

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Dielectric Properties and Ultraviolet Absorption Spectra of Addition Compounds of Sulfur Dioxide and Sulfur Trioxide with Tertiary Amines<sup>1</sup>BY J. A. MOEDE<sup>2</sup> AND COLUMBA CURRAN<sup>3</sup>

Studies on the addition compounds of tertiary amines with sulfur dioxide have been summarized by Bateman, Hughes and Ingold.<sup>4</sup> Later work includes the phase equilibrium studies of VanderWerf and co-workers.<sup>5</sup> An adequate discussion of the type of bonding in these compounds has been given by Burg.<sup>6</sup>

The addition compounds of amines with sulfur trioxide have been less extensively studied. They are higher melting, more stable, less reactive and much less soluble in inert solvents than their sulfur dioxide analogs.<sup>6</sup>

The present investigation was undertaken to evaluate the N-S bond moment, to study the effect of the formation of this bond on ultraviolet absorption spectra, and to determine the extent of dissociation of the addition compounds in solution. Dielectric constant and absorption measurements complement each other in that the latter may be made at solute mole fractions of about one-thousandth of the concentrations required for the former measurements.

## Experimental

**Preparation and Purification of Compounds.**—Sulfur dioxide, an Ohio Chemical Company product, was dried by passing through two phosphoric anhydride towers.

Sulfur trioxide was obtained by distillation from a mixture of fuming sulfuric acid and phosphoric anhydride.

Trimethylamine, an Eastman Kodak Co. product, was purified by passing through sodium hydroxide. Analysis by titration indicated a purity of 99.3%.

Triethylamine and tri-*n*-butylamine, Eastman Kodak Co. white label products, were refluxed over sodium and distilled. The following constants were obtained for tri-*n*-butylamine: b. p. 219° (750 mm.),  $d_{25}^{25}$ , 0.7743,  $n_{25}^{25}$  1.4278.

Pyridine was refluxed over calcium oxide and distilled.

Dimethylaniline, a Merck product, was distilled and stored over activated alumina in an atmosphere of nitrogen.

Triethylamine-sulfur dioxide was prepared under moisture-free conditions by the method of Burg<sup>6</sup>; m. p. 77°.

Pyridine-sulfur dioxide, m. p. -7.0°, was prepared by the addition of sulfur dioxide to pyridine at -20°.

Pyridine-sulfur trioxide, m. p. 137°, was prepared by a variation of the method of Baumgarten.<sup>7</sup>

Dimethylaniline-sulfur trioxide was prepared by the method of Willcox.<sup>8</sup> The dried product melted between 85 and 90° and solutions were prepared immediately after drying, as the compound is not stable over long periods.

Trimethylamine-sulfur trioxide, m. p. 240°, was prepared in the same manner as dimethylaniline-sulfur trioxide and purified by washing with water.

Triethylamine-sulfur trioxide, m. p. 91.5°, was prepared in the same manner as pyridine-sulfur trioxide, using carbon tetrachloride as a solvent. The product was crystallized from acetone and the crystals were dried in a vacuum desiccator over phosphoric anhydride.

Tri-*n*-butylamine-sulfur trioxide was prepared by adding 5 ml. of liquid sulfur trioxide with stirring to 30 ml. of tri-*n*-butylamine in 300 ml. of carbon tetrachloride at 0°. The lower layer was washed with cold concentrated hydrochloric acid and then with water, dried over calcium chloride and decolorized with activated charcoal. The solvent was evacuated off and the product crystallized from acetone, m. p. 94°. Its molecular weight was determined cryoscopically in benzene as 266, compared to the calculated value, 265.4.

Dimethylaniline hydrochloride was prepared as described by Scholl and Escales.<sup>9</sup>

*trans*-Dichloroethylene, obtained from the Columbia Organic Chemicals Company, was washed successively with silver nitrate, hydrochloric acid, sodium carbonate and water and partially dried with calcium chloride. It was then refluxed over phosphoric anhydride and twice fractionally distilled through a 1 meter Fenske column in an atmosphere of nitrogen.

Triethylamine-sulfur dioxide and tri-*n*-butylamine-sulfur dioxide were prepared in solution. For the absorption measurements, all sulfur dioxide addition compounds were prepared in solution.

Chloroform, a U. S. P. grade, was dried over activated alumina. Where alcohol-free chloroform was necessary a technical grade was washed with water, dried over activated alumina and activated silica and used as soon as possible after drying.

*n*-Butyl chloride, an Eastman product, was washed with water and dried with activated alumina and activated silica. Other solvents were purified as in earlier work.

