Discussion

The heats of formation of the six substances are summarized in Table VII. In column (a) are the heats of formation from the elements, in column (b) the heats of formation from magnesium, chlorine gas, and liquid water, and in column (c) the heats of formation from anhydrous magnesium chloride and liquid water.

TABLE VII

HEATS OF FORMATION (CAL. PER MOLE)

	$\Delta H_{298.16}$		
	(a) From elements	(b) From Mg, Cl_2 and H_2O	(c) From $MgCl_2$ and H_2O
MgO	−143,840		
$MgCl_2$	−153,220	−153,220	0
$MgCl_2·H_2O$	−230,970	−162,650	−9,430
$MgCl_2·2H_2O$	−305,810	−169,170	−15,950
$MgCl_2·4H_2O$	−453,820	−180,550	−27,330
$MgCl_2·6H_2O$	−597,240	−187,330	−34,110

The present value for the heat of formation of magnesium oxide compares favorably with the combustion value of von Wartenberg,[10] −143,900 cal. per mole, and with the value Kelley and Anderson[11] computed from heat-of-formation and heat-of-decomposition data of magnesium carbonate, −144,090 cal. per mole. It differs considerably, however, from the value of Moose and Parr,[12] −145,800 cal. per mole. The latter obtained their result by direct combustion of magnesium, but as our oxide had been heated to 1000° there is little reason to believe that the difference in heat of formation is attributable to difference in physical form of the oxide. The work of Marignac and Berthelot leads to values in the range −143,400 to −145,300 cal. per mole, depending on the method of calculation.[13]

Bichowsky and Rossini[14] list the following heats of formation from the elements of the magnesium chlorides at 291°K.: −153,300 cal. per mole for $MgCl_2$, −305,500 for $MgCl_2·2H_2O$, −452,600 for $MgCl_2·4H_2O$ and −596,400 for $MgCl_2·6H_2O$. These values are based largely on heat-of-solution measurements of Thomsen. The agreement between these values and our own is better than would have been expected *a priori*. The greatest difference occurs in the case of the tetrahydrate. This difference is about 0.3% of the heat of formation from the elements or 4.5% of that from magnesium chloride and liquid water, the latter being the more significant.

Summary

The heats of formation of magnesium oxide, anhydrous magnesium chloride, magnesium chloride monohydrate, magnesium chloride dihydrate, magnesium chloride tetrahydrate, and magnesium chloride hexahydrate have been determined by measuring the heats of solution of these materials and magnesium metal in 1 *N* hydrochloric acid.

BERKELEY, CALIFORNIA RECEIVED APRIL 30, 1943

---

[10] von Wartenberg, *Z. Elektrochem.*, **15**, 869 (1909).

[11] Kelley and Anderson, *Bureau of Mines Bulletin* **384**, 1935, p. 26.

[12] Moose and Parr, THIS JOURNAL, **46**, 2656 (1924).

[13] (a) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, Vol. 2, 1923, p. 1519; (b) *ibid.*, 1st Supplement, 1927, p. 825.

[14] Bichowsky and Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Behavior of Trimethylamine, Trimethylammino-sulfur Trioxide and Trimethylamine Oxide toward Sulfur Dioxide

BY ANTON B. BURG[1]

The rapid development of theories explaining the chemical bond, from a mathematical-physical viewpoint, demands a parallel development of purely chemical facts having a fairly simple relation to the new ideas. As a step toward meeting this evident need, it seems appropriate to make comparative studies of complex compounds involving the simpler elements. The present paper describes the behavior of trimethylamine, trimethylammino-sulfur trioxide, and trimethylamine oxide toward sulfur dioxide. These relatively simple compounds were selected because they involve no mobile hydrogen atoms, and form a series suitable for comparisons.

Sulfur dioxide reacts with trimethylamine to form a solid addition product, according to the equation

$$(CH_3)_3N(g) + SO_2(g) \rightleftarrows (CH_3)_3NSO_2(s);\ F^0_{298} = -7 \text{ kcal.}$$

---

[1] The essential results here given were presented at the Detroit meeting of the American Chemical Society, September, 1940. The author wishes gratefully to acknowledge the contribution of Marshall S. Smoler, whose Master's dissertation (University of Chicago Libraries, 1939) describes the preparation and preliminary study of the compound $(CH_3)_3NSO_2$.

This addition compound seems analogous to one which Jander and Wickert formulated as $[(C_2H_5)_3N]_2SO^{++}SO_3^{=}$,[2] but a study of the vapor tensions of its sulfur dioxide solutions gave results favoring the simpler formulation $(CH_3)_3N \rightarrow SO_2$. The SO_2-solution behavior of this compound therefore can properly be compared with that of the compound $(CH_3)_3NSO_3$. Also of interest for comparison are the compounds $(CH_3)_3NOSO_2$ and $(CH_3)_3NO(SO_2)_2$, which can be made by the very cautious treatment of anhydrous trimethylamine oxide with sulfur dioxide at a low temperature.

