

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

## The Dissociation Constants of Some Dihalides of Dimethyl Sulfide and Dimethyl Selenide in Carbon Tetrachloride Solution

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RECEIVED AUGUST 6, 1956

The dissociation constants of dimethylsulfur diiodide, (CH<sub>3</sub>)<sub>2</sub>SI<sub>2</sub>, and dimethylselenium diiodide, (CH<sub>3</sub>)<sub>2</sub>SeI<sub>2</sub>, have been determined spectrophotometrically in carbon tetrachloride solution. The values found are  $K = [(\text{CH}_3)_2\text{S}][\text{I}_2]/[(\text{CH}_3)_2\text{SI}_2] = 1.40 \times 10^{-2} \pm 0.04 \times 10^{-2}$  at  $23 \pm 1^\circ$  and  $K = [(\text{CH}_3)_2\text{Se}][\text{I}_2]/[(\text{CH}_3)_2\text{SeI}_2] = 2.12 \times 10^{-3} \pm 0.02 \times 10^{-3}$  at  $25 \pm 1^\circ$ . Dimethylselenium dibromide was found to have a dissociation constant of less than  $4 \times 10^{-7}$  at  $25^\circ$ . Determination of the dissociation constant of dimethylsulfur dibromide was prevented by bromination of the methyl group with formation of HBr.

In previous communications from these Laboratories, the dissociation constants of a large number of diarylselenium dihalides have been reported.<sup>1</sup> The present communication is concerned with an extension of these studies to the diiodides and dibromides of dimethyl sulfide and dimethyl selenide.

### Experimental

**Materials.**—Dimethyl sulfide (Eastman Kodak Co. white label) was distilled and a 50% center cut retained. This fraction was vacuum distilled and the first half of the distillate used for preparation of a 0.1134 *M* stock solution in dry carbon tetrachloride.

Dimethyl selenide was prepared by Mr. Jordan Bloomfield according to the method of Bird and Challenger.<sup>2</sup> The preparation was distilled, sealed in an ampoule and stored in a light-proof container in a refrigerator until needed. At that time an 8-ml. sample was vacuum distilled and a 50% center cut taken. This fraction was passed as a vapor through Drierite in an evacuated system and frozen out in a weighed glass tube. The tube was sealed off, reweighed and broken under dry carbon tetrachloride to produce a 0.04551 *M* stock solution. Ampoules of this stock solution were refrigerated in light-proof containers until needed.

Bromine (Merck and Co. Reagent) was purified as described previously<sup>3</sup> and a 0.08776 *M* stock solution in dry carbon tetrachloride was prepared.

Iodine (J. T. Baker Reagent) was resublimed and a 0.04532 *M* stock solution in dry carbon tetrachloride was prepared.

Carbon tetrachloride was purified and handled as previously described.<sup>3</sup>

**Spectrophotometric Measurements.**—All spectrophotometric measurements were made on a Cary recording spectrophotometer, Model 11 PMS, using the same general procedure described earlier.<sup>3</sup> Because of the instability of the dihalides involved, these were prepared in solution, as needed, by mixing stock solutions of the components. Each solution studied was prepared independently at least four times on different days. In each case the spectrum was determined shortly after the solution was prepared.

**Method of Calculation.**—The mathematical problem is quite similar to that involved in the selenium-bromine system.<sup>3</sup> However, the difference in stoichiometry leads to different working equations. In the present case, we may write equations 1-4 which hold for a particular solution at a fixed wave length

$$D_n E_n / F_n = K \quad (1)$$

$$S_n = D_n + F_n \quad (2)$$

$$B_n = E_n + F_n \quad (3)$$

$$A_n = b_n(D_n d + E_n e + F_n f) \quad (4)$$

The expression of these equations has been simplified by use of symbols in which the dimethylsulfur diiodide equilibrium is used as an example.

(1) For references to the earlier work see J. D. McCullough and B. A. Eckerson, *THIS JOURNAL*, **73**, 2954 (1951).

(2) M. L. Bird and F. Challenger, *J. Chem. Soc.*, 570 (1942).