**Preparation of Solutions.**—Solutions for dielectric constant measurements were prepared in a dry air box and were introduced into the dielectric cell without contacting moist air. The master solutions for absorption measurements were prepared in a similar manner, but dilutions were made outside the box and the Beckman absorption cells were not sealed. Small amounts of a white solid, probably the bisulfite, formed on the addition of sulfur dioxide to butyl chloride solutions of triethylamine, preventing a quantitative treatment of the absorption measurements on these solutions.

Solutions of sulfur dioxide in *trans*-dichloroethylene were prepared by direct addition of sulfur dioxide gas to the solvent. Concentrations were determined by the addition of excess sodium hydroxide, titration with hydrochloric acid to the phenolphthalein end-point, oxidation of the sulfite with hydrogen peroxide and continued titration to the methyl orange end-point.

**Physical Measurements.**—Dielectric constants were obtained at radio frequencies using a modified Armstrong oscillator in the tuning circuit, constructed with the aid of a circuit diagram kindly furnished by Professor W. D. Kumler. The dielectric cell was similar to that described by Svirbely and co-workers,<sup>10</sup> having a capacity of 110  $\mu\text{mf}$ . As the dielectric constants of dioxane solutions of the sulfur trioxide addition compounds varied with time, capacity readings on these solutions were taken as soon as possible after preparation. The 20-ml. pycnometer used to obtain densities was a modification of that described by

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(4) Bateman, Hughes and Ingold, *J. Chem. Soc.*, 243 (1944).

(5) Hoffman and VanderWerf, *This Journal*, 70, 264 (1943).

(6) Burg, *ibid.*, 65, 1629 (1943).

(7) Baumgarten, *Ber.*, 59, 1166 (1926).

(8) Willcox, *Am. Chem. J.*, 32, 450 (1904).

(9) Scholl and Escales, *Ber.*, 30, 3134 (1897).

(10) Davis, Bridge and Svirbely, *This Journal*, 66, 857 (1943).

Lipkin.<sup>11</sup> Absorption measurements were made with a Beckman DU quartz spectrophotometer. All extinctions were corrected for the difference in transparency of the two 1-cm. fused silica cells. The precision limit of the molar extinction coefficients is estimated as 3%.

### Calculations

The dissociation constant of trimethylamine-sulfur dioxide in chloroform and *n*-butyl chloride was calculated from the variation of the extinction of the solution with solute concentration, assuming Beer's law. For the equilibrium mixture, using 1-cm. cells, the observed extinction  $E = \epsilon_{CC} + \epsilon_{ACA} + \epsilon_{BCB}$ , where  $\epsilon$  is the molar extinction coefficient,  $c$  is the molar concentration and the subscripts A, B and C refer to the amine, sulfur dioxide and the addition compound, respectively. The molar extinction coefficient of the undissociated addition compound could not be obtained experimentally. That value of  $\epsilon c$  was chosen, by trial and error, which gave the smallest variation with concentration of  $K_c = c_A^2/c_2 - c_A$  where  $c_2$  is solute molarity considering no dissociation. The value of the molar extinction coefficient of trimethylaminesulfur dioxide yielding the most consistent set of  $K_c$  values was the same in both solvents, 6250. The dissociation constant of dimethylaniline hydrochloride was calculated in a similar manner; the molar extinction coefficient of this compound was taken as the experimental value obtained in a solution containing a large excess of hydrogen chloride, where the extent of dissociation is negligible.

The solute polarizations at infinite dilution reported in Table II were calculated by the method of Hedstrand. The distortion polarizations were taken as 1.05  $MR_D$ , with the exception of tri-*n*-butylamine for which the atomic polarization was assumed to be zero.<sup>12</sup> The electric moment of trimethylamine-sulfur dioxide in benzene calculated from the data for the three most concentrated solutions listed in Table I is 4.90. The moment calculated assuming a dissociation constant equal to that obtained from spectral measurements in chloroform is 5.0. Dissociation in benzene is expected to be less than in chloroform, and the change in polarization with concentration likewise indicates a smaller degree of dissociation in benzene. Therefore, a mean value, 4.95, has been taken as the moment of this addition compound.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AT

25°

$N_2$	$D$	$d$
Benzene--Tri- <i>n</i> -butylamine		
0.00000	(2.2760)	0.87299
.04079	2.2813	.86156
.05950	2.2843	.85687
.08158	2.2868	.85184

(11) Lipkin, Davison, Harvey and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944).

(12) Le Fevre and Russel, *Trans. Faraday Soc.*, **43**, 374 (1947).