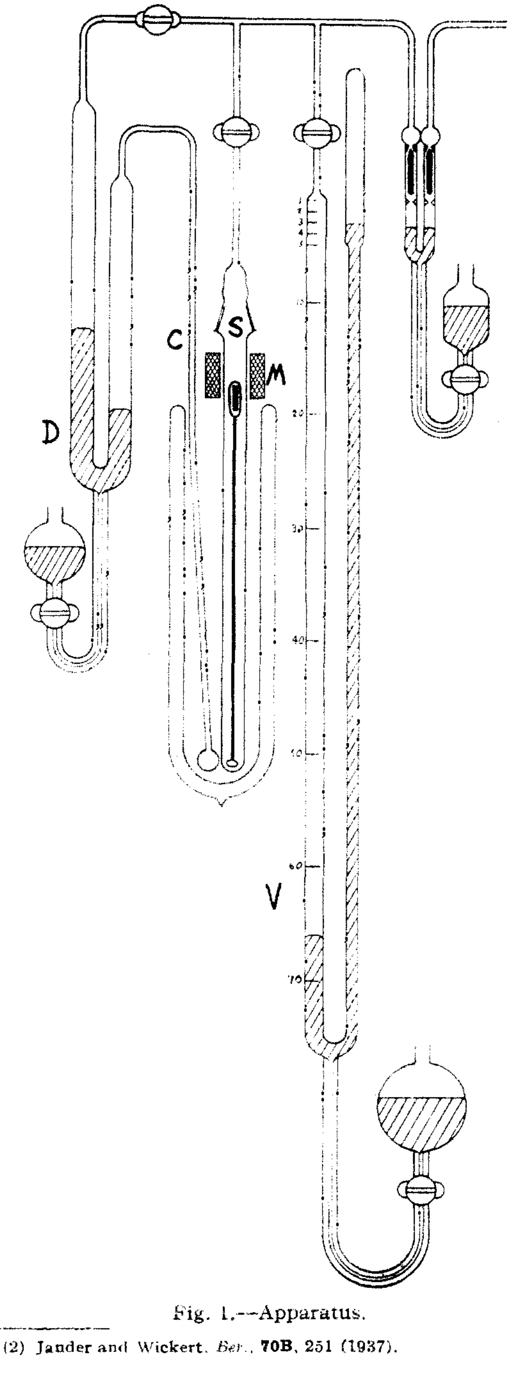


Fig. 1.—Apparatus.

Trimethylamine and Sulfur Dioxide

Apparatus and Technique.—The high-vacuum apparatus, employed in this study, was provided with numerous calibrated tubes, manometers, storage bulbs, a completely immersible bulb for measuring pressures at elevated temperatures,[3] and the differential manometer system shown in Fig. 1, all connected to the pump manifold through mercury float-valves. The differential manometer system was essentially similar to that employed by Stock and Pohland[4] for tensiometric determinations of molecular weight. It was used here for measurement of small depressions of the vapor tension of sulfur dioxide by a solute: each solution was formed and magnetically stirred in tube S and its vapor tension was compared with that of the pure sulfur dioxide contained in C. Whenever the depression was too large for use of the differential manometer, the vapor tension of the solution was measured directly (using the float-valve as a null-manometer), and the result was compared with the vapor tension of the pure solvent at the temperature of the measurement.

Relatively large portions of the solvent sulfur dioxide were determined by weighing the liquid, contained in a small tube carrying a mercury-protected stopcock.[5] The slant-bored plug of this stopcock was ground to an incipient polish, lubricated by Apiezon L grease, and secured against the internal pressure (4 atm.) by means of a tightly-stretched rubber band. Small variations in the quantity of sulfur dioxide were determined by the gas-volumetric method, using the measuring tube V.

Preparation and Purification of Reagents.—Sulfur dioxide was drawn from a commercial cylinder and purified by the aid of a vacuum-jacketed fractionating column, temporarily attached to the high-vacuum apparatus. The reflux temperature was approximately −70°. After two operations, in which the first and last fractions were discarded, a third operation yielded first and last fractions whose vapor tensions at 0° (compared by means of the differential manometer and a cathetometer) differed no more than 0.01 mm. The middle fraction then was selected for the work here described. Its vapor tension at 0° was 1171 mm. (mercury at 24°).

Anhydrous trimethylamine was obtained by distillation of a commercial 25% solution, using a receiver cooled by solid carbon dioxide. The last trace of moisture was removed by allowing the redistilled amine to remain for two days (with occasional shaking) in a sealed tube containing freshly-sublimed phosphoric anhydride (P_4O_{10}). This treatment served also for the removal of all substances containing N–H links.[6] The final product showed a vapor tension of 680 mm. (cor.) at 0°, in agreement with the value reported by Simon and Huter.[7] Further treatment of the sample with phosphoric anhydride, this time

---

(2) Jander and Wickert, *Ber.*, **70B**, 251 (1937).

(3) Burg and Schlesinger, THIS JOURNAL, **59**, 785 (1937).