(3) N. W. Tideswell and J. D. McCullough, *THIS JOURNAL*, **78**, 3026 (1956).

$D_n$ ,  $E_n$  and  $F_n$  represent the molar (equilibrium) concentrations of the species (CH<sub>3</sub>)<sub>2</sub>S, I<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>SI<sub>2</sub>, respectively, in the *n*th solution.

$d$ ,  $e$  and  $f$  represent the molar absorptivities of the above species, respectively, at some fixed wave length.

$S_n$  and  $B_n$  represent the total moles of (CH<sub>3</sub>)<sub>2</sub>S and of I<sub>2</sub> per liter (*i.e.*, the formal concentrations), respectively, in the *n*th solution.

$A_n$  represents the measured absorbance of the *n*th solution at the wave length considered.

$b_n$  represents the optical path length for the *n*th solution.

Since these four equations involve five unknowns, it is necessary to consider a second solution at the same wave length. In this way, we obtain four more equations involving only three additional unknowns. A convenient solution to this set of eight equations involving the eight unknowns  $D_1$ ,  $E_1$ ,  $F_1$ ,  $D_2$ ,  $E_2$ ,  $F_2$ ,  $f$  and  $K$  is the following in which the only unknown is the desired equilibrium constant,  $K$

$$\frac{B_1 + S_1 + K - \sqrt{(B_1 + S_1 + K)^2 - 4S_1B_1}}{B_2 + S_2 + K - \sqrt{(B_2 + S_2 + K)^2 - 4S_2B_2}} = \frac{b_2[A_1 - b_1dS_1 - b_1eB_1]}{b_1[A_2 - b_2dS_2 - b_2eB_2]}$$

Use of the above equation in the determination of  $K$  is similar to the procedure previously described.<sup>3</sup>

Molar absorptivities of dimethyl sulfide, dimethyl selenide and the halogens were independently determined and are given in Table I. The molar absorptivities of the dihalides given in the table are those calculated from the absorbance data after the respective equilibrium constants were known. The spectra are shown in graphical form in Fig. 1. Finally, as a check on the consistency of the results, absorbance values for all measured solutions of the iodides were calculated by use of equation 4. In the range of maximum accuracy (from 400 to 450  $\mu$ ), the calculated absorbances agreed with the observed values within the experimental error of the latter. The average deviation was 0.005 for (CH<sub>3</sub>)<sub>2</sub>SI<sub>2</sub> and 0.004 for (CH<sub>3</sub>)<sub>2</sub>SeI<sub>2</sub>. The observed absorbances for solutions used in the determination of the dissociation constants of dimethylsulfur diiodide, dimethylselenium diiodide and dimethylselenium dibromide are given in Tables II, III and IV, respectively.

TABLE I  
MOLAR ABSORPTIVITIES IN CARBON TETRACHLORIDE

$\lambda$ $\mu$	(CH <sub>3</sub> ) <sub>2</sub> S	(CH <sub>3</sub> ) <sub>2</sub> Se	Br <sub>2</sub>	I <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> - SI <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> - SeI <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> - SeBr <sub>2</sub>
350	0.20	0.12	14.1	23.3	5020	14800	..
360	.18	.08	33.6	15.8	2660	8700	615
370	.18	.06	64.7	11.4	1470	4950	299
380	.16	< .05	107	8.6	967	2940	138
390	.13	< .05	151	7.5	920	2100	64
400	.10	< .05	186	8.3	1140	2030	30
410	.09	< .05	206	12.5	1490	2310	15
420	.08	< .05	207	23.2	1830	2660	8
430	.05	< .05	196	47.0	2020	2850	5
440	< .05	< .05	178	89.0	2040	2790	3
450	< .05	< .05	162	158	1860	2500	2