<i>trans</i> -Dichloroethylene-Sulfur dioxide		
0.00000	2.1886	1.24658
.00217	2.1968	1.24648
.00341	2.2008	1.24642
.00422	2.2030	.....
Benzene--Trimethylamine-sulfur dioxide		
0.00000	2.276	0.8738
.00343	2.390	.....
.00376	2.402	.8749
.00538	2.456	.8756
Benzene--Triethylamine-sulfur dioxide		
0.00000	2.2760	0.87315
.00153	2.3088	.87360
.00238	2.3348	.87382
.00557	2.4261	.87469
.00877	2.5259	.87562
Benzene--Tri- <i>n</i> -butylamine-sulfur dioxide		
0.00000	2.2760	0.87318
.00169	2.3062	.87355
.00229	2.3220	.87366
.00464	2.3840	.87404
.00686	2.4491	.87461
.01022	2.5450	.87549
Benzene--Pyridine-sulfur dioxide		
0.00000	2.276	0.8735
.00507	2.335	.8756
.00698	2.360	.8769
.00813	2.372	.8769
.00931	2.390	.8774
.01099	2.412	.8779
.01256	2.437	.8784
Benzene--Triethylamine-sulfur trioxide		
0.00000	2.275	0.8731
.00567	2.644	.8767
.00895	2.856	.8789
.01043	2.951	.....
.01223	3.064	.8810
Dioxide--Triethylamine-sulfur trioxide		
0.00000	2.212	1.0291
.00198	2.362	1.0295
.00200	2.365	1.0296
.00345	2.468	1.0304
Benzene--Tri- <i>n</i> -butylamine-sulfur trioxide		
0.000000	2.2750	0.87313
.000717	2.3282	.87342
.000797	2.3332	.....
.002035	2.4215	.87414
.005260	2.6582	.87595
CCl <sub>4</sub> --Tri- <i>n</i> -butylamine-sulfur trioxide		
0.000000	2.2332	1.5851
.000681	2.2777	.....
.001093	2.3055	.....
.002218	2.3831	.....
.004600	2.5875	1.5793
.006039	2.7349	1.5776
.008480	2.9970	1.5748

Both the  $\Delta D/N_2$  and  $\Delta d/N_2$  ratios for benzene solutions of the addition compounds of triethylamine, tri-*n*-butylamine and pyridine with sulfur dioxide decreased sharply with decreasing solute concentration, indicating appreciable dissociation. Assuming that these compounds were in equilibrium in solution with the amines and sulfur dioxide, dissociation constants were calculated in the following manner: The electric moments of triethylamine-sulfur dioxide and tri-*n*-butylamine-sulfur dioxide were assumed to be 0.05 and 0.10 debyes greater than the moment of trimethylamine-sulfur dioxide. The calculation of the moment of pyridine-sulfur dioxide is indicated in the Discussion. The polarizations at infinite dilution of these compounds were calculated from the moments and molar refractions. The polarizations of tri-*n*-butylamine and sulfur dioxide are listed in

TABLE II

POLARIZATIONS AND ELECTRIC MOMENTS			
Compound	$P_{2\infty}$	$MR_D$	$\mu$
Sulfur dioxide	63.2	11.5	1.6
Tri- <i>n</i> -butylamine	73.6	61.6	0.77
Trimethylamine-sulfur dioxide	522	31.5	4.95
Triethylamine-sulfur trioxide (benzene)	985	44.7	6.84
Triethylamine-sulfur trioxide (dioxane)	1136	44.7	7.3
Tri- <i>n</i> -butylamine-sulfur trioxide (benzene)	1149	72.6	7.2
Tri- <i>n</i> -butylamine-sulfur trioxide (CCl <sub>4</sub> )			
$N_2 = 0.008480$	1533	72.6	8.4
$N_2 = 0.000681$	1132	72.6	7.2

TABLE III

POLARIZATIONS AND DISSOCIATION CONSTANTS IN BENZENE AT 25°			
$N_2$	$V$	$P_T$	$K_c$
Triethylamine-Sulfur Dioxide			
0.00877	90.07	30.07	0.0084
.00557	89.86	28.95	.0069
.00238	89.63	27.60	.0047
.00153	89.56	27.20	.0063
		Mean	.007
Tri- <i>n</i> -butylamine-Sulfur Dioxide			
0.01022	91.22	31.01	0.0173
.00686	90.66	29.53	.0134
.00464	90.27	28.50	.0130
.00229	89.85	27.48	.0122
.00169	89.75	27.22	.0136
		Mean	.013
Pyridine-Sulfur Dioxide			
0.01256	89.86	29.10	3
.01099	89.79	28.74	4
.00931	89.72	28.41	4
.00813	89.68	28.14	5
.00698	89.59	27.95	4
.00507	89.58	27.58	5
		Mean	4

Table II. The values for triethylamine and pyridine were taken from the literature. It was assumed that at the low solute concentrations listed in Table III the polarization of each component was independent of concentration. The concentration of each component and the value of  $K_N$  were calculated from the total polarization of each solution by relations similar to those used by Earp and Glasstone.<sup>13</sup> Values of  $K_c$  were obtained from the equation  $K_c = K_N/V$  where  $V$  is the molar volume of the solution in liters.