(4) Stock and Pohland, *Ber.*, **58**, 657 (1925).

(5) As described by Stock and Somieski, *ibid.*, **49**, 127 (1916).

(6) Daniel P. Ingram, M.S. Dissertation, The University of Chicago Libraries, 1939.

(7) Simon and Huter, *Z. Elektrochem.*, **41**, 32 (1935).

in a sealed tube at 90°, had no effect upon the vapor tension.

The Compound $(CH_3)_3NSO_2$.—Trimethylamine and sulfur dioxide react instantaneously at ordinary temperatures, yielding a readily sublimable white solid containing equimolecular proportions of the two reactants. Thus when nearly equal volumes of $(CH_3)_3N$ and SO_2 (measured successively in the same part of the apparatus, each registering 398 mm. at 21° in a space of 121.3 cc.) were brought together in the closed system, the resulting pressure at room temperature was 17 mm. The product was cooled to $-45°$ and the excess gas (removed by condensation elsewhere) amounted to 0.5 cc., or 0.4% of the whole. Similarly, 11.6 cc. of $(CH_3)_3N$ and 11.5 cc. of SO_2 reacted to give a solid, leaving a residual pressure of 2.8 mm. at 19.7°, which became less than 0.01 mm. at $-70°$. In many other experiments a considerable excess of either component was easily removed by distillation from a tube at $-45°$, and the residue always exhibited pressures agreeing with those in Table II. Neither a secondary addition compound nor much adsorption could be recognized.

The vapor of the 1:1 compound is dissociated almost completely, as indicated by the data of Table I (obtained by the use of the completely immersed bulb[3]). In this table, the symbol V_{gas} refers to the total volume of vapor, corrected to standard conditions. The calculated V (based upon weighed samples) is the standard volume predicted for complete dissociation of the compound into the original reactants. It appears that the compound $(CH_3)_3NSO_2$ may exist to a slight extent in the vapor phase, but the extent of combination evidently was scarcely greater than 10% under the conditions of the experiment, and a large part of the effect might be attributed to van der Waals attractions.

TABLE I

VAPOR-PHASE DISSOCIATION OF $(CH_3)_3NSO_2$

$V_{app.}$, cc.	163.7	164.1	165.8	164.8	164.8	164.8	164.4
T, °K.	337.9	343.1	348.3	358.9	367.7	373.1	356.0
p, mm.	77.6	79.1	80.85	83.8	86.5	88.2	179.7
V_{gas}, cc.	13.49	13.59	13.72	13.80	13.92	13.97	29.81
$V_{calcd.}$	14.10	14.10	14.10	14.10	14.10	14.10	31.50

The same samples and immersed bulb[3] were used in obtaining the dissociation pressures recorded in Table II. These values represent conditions ranging from nearly complete condensation to nearly complete vaporization, and the good agreement with the equation $\log p = 11.276 - (3165/T)$ (the source of the calculated pressures) thus is convincing evidence that the solid material is a single substance. The assumption of complete dissociation in the vapor phase, whereby $\log K_{atm.} = 16.188 - (6330/T)$, leads to the rough expression $\Delta F^0 = 28.95 - 0.07404T$, for the standard molar free energy (in kilogram-calories) of the process $(CH_3)_3NSO_2(s) \rightleftarrows (CH_3)_3N(g) + SO_2(g)$. This result is subject to the deviations indicated in Table I.

TABLE II

DISSOCIATION PRESSURES OF $(CH_3)_3NSO_2$

(SOLID $\rightleftarrows$ VAPOR)

t, °C.	19.8	30.6	44.2	54.7	61.0	67.3	75.7
p, mm., obsd.	2.94	7.07	20.1	41.8	63.6	94.7	159.2
p, mm., calcd.	2.95	7.15	20.0	41.74	63.5	95.1	159.2

$(CH_3)_3NSO_2$ with Excess Trimethylamine.—The addition compound $(CH_3)_3NSO_2$, not only fails to add a second molecule of trimethylamine, but it seems to be almost insoluble in the liquid amine.

$(CH_3)_3NSO_2$ with Excess Sulfur Dioxide.—The 1:1 addition compound is highly soluble in liquid sulfur dioxide, but a search for a definite secondary addition, by the study of pressure–composition isotherms at five different temperatures, showed only that saturated solutions began to form as soon as the condensed phase contained more sulfur dioxide than that corresponding to a 1:1 molecular ratio of the reactants. The pressures remained strictly constant as more and more sulfur dioxide was added, until all of the solute was dissolved. The point of complete dissolving (determining solubility) could be located accurately, as the point beyond which the pressure–composition curve suddenly began to rise. The apparent degree of solvation of the amine in each saturated solution was calculated according to Raoult's law, whereby the mole fraction of unbound sulfur dioxide was assumed to be given by the ratio of the observed vapor tension to that of pure sulfur dioxide. The results, given in Table III, indicate that the solvation of the compound $(CH_3)_3NSO_2$ is of indefinite character, not to be confused with true compound formation.