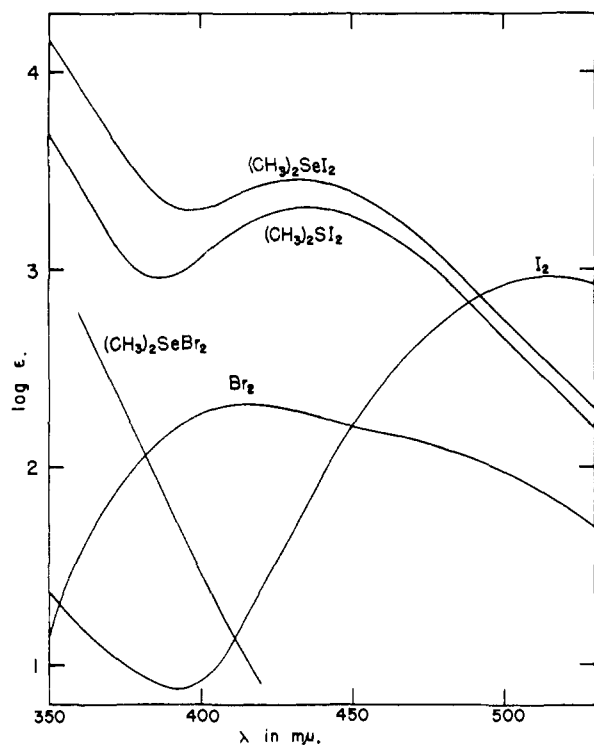


Fig. 1.

### Results and Discussion

The dissociation constants for the dimethyl compounds found in the present study are given in Table V, together with those for the diphenylselenium dihalides found in previous investigations.

The dissociation constants listed for the diiodides of the dimethyl compounds are the averages of values resulting from the comparison of several pairs of solutions. Estimated standard deviations

TABLE II  
ABSORBANCES OF CARBON TETRACHLORIDE SOLUTIONS *S*  
FORMAL IN  $(\text{CH}_3)_2\text{S}$  AND *B* FORMAL IN  $\text{I}_2$   
Optical path, *b*, 0.100 cm.; temperature  $23 \pm 1^\circ$

Soln. no. →	1	2	3	4
$S \times 10^3 \rightarrow$	9.072	4.536	90.72	95.04
$B \times 10^3 \rightarrow$	9.064	9.064	9.064	0.691
$\lambda$ , $m\mu$				
400	0.326	0.180	0.899	0.550
410	.428	.238	1.168	.714
420	.532	.301	1.426	.879
430	.600	.348	1.587	.974
440	.631	.384	1.591	.977
450	.627	.405	1.460	.898

TABLE III  
ABSORBANCES OF CARBON TETRACHLORIDE SOLUTIONS *S*  
FORMAL IN  $(\text{CH}_3)_2\text{Se}$  AND *B* FORMAL IN  $\text{I}_2$   
Temperature  $25 \pm 1^\circ$

Soln. no. →	1	2	3	4
$S \times 10^3 \rightarrow$	0.4551	4.551	18.20	1.820
$B \times 10^3 \rightarrow$	0.4532	4.532	3.626	9.064
<i>b</i> , cm. →	1.000	0.100	0.100	0.100
$\lambda$ , $m\mu$				
400	0.145	0.464	0.644	0.298
410	.167	.532	.737	.334
420	.196	.612	.852	.390
430	.214	.664	.916	.433
440	.226	.659	.900	.460
450	.235	.606	.815	.469

TABLE IV  
ABSORBANCES<sup>a</sup> OF CARBON TETRACHLORIDE SOLUTIONS *S*  
FORMAL IN  $(\text{CH}_3)_2\text{Se}$  AND *B* FORMAL IN  $\text{Br}_2$   
Temperature  $25 \pm 1^\circ$

Soln. no. →	1	2	3	4	5
$S \times 10^3 \rightarrow$	0.3641	3.641	43.69	3.641	0
$B \times 10^3 \rightarrow$	0.3510	3.510	3.510	7.020	3.510
<i>b</i> , cm.	10.00	1.000	1.000	1.000	1.000
$\lambda$ , $m\mu$					
400	0.100	0.106	0.106	0.750	0.653
410	.047	.055	.058	.757	.723
420	.026	.027	.030	.732	.726
430	.015	.017	.019	.681	.688
440	.008	.008	.016	.615	.625
450	.006	.006	.009	.554	.569

<sup>a</sup> The absorbance of  $3.641 \times 10^{-3}$   $F(\text{CH}_3)_2\text{Se}$  is negligible at these wave lengths.