TABLE IV

EXTINCTIONS AND THE DISSOCIATION CONSTANT OF TRIMETHYLAMINE-SULFUR DIOXIDE AT 24 ± 3°		
$c$	$E$	$K_c \times 10^4$
In <i>n</i> -Butyl Chloride at 267 m $\mu$		
0.000561	2.020	1.9
.000448	1.560	1.8
.000420	1.395	2.0
.000374	1.187	2.0
.000187	0.467	1.9
		Mean 1.9 ± 0.4
In Chloroform at 260 m $\mu$		
0.000539	1.985	1.7
.000359	1.126	2.0
.000270	0.800	1.8
.000180	0.462	1.7
.000135	0.280	2.1
		Mean 1.9 ± 0.4

TABLE V

EXTINCTIONS OF DIMETHYLANILINE HYDROCHLORIDE IN CHLOROFORM AND THE VARIATION OF $K_c$ WITH CONCENTRATION AT 24 ± 3°		
$c$	$E$	$K_c \times 10^6$
0.008442	1.675	0.38
.008120	1.630	0.71
.005627	1.160	1.9
.005413	1.105	1.4
.004221	0.910	5.3
.004060	.845	3.2
.003248	.695	4.5
.002814	.602	4.6
.002707	.600	8.2
.001407	.325	14
.001203	.300	31
(0.000000)		200

### Discussion of Results

The low moment obtained for tri-*n*-butylamine in benzene, 0.77, compared to the values reported<sup>12</sup> for triethylamine, 0.90, and trimethylamine, 0.86, suggest a slight increase in the nitrogen valence angle in tri-*n*-butylamine due to steric hindrance.

A consideration of the configurations of sulfur dioxide,<sup>14</sup> thionyl chloride<sup>15</sup> and sulfur chloride<sup>15</sup> has led the authors to choose 55° as the angle between the N → S and SO<sub>2</sub> moment vectors in the

(13) Earp and Glasstone, *J. Chem. Soc.*, 1709 (1935).(14) Cross and Brockway, *J. Chem. Phys.*, 3, 821 (1935).(15) Palmer, *THIS JOURNAL*, 60, 2360 (1938).

amine-sulfur dioxide addition compounds. Assuming the moments of the amine, 0.86, and sulfur dioxide, 1.6, each to be increased by 0.2 in the addition compound, the moment calculated for the N  $\rightarrow$  S bond from the moment of trimethylamine-sulfur dioxide, 4.95, is  $2.7 \pm 0.4$ .

This N  $\rightarrow$  S moment is appreciably lower than the N  $\rightarrow$  O bond moment, 4.2, in amine oxides,<sup>16</sup> and the difference is greater than expected from a comparison of the C-S and C-O bond moments. It has been suggested by one of the authors<sup>17</sup> that a coordinate bond may result from resonance between a dipole-dipole bond,  $R_3N \cdots SO_2$ , and a purely covalent bond in which the electrons are equally shared,  $R_3\overset{+}{N}-\overset{-}{S}O_2$ . The dipole-dipole structure should make an appreciable contribution to the amine-sulfur dioxide molecule and thus reduce the N  $\rightarrow$  S moment appreciably below the N  $\rightarrow$  O moment in amine oxides, as the latter bond can have practically no dipole-dipole character.

The moment of pyridine-sulfur dioxide,  $6.2 \pm 0.7$ , used in calculating the dissociation constant for this compound in benzene listed in Table III was approximated as the vector sum of the pyridine, N  $\rightarrow$  S and  $SO_2$  moments.

Compound formation between trimethylamine and sulfur dioxide is accompanied by a marked increase in ultraviolet absorption, as is evident from Fig. 1. The lower absorption maxima of the addition compounds of sulfur dioxide with triethylamine and tri-*n*-butylamine are attributed to the greater dissociation of these compounds at corre-

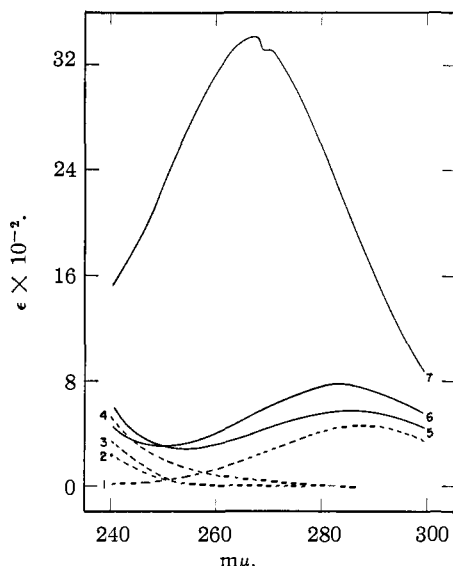


Fig. 1.—Absorption spectra in *n*-butyl chloride: (1) sulfur dioxide; (2) trimethylamine; (3) triethylamine; (4) tri-*n*-butylamine; (5) tri-*n*-butylamine-sulfur dioxide,  $c = 5.1 \times 10^{-4}$ ; (6) triethylamine-sulfur dioxide,  $c = 2.9 \times 10^{-4}$ ; (7) trimethylamine-sulfur dioxide,  $c = 5.6 \times 10^{-4}$ .