TABLE III

SOLUBILITY AND SOLVATION OF TRIMETHYLAMINE IN SO_2

t, °C.	-17.0	-8.0	0.0	9.9	19.4
$P_{sat.}$, mm., cor.	162	226	296	394	494
Mole ratio SO_2/amine	2.50	2.30	2.18	2.04	1.87
Solubility, mole % amine	28.5	30.3	31.4	32.9	34.8
Apparent solvation (mole ratio bound SO_2 to amine)	2.08	1.93	1.84	1.74	1.61

The Effect of Dimethylamine.—In some preliminary experiments of the sort just described, the shape of the isotherm at 0° suggested the formation of solid solutions of sulfur dioxide in $(CH_3)_3NSO_2$; the apparent "saturation point" occurred when the total SO_2 was 1.20 moles per mole of amine. This illusory effect was traced to the presence of dimethylamine: only three mole per cent. of dimethylamine, added to the pure trimethylamine, led to results exactly similar to the "solid solution" effect noted in the cruder experiments.

The Vapor Tensions of SO_2-Solutions of $(CH_3)_3N$ at 0°.—It was considered desirable to learn as much of the nature of the solute, present when trimethylamine is dissolved in liquid sulfur dioxide, as the measurement of vapor tensions could indicate. The study of the isotherm at 0° therefore was extended to include the entire feasible range of concentrations. The results, presented in Table IV, are plotted as deviations from Raoult's law in Fig. 2.

As the solution becomes very dilute, it appears that the lowering of the vapor tension by the solute approaches that expected on the basis of Raoult's law, on the assumption that trimethylamine was dissolved without association

TABLE IV

VAPOR TENSION LOWERING BY $(CH_3)_3NSO_2$, DISSOLVED IN LIQUID SO_2

Volume of amine, cc. of gas	Total SO_2 in cond. phase, cc. gas	Δp, mm.	Apparent mole fr., $\Delta p/p_0$	x = Calcd. mole fr. $(CH_3)_3NSO_2$	Ratio: $\frac{\Delta p/p_0}{x}$	Apparent solvation[a]
1.98	763	3.12	0.00266	0.00260	1.023	10
4.43	765	7.14	.00609	.00582	1.046	9
11.10	774	18.2	.01554	.01454	1.069	6.4
16.96	583	39.2	.03346	.02994	1.118	5.5
31.85	602	79.2	.0675	.0558	1.209	5.1
52.70	633	141.7	.1209	.0909	1.330	4.7
166.7	741	441	.376	.225	1.672	2.79
193.7	742	522	.445	.260	1.712	2.58
218.1	751	589	.503	.290	1.735	2.46
247.3	757	668	.569	.326	1.745	2.30
45.6	115.4	790	.674	.395	1.707	2.05
45.6	107.2	849	.724	.436	1.661	1.97
58.3	126.9	874	.746	.459	1.625	1.84

[a] Calculated according to Raoult's law, and expressed as ratio of bound SO_2 to trimethylamine.

or dissociation. Hence the molecular weight in dilute solution corresponds to the formula $(CH_3)_3N(SO_2)_x$.

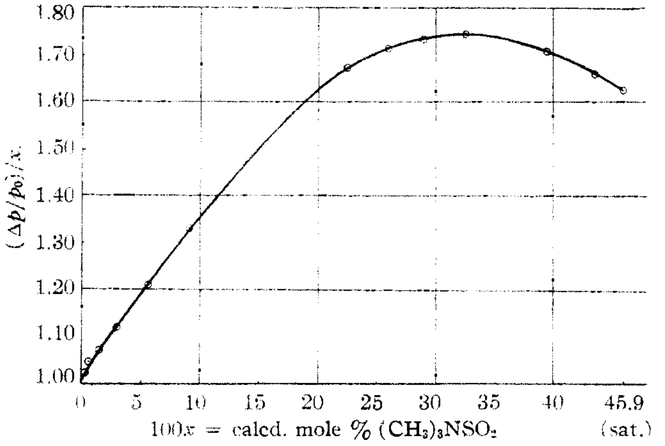


Fig. 2.—Temperature, 0°.

Furthermore, as the solution becomes more concentrated, the deviations from Raoult's law (Fig. 2) increase positively, in direct contradiction to the behavior expected in case of either an ionic or an associative equilibrium. It therefore is evident that an ionic structure like that proposed by Jander and Wickert[2] for the 1:1 compound of triethylamine with sulfur dioxide, is not present here to an appreciable extent. This conclusion is supported by a measurement of the electrical conductivity, indicating that ionization is of the order of 1% in a solution of medium concentration.[8]

The entire curve of Fig. 2 is easily and naturally explained in terms of an increase in the degree of solvation of the solute, with increasing dilution. As sulfur dioxide is added to the saturated solution, the increase in solvation evidently is such as to increase the deviation from Raoult's law, in spite of the opposite effect of dilution. The curve thus passes through a maximum, and then drops off as the quantity of bound sulfur dioxide becomes less and less important in comparison with the total. At the lowest concentrations, it seems that the effect of solvation becomes practically negligible, and so the apparent "molecular weight" of the solute becomes normal.