TABLE V  
DISSOCIATION CONSTANTS OF  $\text{R}_2\text{SX}_2$  AND  $\text{R}_2\text{SeX}_2$  COM-  
POUNDS IN CARBON TETRACHLORIDE AT  $25^\circ$

	Dibromide	Diiodide
$(\text{CH}_3)_2\text{S}$	(Not determined)	$1.40 \times 10^{-2}$
$(\text{CH}_3)_2\text{Se}$	$< 4 \times 10^{-7}$	$2.12 \times 10^{-3}$
$(\text{C}_6\text{H}_5)_2\text{Se}$	$4.8 \times 10^{-4}$	$3.6 \times 10^{-2}$

for the dissociation constants are  $0.04 \times 10^{-2}$  for  $(\text{CH}_3)_2\text{SI}_2$  and  $0.02 \times 10^{-3}$  for  $(\text{CH}_3)_2\text{SeI}_2$ .

An upper limit for the dissociation constant for  $(\text{CH}_3)_2\text{SeBr}_2$  was derived on the basis of the following considerations. Examination of the absorbance data for solutions 1 and 2 in Table IV shows that Beer's law ( $\log_{10} P_0/P = \epsilon bc = A$ ) is followed fairly well. This indicates that  $(\text{CH}_3)_2\text{SeBr}_2$  is either nearly completely dissociated or very slightly dissociated in both solutions. The former possibility is ruled out by the very low observed absorbances of the solutions at wave lengths above 430  $m\mu$  where  $\text{Br}_2$  absorbs strongly. An estimate of the maximum amount of free  $\text{Br}_2$  in solution 1 may be made on the basis of the observed absorbance of 0.004 at  $\lambda$  460 and the molar absorptivity of 148 for  $\text{Br}_2$  at this wave length. This leads to a concentration of  $3 \times 10^{-6}$  for  $\text{Br}_2$  and a value of  $1.5 \times 10^{-7}$  for  $K$ . However, the measured absorbance might be lower than the true value, allowing both of the above values to be higher. The observed absorbances in the tables are, in all cases, the result of averaging spectra from four independently prepared solutions. For solution 1, the value of 0.004 at  $\lambda$  460 has a mean deviation of 0.0025. It was estimated that the error in the absorbance due to various causes was probably less than 0.006. If we thus take the upper limit for the absorbance at  $\lambda$  460 as 0.010, the corresponding upper limit for  $K$  is  $4 \times 10^{-7}$ .

The absorbances of solutions containing dimethyl sulfide and bromine change with time and  $\text{HBr}$  is evolved, making it impractical to determine the dissociation constant of  $(\text{CH}_3)_2\text{SBr}_2$ .

It is of interest to compare the dissociation constant for  $(\text{CH}_3)_2\text{SI}_2$  determined in the present study with the results of some cryoscopic measurements reported by Jensen for dibenzylsulfur diiodide in benzene solution.<sup>4</sup> On converting mole fractions to molar concentrations by use of the density data given for the solutions, one calculates a dissociation constant of approximately  $9.3 \times 10^{-3}$  for

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

(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>SI<sub>2</sub> in benzene at 5°. Considering the differences in the organic groups, the temperature and the solvent, this is consistent with the value found for (CH<sub>3</sub>)<sub>2</sub>SI<sub>2</sub> in the present study.

Additional work on the dissociation constants of compounds of the type R<sub>2</sub>SI<sub>2</sub>, R<sub>2</sub>SeI<sub>2</sub> and R<sub>2</sub>TeI<sub>2</sub> is planned.