(16) Linton, *ibid.*, **62**, 1945 (1940).

(17) McCusker and Curran, *ibid.*, **64**, 614 (1942).

sponding concentrations. The absorption maxima for these two compounds shifted with decreasing concentration and the absorption curves approached the envelopes of the amine and sulfur dioxide curves at very low concentrations. The variation of the molar extinction coefficients with concentration is illustrated in Fig. 2. The disso-

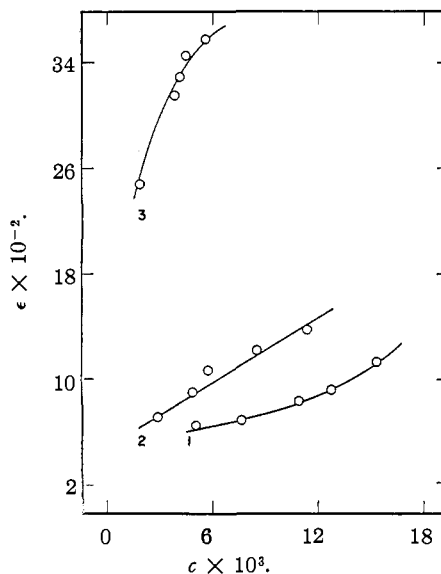


Fig. 2.—Change in molar extinction coefficient in *n*-butyl chloride with concentration: (1) tri-*n*-butylamine-sulfur dioxide at 284  $m\mu$ ; (2) triethylamine-sulfur dioxide at 284  $m\mu$ ; (3) trimethylamine-sulfur dioxide at 267  $m\mu$ .

ciation constant calculated for trimethylamine-sulfur dioxide from spectral data is  $1.9 \times 10^{-4}$  in both chloroform and butyl chloride, compared to the values 0.007, 0.013 and 4 calculated for the sulfur dioxide addition compounds of triethylamine, tri-*n*-butylamine and pyridine from the changes in polarization with concentration in benzene. The variation with time of the extinction values observed for U.S.P. chloroform, alcohol-free chloroform and *n*-butyl chloride solutions of triethylamine-sulfur dioxide and tri-*n*-butylamine-sulfur dioxide prevented the calculation of dissociation constants for these compounds from spectral data. It is evident from Fig. 3 that pyridine-sulfur dioxide is practically completely dissociated at concentrations of the order of  $10^{-4}$  molar.

Both the dielectric and absorption data reveal that the order of decreasing dissociation of the sulfur dioxide addition compounds is pyridine > tri-*n*-butylamine > triethylamine > trimethylamine. The chief factors determining this order appear to be the weak basicity of pyridine and the steric effects of alkyl groups. The steric factors affecting the stability of this type of compound have been characterized by Brown.<sup>18</sup>

The dielectric and density data reveal that the sulfur trioxide addition compounds of triethylam-

(18) Brown and Pearsall, *ibid.*, **67**, 1765 (1945).

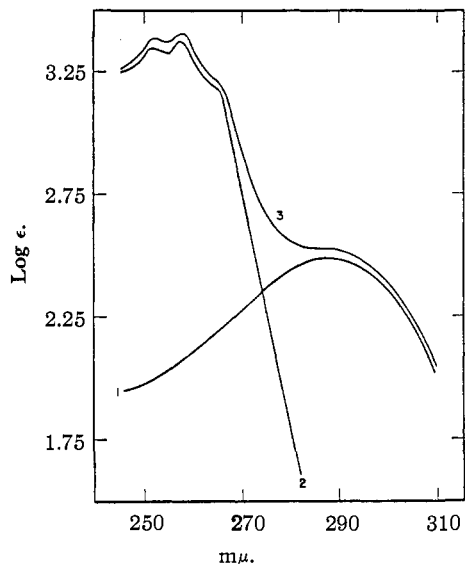


Fig. 3.—Absorption spectra in chloroform: (1) sulfur dioxide; (2) pyridine; (3) pyridine-sulfur dioxide,  $c = 5.4 \times 10^{-4}$ .

ine and tri-*n*-butylamine do not dissociate in benzene solution. This lack of dissociation is also evidenced by the molecular weight obtained for tri-*n*-butylamine-sulfur trioxide from a freezing point measurement on a benzene solution. Association of this compound in carbon tetrachloride at solute mole fractions in excess of 0.001 is indicated by the large  $\Delta D/N_2$  ratios that increase with increasing concentration. To illustrate this effect the electric moment of tri-*n*-butylamine-sulfur trioxide has been calculated from  $\Delta D/N_2$  ratios for two concentrations in carbon tetrachloride and listed in Table II. The solubilities of the addition compounds of sulfur trioxide with trimethylamine, pyridine and dimethylaniline in non-polar solvents were too low for dielectric constant measurements.