This explanation of the shape of the curve becomes more readily acceptable if one considers the values given in Table IV, for the apparent solvation of the dissolved amine. These values were calculated by means of the equation $S = \frac{\text{moles SO}_2}{\text{moles amine}} - \frac{p}{\Delta p}$, which is easily derived from Raoult's law, on the assumption that solvation is the only cause of the deviations. The regular increase in the apparent solvation, as a higher proportion of sulfur dioxide becomes available, is quite in accord with the hypothesis of solvation.

Trimethylammino-sulfur Trioxide and Sulfur Dioxide

Preparation.—Trimethylammino-sulfur trioxide was prepared by the direct reaction of sulfur trioxide (vapor, carried in a stream of nitrogen) with dry trimethylamine vapor, continuously fed into the reaction flask.[9] Some tar-like material was formed; this was eliminated by repeated recrystallization from water. The colorless crystals of the purified material melted at 240°, in good agreement with the report of Traube, Zander, and Gaffron[10] on the same compound, which they prepared by other methods. In the high-vacuum system, this compound, $(CH_3)_3NSO_3$, sublimed cleanly at 130–140°, leaving no detectable residue, and evolving no trace of any more volatile substance. The purity of the compound was further established by analysis, with determination both of $(CH_3)_3N$ and of SO_3.

Tensiometric Behavior of $(CH_3)_3NSO_3$ in Liquid SO_2 at 0°.—Weighed samples of $(CH_3)_3NSO_3$ and sulfur dioxide were brought together in the tube S (Fig. 1), and the difference of pressure between the solution and pure sulfur dioxide, both immersed in the same ice-bath, was measured by means of the differential manometer. The results are presented in Table V.

TABLE V

TENSIOMETRIC EFFECTS OF $(CH_3)_3NSO_3$ IN LIQUID SO_2 AT 0°

$(CH_3)_3$-NSO_3, millimoles	SO_2 in cond. phase, mmols.	Δp, mm.	Apparent mole fr., $\Delta p/p_0$	x = calcd. mole fr. solute	Ratio: $\frac{\Delta p/p_0}{x}$	Apparent solvation
0.974	35.1	33.0	0.0282	0.0270	1.043	1.6
0.974	14.3	81.0	.0691	.0636	1.086	1.22
3.743	39.35	114.2	.0975	.0868	1.122	1.26
3.743	36.75	121.7	.1039	.0924	1.123	1.19
3.743	35.78	124.4	.1062	.0947	1.121	1.16
3.743	35.40	125.5	.1072	.0956	1.122	1.13
3.743	35.03	127.0	.1085	.0965	1.125[a]	1.13
3.743	35.17	126.2	.1078	.0962	1.121[b]	1.12
3.743	34.83	126.2	.1078	Crystals appear		

[a] Supersaturated solution. [b] Saturated solution.

From these results it appeared that the solvation of $(CH_3)_3NSO_3$ in liquid sulfur dioxide might involve a

---

(8) A result taken from the Master of Science thesis of Joseph U. Messenger, University of Southern California Libraries, 1942.

(9) This method of preparation, based upon the preparation of $(C_2H_5)_3NSO_3$ by Beilstein and Wiegand, *Ber.*, **16**, 1267 (1883), was developed by S. J. Collender, working under the direction of the author at The University of Chicago.

(10) Traube, Zander and Gaffron, *ibid.*, **57B**, 1049 (1924).

definite 1:1 addition compound. However, an attempt to find decomposition pressures, corresponding to such a compound, met with failure. The solution was evaporated at −70°, until the molecular ratio of solvent to solute was far less than one. The pressure over the residue at −78° then approximated that of pure sulfur dioxide (9 mm.) instead of some lower value, which would have appeared to be the decomposition pressure of a compound. This evidence against the existence of even a very unstable addition compound leads one to assume that any solvation in solution must be of indefinite character. In this case, in fact, solvation of any kind is open to doubt.

Solubility of $(CH_3)_3NSO_3$ in Liquid SO_2.—From the results in Table V, it is noted that the solubility of $(CH_3)_3NSO_3$ in liquid sulfur dioxide at 0° is 9.62 mole per cent. Since the deviations from Raoult's law are not very great, it is possible to estimate the values of solubility at lower temperatures, from measurements of the lowering of the vapor tension in saturated solutions. The results of such measurements appear in Table VI. The true solubilities should be approximately 10% lower than the apparent mole fractions given in this table.

