); *Chem. Abstr.*, 50, 4693b (1956), have studied the iodine complexes of ethyl sulfide, benzyl sulfide, propyl sulfide, ethyl amyl sulfide, phenyl sulfide, propyl disulfide and isoamyl selenide. Unfortunately we could not obtain a copy of this report. H. V. Drushel, Ph.D. Thesis, University of Pittsburgh, Penna., 1956, has studied the iodine complexes of thianaphthene, 1-(*p*-methylphenyl)-1-thiaethane, 1,3-diphenyl-2-thiapropene, 2-thiapropene, thiacyclobutane, 2-thiabutane, 2-thiapentane, 2,6-dimethyl-4-thiaheptane, 3-methyl-2-thiabutane, thiacyclohexane, 2,2,4,4-tetramethyl-3-thiapentane, 4-thiatridecane, 3-thiapentane, 6-thiaundecane, 8-thiapentadecane, 5-thianonane, thiacyclopentane and 2,8-dimethyl-5-thianonane. This latter study is a particularly thorough one.

weaker complex than the monosulfide. Thus, at least with respect to iodine complexation, the disulfide is the better Lewis acid and the monosulfide the better Lewis base; this order causes no surprise since a similar behavioral difference exists between  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$ . However, in terms of charge transfer theory this may not be so readily explained. Since  $\lambda_{\text{CT}}$  and  $I_d$  are roughly equal for both the disulfide- and sulfide-iodine complexes and since the dipole moment of the disulfide is larger than that of the monosulfide (1.98 as compared with 1.47 $d^{17}$ ), the comparative instability of the disulfide-iodine complex must be sought in a comparative smallness of the DA overlap,  $\int \varphi_A \varphi_D d\tau$ , for this complex or in some steric factor. If we follow Hassel,<sup>18</sup> the structure of the diethyl sulfide-iodine complex is that depicted in Fig. 3a and the DA overlap integral is  $\int \varphi(3p_y\text{S})\varphi(5d_{zy}\text{I})d\tau$ , with the three atoms,  $\text{SI}_2$ , collinear. On the other hand, if we presume a structure for the diethyl disulfide complex with iodine similar to that in Fig. 3b the DA overlap integral is

$$\int \varphi(3p_x\text{S}^1 - 3p_y\text{S}^2)\varphi(5d_{(x+y)(x+y)})d\tau$$

where the nomenclature used should be apparent from the figure. Since the acceptor orbital is the same in both cases, it is concluded that the magnitude of the DA integral is determined by the donor orbitals, at least for equal separation of donor and acceptor centers. Assuming reasonable values for the S—S distance and for the radial distance to the point of maximum amplitude of the 3p wavefunction of sulfur, it may be shown that the operative centers of maximum amplitude are  $\sim 3/2$  to 2 times as far apart in the donor orbital of the disulfide as in the monosulfide. It would not be unreasonable on this basis to expect the DA overlap integral for the disulfide to be less than that for the monosulfide, and other things being equal to expect also a comparative instability of the complex

(17) C. C. Woodrow, M. Carmack and J. G. Miller, *J. Chem. Phys.*, **19**, 951 (1951).

(18) O. Hassel, *Proc. Chem. Soc.*, 250 (1957).

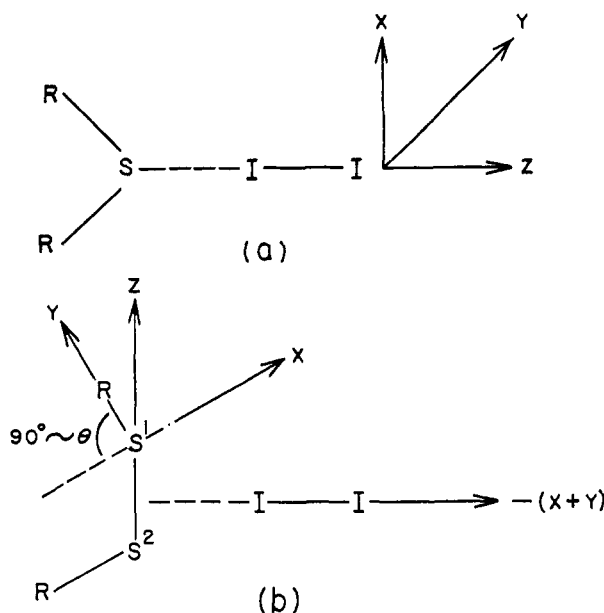


Fig. 3.—(a) The assumed structure of  $(\text{C}_2\text{H}_5)_2\text{S}\cdot\text{I}_2$ ; it has been presumed that the structure of this complex is the same as that of diphenyl sulfide-iodine studied by Hassel<sup>18</sup> by X-ray diffraction. (b) The assumed structure of  $(\text{C}_2\text{H}_5)_2\text{S}_2\cdot\text{I}_2$ . The axes here are defined independently of the definition in (a). The dihedral angle  $\theta$  has been assumed equal to  $90^\circ$  and the superscripts on the sulfurs merely afford a method of labelling.

of the former with iodine. The fact that such is the case is presumed to favor structure b for the disulfide-iodine complex; it must be realized, however, that these latter conclusions can hardly be considered quantitative and should be accepted only with the proverbial grain of salt.

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## The Acid $\text{CF}_3\text{PO}_2\text{H}_2$ , its Esters, Association and Structure<sup>1</sup>

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The phosphonous esters  $\text{CF}_3\text{P}(\text{OCH}_3)_2$  (b.p.  $89^\circ$ ) and  $\text{CF}_3\text{PO}_2\text{C}_2\text{H}_4$  (m.p.  $-33^\circ$ ; b.p.  $113^\circ$ ) were made from  $\text{CF}_3\text{PCl}_2$  and  $\text{CH}_3\text{OH}$  or  $\text{C}_2\text{H}_4(\text{OH})_2$  respectively. Their infrared spectra agree with the formulas as written. The formation of the ring ester  $\text{CF}_3\text{PO}_2\text{C}_2\text{H}_4$  was accompanied by considerable yields of less volatile products believed to be higher polymers of the same unit. Neither phosphonous ester showed any tendency for spontaneous rearrangement to the phosphinic ester form  $\text{CF}_3\text{RPOOR}$ , but the free acid  $\text{CF}_3\text{PO}_2\text{H}_2$  gave infrared spectral evidence of existing almost wholly as the phosphinic acid dimer  $(\text{CF}_3\text{HPOOH})_2$ . For its vapor-phase dissociation to the monomer,  $\Delta F^\circ = 16.00 - 0.0247T$  kcal. per mole of dimer, indicating  $\Delta H^\circ = 8.00$  kcal. for each O—H—O bond. It is argued that the monomer is mostly  $\text{CF}_3\text{HPOOH}$  rather than  $\text{CF}_3\text{P}(\text{OH})_2$ .

The phosphonous acid  $\text{CF}_3\text{P}(\text{OH})_2$  has not been proved to exist as such; indeed, the corresponding

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sodium salt was shown to be the phosphinate  $\text{Na}^+\text{CF}_3\text{HPO}_2^-$ , while the character of the free acid remained uncertain.<sup>2</sup> We now have made the dimethyl and dimethylene phosphonous esters  $\text{CF}_3\text{P}-$

(2) F. W. Bennett, H. J. Emel us and R. N. Haszeldine, *J. Chem. Soc.*, 3598 (1954).