Assuming tetrahedral valence angles in sulfur trioxide addition compounds and an increase of 0.3 in the triethylamine moment, the sum of the  $N \rightarrow S$  and  $S-O$  bond moments in triethylamine-sulfur trioxide is 5.6. As a fair approximation a value of 3.6 is assigned to the  $N \rightarrow S$  vector and 2.0 to the  $S-O$  bond moment. The increase in the  $N \rightarrow S$  moment from the sulfur dioxide to the sulfur trioxide addition compounds is probably due to the greater residual positive charge on the trioxide sulfur and to the distorted character of the sulfur bond angles in the  $R_3N--SO_3$  dipole-dipole structure, resulting in an increased contribution of the  $R_3N^+-\bar{S}O_3$  structure to the molecule. The large moment of the  $S-O$  bond in this addition compound indicates a decrease in the  $S=O$  double bond character compared to that in sulfur dioxide.

The transparency of sulfur trioxide in the near ultraviolet limits the study of compound forma-

tion from absorption spectra to a comparison of the spectrum of the addition compound with that of the amine. Trimethylamine-sulfur trioxide and triethylamine-sulfur trioxide were observed to be transparent in the region available with chloroform, above 240  $m\mu$ , indicating, in support of the interpretation of dielectric data, that these compounds are not dissociated in solution. The absorption of tri-*n*-butylamine-sulfur trioxide, Fig. 4, is about 0.2% of that of the amine at 243  $m\mu$ , suggesting the possibility of a small amount of dissociation. The molar extinction coefficient of this compound increased slightly with decreasing concentration, but the change was less than the precision error of the measurements at these low extinction values.

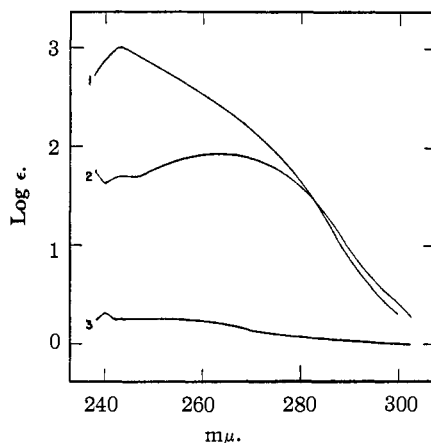


Fig. 4.—Absorption spectra in chloroform: (1) tri-*n*-butylamine; (2) tri-*n*-butylamine + 0.04 molar hydrogen chloride; (3) tri-*n*-butylamine-sulfur trioxide,  $c = 0.1$ .

The transparency of sulfur trioxide and its addition compounds compared to the absorption by sulfur dioxide and the amines and the strong absorption by the sulfur dioxide addition compounds suggests that absorption by these compounds is associated with excitation of the unshared nitrogen and sulfur electrons. This view is consistent with the decrease in the absorption by butylamine in acid solution illustrated in Fig. 4. The very strong absorption by trimethylamine-sulfur dioxide suggests that compound formation results in a loosening of the unshared sulfur electrons, perhaps by increasing the  $sp^3$  hybrid character of the orbitals of these electrons.

The addition of a proton to pyridine increases the electron demand of the nitrogen atom and thus facilitates electron migration from the ortho and para carbon atoms, resulting in stronger absorption. The addition of sulfur trioxide alters the pyridine spectrum in a similar manner, as illustrated in Fig. 5. Lewis and Bigeleisen have shown a similar relation between the proton and stannic chloride in altering the spectrum of methylene blue.<sup>19</sup> The slightly lower maximum of pyridine-

(19) Lewis and Bigeleisen, *ibid.*, **65**, 1144 (1943).

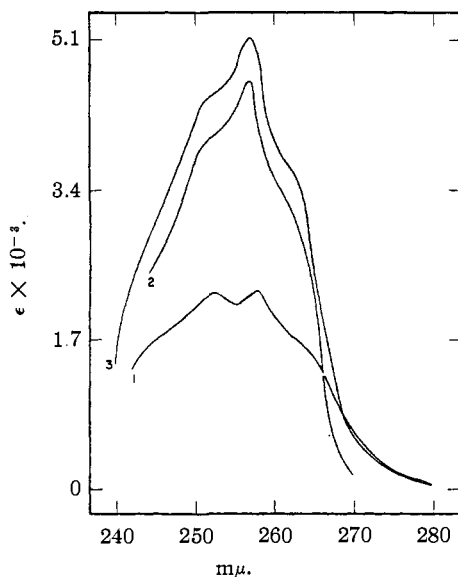


Fig. 5.—Absorption spectra in chloroform: (1) pyridine; (2) pyridine-sulfur trioxide + 1% ethyl alcohol; (3) pyridine + 0.1 molar hydrogen chloride.

sulfur trioxide compared to the pyridinium ion may result from the action of the alcohol required to dissolve the addition compound. The very low solubility of this compound prevented a study of the effect of concentration on the molar extinction coefficient.