TABLE VI

APPARENT SO_2-SOLUBILITIES OF $(CH_3)_3NSO_3$ AT LOWER TEMPERATURES

t, ° C.	−8.0	−16.0	−24.3	−31.8	−45.8
Δp, mm., Hg at 21°	89.5	57.0	36.3	23.0	8.75
p_0, mm., Hg at 21°	832.0	579.0	387.5	261.0	114.0
Apparent mole fr.	0.104	0.098	0.090	0.084	0.073

Trimethylamine Oxide and Sulfur Dioxide

Preparation.—Trimethylamine oxide was prepared in solution by the action of hydrogen peroxide, as recommended by Dunstan and Goulding.[11] The anhydrous material was obtained by vacuum drying at 100° and subsequent sublimation, much as described by Meisenheimer and Bratring.[12] The practical limit of the drying at 100° was marked by the appearance of a white sublimate in the cooler part of the apparatus. After the first sublimation (in high-vacuum at 120°), the product was transferred to the closed end of the long tube shown in Fig. 3, and resublimed several times before a small sample finally was collected at B, by sublimation through the standard ground-joint J. The apparatus now was filled with dry air and the (previously weighed) reaction tube S was immediately closed by a clean, weighed rubber stopper, and weighed at once. The tube, with contents now of known weight, was jointed to the differential manometer system and evacuated. As a final test of freedom from water, the trimethylamine oxide was resublimed within the reaction tube; water, which would have collected in the trap leading to the high-vacuum pump, never was found.

The Compound $(CH_3)_3NOSO_2$.—Preliminary experiments showed that the action of sulfur dioxide upon anhydrous trimethylamine oxide was very energetic, and quite likely to produce black products of indefinite character. For the smooth addition of sulfur dioxide to the amine oxide, it was necessary to keep the latter at −80° or colder, while the gas was allowed to make contact at low pressure. It was found most convenient to condense the sulfur dioxide in the comparison tube (C, Fig. 1) of the differential manometer system, to immerse both that tube and the reaction tube in the same bath at −100°, and then open the connecting stopcocks. After several hours, the reaction would be complete, and the excess sulfur dioxide could be distilled away (reaction tube finally at room temperature) and measured. In two experiments of this sort, the respective combining ratios were 1.007 and 0.96 moles of SO_2 per mole of amine oxide.

The compound $(CH_3)_3NOSO_2$ appears to be extremely stable, in the sense that its formation is not reversed by heating *in vacuo*. However, it does decompose, at 120°, yielding a variety of products: a nearly non-volatile oil, a white, deliquescent solid (sublimable *in vacuo* at 60–70°), a less volatile sublimate which might be the compound $(CH_3)_3NSO_3$ (though not definitely identified), a fair proportion of $(CH_3)_3NSO_2$, and a black, tarry residue. This behavior contrasts sharply with that of $(CH_3)_3NSO_3$, which, regardless of attempts to catalyze its decomposition by addition of traces of amine oxide and sulfur dioxide, sublimes quite cleanly on heating *in vacuo*. The two compounds $(CH_3)_3NOSO_2$ and $(CH_3)_3NSO_3$ thus are recognized as quite different.

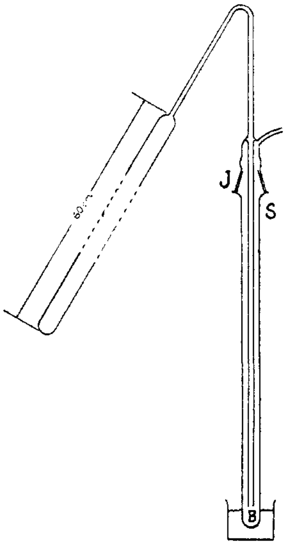


Fig. 3.

Secondary Addition of Sulfur Dioxide to $(CH_3)_3NOSO_2$.—A 0.1005-g. sample of trimethylamine oxide (equivalent to 30.0 cc. of gas at standard conditions) was treated with sulfur dioxide in the manner described above. The solid reaction product was washed to the bottom of the reaction tube, by refluxing sulfur dioxide above it. The excess of sulfur dioxide was removed by slow sublimation at −80°, leaving a spongy residue. The original sulfur dioxide amounted to 2.1756 g.; that recovered, 2.0996 g. The difference was equivalent to 26.6 cc. The total quantity of sulfur dioxide which now had combined with the amine oxide thus was 56.6 cc., or 1.88 moles SO_2 per mole of $(CH_3)_3NO$.

A study of the pressure–composition isotherm for the removal and addition of sulfur dioxide at −20° yielded the data presented in Table VII. These data constitute fairly clear evidence of the existence of the secondary addition product $(CH_3)_3NOSO_2 \cdot SO_2$. The small variation of the decomposition pressure with changing composition probably is to be attributed to the considerable difficulty involved in the establishment of equilibrium. The definite rise of pressure at ratios above 1.90 (agreeing with the original combining ratio 1.88) indicates that an inert impurity was present in the proportion of ten to

---

(11) Dunstan and Goulding, *J. Chem. Soc.*, **75**, 1005 (1899).

(12) Meisenheimer and Bratring, *Ann.*, **397**, 286 (1913).