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## Spectrophotometric Studies on the Interaction between Acetone and Sulfuric Acid<sup>1</sup>

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RECEIVED OCTOBER 25, 1956

One of the problems treated in the present paper is the mechanism of the blue shift of the  $\pi^* \leftarrow n$  transition band of acetone in sulfuric acid. As the result of careful measurements of this absorption band in various concentrations of sulfuric acid, it is shown that the blue shift in the acid should principally be due to the formation of the onium ion of acetone (H<sub>3</sub>C)<sub>2</sub>C=O<sup>+</sup>H and moreover that the basic strength of acetone can be discussed quantitatively by the use of spectrophotometric methods. Another problem is the mechanism of coloration of acetone, that is, the remarkable change of absorption spectrum observed on mixing it with concentrated sulfuric acid. This mechanism seemed to be complicated, but finally it was concluded that the change could be explained by the formation of condensation products of acetone, especially

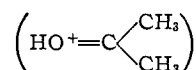
mesityl oxide (H<sub>3</sub>C)<sub>2</sub>C=C(C=O)CH<sub>3</sub>. Furthermore, the mechanism of the anomalously large red shift of the 231  $\mu$ m

band of mesityl oxide in *n*-heptane to 284  $\mu$ m in concentrated sulfuric acid is discussed on the basis of the conception of intramolecular charge transfer absorption.

### Introduction

In this paper, two phenomena which are observed with acetone in sulfuric acid are studied by the use of the spectrophotometric method. One of them is the effect of the acid on the weak absorption due to the  $\pi^* \leftarrow n$  transition of acetone. It is well known that this type of absorption generally shifts to shorter wave lengths with increasing dielectric constant of solvent and that this wave length shift is especially large in acid media. This blue shift is regarded as one of the typical properties by which the  $\pi^* \leftarrow n$  transition can be distinguished from the ordinary  $\pi^* \leftarrow \pi$  transition.<sup>3-5</sup> As to the mechanism of the large blue shift in acid, Kasha suggested that it may be caused by the attachment of a proton to the atom containing non-bonding electrons, for instance, the oxygen atom of acetone. As far as the authors know, however, no substantiating experimental evidence has been published for the system of acetone and sulfuric acid. Furthermore, this interaction seems to be interesting from the standpoint of organic chemistry, too, because the formation of acetonium cation [HO<sup>+</sup>=C(CH<sub>3</sub>)<sub>2</sub>] is predicted as the intermediate state for some reactions of acetone in acid media.<sup>6</sup> In order to obtain some experimental knowledge on these problems, we have measured the near ultraviolet

absorption of acetone in various concentrations of sulfuric acid. Consequently, we were led to the conclusion that the blue shift of the  $\pi^* \leftarrow n$  transition band of acetone in acid is actually due to specific interaction between these two species, namely, to the formation of acetonium cation



Moreover, on the basis of this interpretation of the blue shift, we have succeeded in obtaining a somewhat quantitative knowledge about the basic strength of acetone.

The blue shift phenomenon is observed in relatively dilute sulfuric acid. On the other hand, in concentrated sulfuric acid (93%), acetone becomes colored yellow or brown, and the ultraviolet absorption spectrum changes remarkably compared with that in the dilute acid or an organic solvent. This coloration, which may be regarded as one of the most typical examples of halochromy, is another problem considered in the present paper. Although the mechanism of this coloration already has been studied by Poggi and others,<sup>7</sup> no final conclusion has ever been obtained. We undertook to study this phenomenon, because we thought it might be intimately related with the intermolecular charge transfer absorption which has frequently been observed in the case of molecular complex formation between an electron donor and acceptor and whose mechanism had already been studied by Mulliken.<sup>8</sup> The results obtained actually were more complicated than our initial expectation, but

(1) (a) This work was assisted in part by the Office of Ordnance Research under Project TB2-0001(505) of Contract DA-11-022-ORD-1002 with the University of Chicago. (b) Some parts of this work were done in the Institute of Science and Technology, Tokyo University.

(2) Institute of Science and Technology, Tokyo University, Meguro-ku, Tokyo, Japan.

(3) M. Kasha, *Disc. Faraday Soc.*, **9**, 14 (1950).

(4) (a) F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951); (b) H. McConnell, *ibid.*, **20**, 700 (1952).

(5) S. Nagakura and A. Kuboyama, *THIS JOURNAL*, **76**, 1003 (1954).

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.

(7) A. Paul Poggi, G. Serchi, G. Adembri and A. Monaci, *Gazz. chim. ital.*, **79**, 80 (1949).

(8) R. S. Mulliken, *THIS JOURNAL*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).