The addition of a proton to dimethylaniline prevents the migration of the nitrogen electrons to the ring and decreases sharply the absorption maxi-

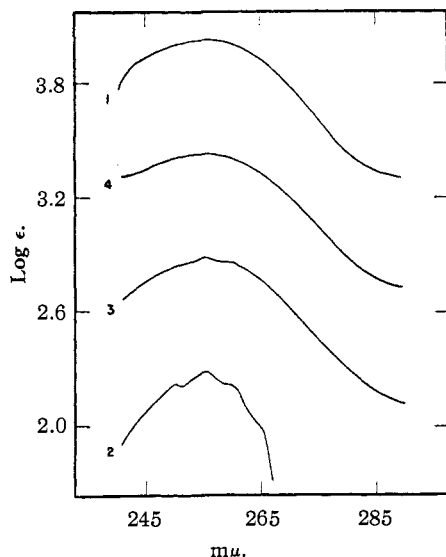


Fig. 6.—Absorption spectra of (1) dimethylaniline in chloroform and (2) dimethylaniline hydrochloride in chloroform + 0.1 molar hydrogen chloride compared with (3)  $1.2 \times 10^{-3}$  molar and (4)  $2.0 \times 10^{-4}$  molar dimethylaniline-sulfur trioxide in U. S. P. chloroform.

um at 255  $m\mu$ .<sup>20</sup> Figure 6 reveals that sulfur trioxide addition has a similar effect on the spectrum of dimethylaniline. The change in the molar extinction coefficient with concentration in U.S.P. chloroform indicates appreciable dissociation of the addition compound in this solvent. In alcohol-free chloroform, as illustrated in Fig. 7, this dissociation is decreased considerably; the extent of dissociation of the sulfur trioxide complex is very little different from that of the dimethylanilinium ion in this solvent. The absorption maxima for dimethylaniline-sulfur trioxide at varying concentrations in alcohol-free chloroform could not be determined with sufficient precision (the extinction values changed slightly with time) to obtain a reliable dissociation constant for this compound.

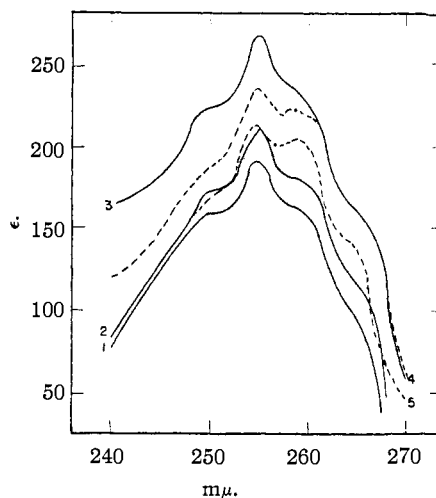


Fig. 7.—Absorption spectra in alcohol-free chloroform: (1) dimethylaniline hydrochloride + 0.1 molar hydrogen chloride; (2) 0.0081 *M* and (3) 0.0012 *M* dimethylaniline hydrochloride; (4) 0.0017 *M* and (5) 0.0069 *M* dimethylaniline-sulfur trioxide.

The values of the dissociation constant calculated for dimethylaniline hydrochloride in chloroform from observed extinctions at different concentrations increased with decreasing concentration. Dr. W. H. Hamill suggested to the authors that this increase might be due to the salt effect of the hydrochloride. The conductance of a 0.1 molar solution of dimethylaniline hydrochloride in chloroform was observed to be about a thousand times that of hydrogen chloride in chloroform. The dissociation constant was therefore calculated considering the equilibrium to be  $C_8H_{11}NH^+ + Cl^- \rightleftharpoons C_8H_{11}N + HCl$ . The values of  $K_c$  are given in Table V. From the Debye-Hückel limiting law it follows that  $-\log K_c = -\log K_a + 2k\sqrt{\mu}$ , where  $k$  for chloroform at 25° is 32.8. The plot of

(20) This is actually a comparison of the primary band of dimethylaniline with the secondary band of the ion. For simplicity of illustration the shift of the dimethylaniline secondary band to higher frequencies on ionization is ignored. See Doub and Vandenberg, *ibid.*, **69**, 2714 (1947).