TABLE VII

PRESSURE-COMPOSITION ISOTHERM OF SYSTEM $(CH_3)_3NO-SO_2$ AT −20°

SO_2 in cond. phase, cc.[a]	59.3	57.0	54.0	52.5	41.8	31.2	29.7
Pressure, mm.	144	28	27	27	26	25.5	0.0
Molecular ratio of SO_2 to amine oxide	1.98	1.90	1.80	1.75	1.39	1.04	0.99

[a] The material remained completely solid at all compositions recorded.

twelve mole per cent. Since the SO_2-content of the compound, remaining after pumping at −20°, was within 1% of that represented by the formula $(CH_3)_3NOSO_2$, it seems likely that the impurity was $(CH_3)_3NSO_3$, which has been shown to be practically inert toward sulfur dioxide. Another indication of such a by-product is found in the tensiometric behavior of the mother liquor remaining after crystallizing out a large part of the $(CH_3)_3NOSO_2 \cdot SO_2$ from a sulfur dioxide solution (Table VIII).

Change of Decomposition Pressure of $(CH_3)_3NOSO_2 \cdot SO_2$ with Temperature.—To the decomposition pressure of $(CH_3)_3NOSO_2 \cdot SO_2$ at −20°, namely, 26 mm., two other determinations were added: 141 mm. at −9.3° and 570 mm. at 0.0°. The three values indicate the equation $\log p_{mm.} = 19.918 - (4687/T)$, from which the check values 25.1 mm. at −20°, 141.6 mm. at −9.3°, and 570 mm. at 0.0° are calculated. The agreement is further evidence that a true compound was formed. The equation implies that $\Delta F^0 = 21.44 - 0.0779T$ (in kilogram calories). The temperature at which $\Delta F^0 = 0$ (*i. e.*, $p = 760$ mm.) is computed to be +2.4°.

Tensiometric Behavior of $(CH_3)_3NOSO_2$ in Liquid SO_2 at 0°.—The second of the two samples of $(CH_3)_3NOSO_2$—a quantity equivalent to 27.6 cc. of normal gas—was used in a preliminary study of the effect of the compound upon the vapor tension of sulfur dioxide. The results, shown in Table VIII, indicate a very considerable degree of dimerization in solution, probably complicated by the effect of solvation. The increase of the apparent mole fraction, during crystallization from the saturated solution, indicates the presence of a soluble impurity. Since the composition of the pumped material is given accurately as $(CH_3)_3NOSO_2$, it seems likely that the by-product is $(CH_3)_3NSO_3$. Other evidence of a relatively inert impurity has been seen in the results of the study of the pressure-composition isotherm at −20°.

TABLE VIII

TENSIOMETRIC EFFECT OF $(CH_3)_3NOSO_2$ IN LIQUID SO_2

Sample equivalent to 27.6 cc. of gas

SO_2 in cond. phase, millimoles	Δp	$\Delta p/p_0$ (app. mole fr.)	Calcd. mole fr. solute	Ratio apparent/calcd. mole fraction
474.0	41.7	0.0356	0.0618	0.576
265.0	78.0	.0665	.1166	.570
213.4	104.7	.0894	.148	.604
183.8	128.2	.1094	.177	.618
181.0	131.6	.1123	.181	.621
178.7	134.2	.1146	.184	.623
175.5	138.2	.1180	.187	.631
165.0	150.6	.1285	.201	.640
169.5	104.5	.0893	Crystals	
149.3	118	.1008		
131.2	136	.1120		

After all of the excess sulfur dioxide had been removed, by distillation at room temperature, the tube was opened to the air. The powdery sample was found to be non-deliquescent.

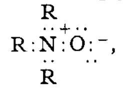
Discussion

The facts here reported constitute the basis for a comparison of five different compounds, in regard to their power to employ their unshared electrons for bonding the electron acceptor molecule, SO_2. The order of increasing attraction for sulfur dioxide appears to be $(CH_3)_3NSO_3$, $(CH_3)_3NSO_2$, $(CH_3)_3NOSO_2$, $(CH_3)_3N$, $(CH_3)_3NO$. This comparison is chiefly significant in relation to the structures of the compounds, consideration of which will next be in order.

The compound $(CH_3)_3NSO_3$ has been called a "betaine" of dimethylaminosulfonic acid,[10] but this seems artificial when compared with the simpler statement that SO_3 is attached to N through its otherwise unshared pair of electrons. The relative inertness of the compound, toward sulfur dioxide, is explained by the assumption that the oxygen atoms of the SO_3 are chiefly double-bonded to sulfur, and thus retain very little electron-dative external bonding power. This assumption may be justified by reference to the otherwise unoccupied *3d* orbitals of sulfur. It appears to be required also to explain the stability of the compound, since the single-bonding of more than one of the three oxygen atoms would lead to a violation of the adjacent charge rule.

The compound $(CH_3)_3NSO_2$ appears to be formed simply by electron sharing between nitrogen and sulfur. Its tensiometric behavior in liquid sulfur dioxide offers clear evidence against an ionic dimer of the type $(R_3N)_2SO^{++}SO_3^{=}$, although the small conductivity would suggest that there might be an equilibrium between much $(CH_3)_3NSO_2$ and little $[(CH_3)_3N]_2SO^{++}SO_3^{=}$. The latter form, if present at all, would not seriously affect the interpretation of results.