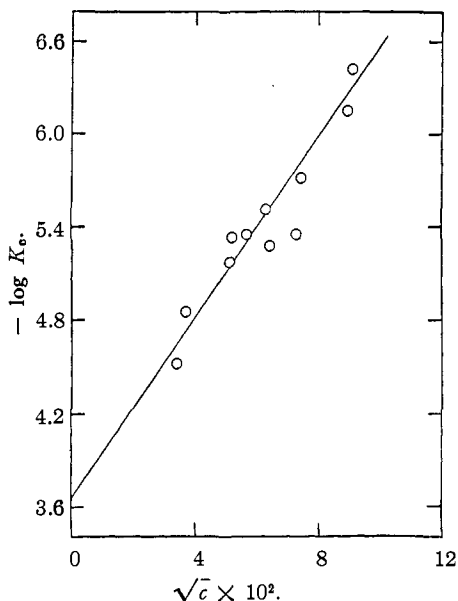


Fig. 8.—Variation of  $-\log K_e$  for the reaction  $C_6H_{11}NH^+ + Cl^- \rightleftharpoons C_6H_{11}N + HCl$  with concentration of dimethylanilinium ions.

$-\log K_e$  versus  $\sqrt{c}$  given in Fig. 8, where  $c$  is the concentration of dimethylanilinium ions calculated from the spectral data, yielded a value of  $K_a = 2 \times 10^{-4}$  and a value of  $k = 14$ . Other authors have reported low values of  $k$  for solvents of low dielectric constant from conductance measurements. In this instance the low value appears to

be due in part to the presence of a large number of  $C_6H_{11}NH^+ \cdots Cl^-$  ion pairs, which reduces the ionic strength below the calculated value.

### Summary

Electric moments have been determined for sulfur dioxide, tri-*n*-butylamine, trimethylamine-sulfur dioxide, triethylamine-sulfur trioxide and tri-*n*-butylamine-sulfur trioxide. The N  $\rightarrow$  S bond moments in these addition compounds have been evaluated.

Dissociation constants have been calculated for trimethylamine-sulfur dioxide and dimethylaniline hydrochloride in chloroform from ultraviolet absorption measurements, and for the sulfur dioxide addition compounds of pyridine, triethylamine, and tri-*n*-butylamine in benzene from dielectric constant and density measurements. Both absorption and dielectric constant measurements reveal that the order of decreasing stability of the sulfur dioxide addition compounds is trimethylamine > triethylamine > tri-*n*-butylamine > pyridine. The sulfur trioxide addition compounds of trimethylamine and triethylamine appear to be undissociated in benzene and chloroform solutions.

Interaction of trialkylamines with sulfur dioxide results in a very large increase in absorption in the 270  $m\mu$  region. The addition compounds of sulfur trioxide with trialkylamines are transparent in this region. Sulfur trioxide shows an effect similar to that of the proton in altering the spectra of pyridine and dimethylaniline.

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## Rate of Adsorption of Barium Ions in Extreme Dilution, by Hydrous Ferric Oxide

BY M. H. KURBATOV

### Introduction

In earlier work it was realized that the extent of adsorption of divalent ions from very dilute solutions on hydrous ferric oxide depended not only on the usually recognized factors of temperature,  $pH$ , amount of adsorbent, volume and salt concentration but also on the duration of adsorption. It was observed that adsorption was not discontinued with the separation of the solid adsorbent, but that when the co-precipitation procedure was used in the case of very dilute solutions, there was an observable adsorption rate. Particularly was this true when the amount of adsorbate was less than  $10^{-6}$  gram atom, the volume of solution of the order of 10–30 ml. and the quantity of adsorbent 1 or  $2 \times 10^{-5}$  gram atom of iron, the effect being more pronounced with decreased amounts of adsorbate. From this observation there arose the possibility of determining a rate of ion adsorption from solution.

### Procedure

The adsorption procedure and the preparation of barium 133 as carrier-free tracer are described in a previously published paper.<sup>1</sup> For the rate studies,  $2 \times 10^{-5}$  gram mole ferric chloride was mixed with the chosen quantity of stable barium chloride and tracer, all in acid solution, and the mixture titrated rapidly with ammonium hydroxide to the selected  $pH$ . Thus, the so-called co-precipitation procedure, in which hydrous ferric oxide was precipitated in the presence of barium ions, was used. Some barium was adsorbed during titration in the  $pH$  interval from the formation of the solid phase to the selected  $pH$  of a particular series of experiments, the amount adsorbed during titration increasing with  $pH$  (see Table II).

The co-precipitation procedure has some advantage over the "real" adsorption procedure (in

(1) M. H. Kurbatov, Fu-Chun Yu and J. D. Kurbatov, *J. Chem. Phys.*, **16**, 87 (1948).