Assuming, therefore, that this compound differs from $(CH_3)_3NSO_3$ only in the absence of one neutral oxygen atom, one can understand its greater solubility and apparent solvation in liquid sulfur dioxide, since the sulfur atom of $(CH_3)_3NSO_2$ would have an unshared pair of electrons. This would imply a greater electron density in sulfur, and the effect would be a greater electron-dative bonding power in the SO_2 unit of $(CH_3)_3NSO_2$. It is also not difficult to understand the wide difference of stability, between $(CH_3)_3NSO_3$ and $(CH_3)_3NSO_2$, since greater electron density in the latter would tend to weaken the N→S link. Since both compounds are fairly soluble, it seems unlikely that the difference of lattice energy would be an important factor.

The high dative bonding power of trimethylamine oxide already was discernible in the considerable stability of the dihydrate,[12] and now is still more clearly evident. It is easily explained in terms of the singly-bonded oxygen atom in the structure  $\mathrm{R}:\overset{\mathrm{R}}{\underset{\mathrm{R}}{\overset{+}{\mathrm{N}}}}:\ddot{\underset{..}{\mathrm{O}}}:^{-}$, an oxygen atom which appears to be in essentially the same condition as that in the hydroxyl ion, an unusually strong electron-donor. It therefore would have been reasonable to expect an attachment to sulfur dioxide, so strong that only the destruction of the amine oxide structure would allow a release of the sulfur dioxide, and also strong enough to destroy the attraction of the amine oxide toward water.

The attachment of more sulfur dioxide to $(CH_3)_3NOSO_2$, to form a definite secondary addition compound, may be regarded as a residual effect of the high external bonding power of the amine oxide oxygen atom. It seems useless to attempt a decision of the question whether the second sulfur dioxide molecule links to the oxygen of the amine oxide or to one of the SO_2 oxygen atoms, since the tensiometric evidence of dimerization in SO_2 solution leaves doubt concerning the structural plan of this compound. The dimerization might be only a dipole effect, or it might represent a structure quite different from that implied by the formula $(CH_3)_3NOSO_2$.

Summary

Trimethylamine reacts with sulfur dioxide, yielding the solid compound $(CH_3)_3NSO_2$. For the reverse reaction, $\Delta F^0 = 28.95 - 0.07404\,T$ (kcal.). No definite secondary addition compounds could be recognized, but extensive solvation seems to occur in liquid sulfur dioxide solutions. Neither ionization nor association was evident. The compound $(CH_3)_3NSO_3$ is less soluble and less evidently solvated.

Anhydrous trimethylamine oxide absorbs sulfur dioxide at −80°, forming the compound $(CH_3)_3NO(SO_2)_2$. This easily loses SO_2 to form the very stable $(CH_3)_3NOSO_2$, distinctly different from $(CH_3)_3NSO_3$. The amine oxide addition compound appears to be dimeric in solution in sulfur dioxide.

The relation of the results to the electron theory of chemical bonding is discussed.

LOS ANGELES, CALIFORNIA RECEIVED JANUARY 9, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Addition of Boron Fluoride to Hexamethylenetetramine

BY ANTON B. BURG AND LA VERNE LEE MARTIN[1]

Hexamethylenetetramine, which contains four equivalent tertiary-amine nitrogen atoms,[2,3] appears to offer interesting possibilities for the study of the effect of complex bonding at one nitrogen atom upon the dative bonding power of nearby nitrogen atoms. Such an effect should be most clearly recognizable if one employs only singly-coördinating molecules, such as the boron halides, sulfur trioxide, or phosphorus pentafluoride, for forming the complex compounds with the polynitrogen tertiary amine. Studies of this character, insofar as they may yield intelligible results, should aid the understanding of numerous metal-complexes of polyfunctional bases.

Each of the four nitrogen atoms of hexamethylenetetramine might be expected to employ its unshared pair of electrons for bonding a molecule of boron fluoride; hence one would expect the addition of four equivalents of boron fluoride as an upper limit. This limit actually can be reached, but only by a very special method.

Treatment of $(CH_2)_6N_4$ with BF_3.—When boron fluoride, generated from potassium fluoborate and purified by a B_2O_3-H_2SO_4 washing tube,[4] was passed into a chloroform

---

[1] Most of the results here described were taken from a thesis presented by La Verne Lee Martin to the Graduate School of the University of Southern California, in partial fulfillment of the requirements for the degree of Master of Arts, June, 1940. Much of the experimental work was performed in the laboratories at La Verne College, La Verne, California.

[2] Dickinson and Raymond, THIS JOURNAL, **45**, 22 (1923).

[3] Hampson and Stosick, *ibid.*, **60**, 1814 (1938).

[4] Booth and Willson, *ibid.*, **57**, 2273 (1935); "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, Vol. I, p. 21.