63. *Molecular Compounds between Amines and Sulphur Dioxide. A Comment on Jander's Theory of Ionic Reactions in Sulphur Dioxide.*

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Jander's theory of ionic reactions in liquid sulphur dioxide (cf. *Ann. Reports*, 1939, **36**, 141) is based essentially on (*a*) the occurrence of reactions in which chlorine is displaced as chloride ion from thionyl chloride by means of other anions including sulphite ion, and (*b*) a supposed demonstration that amine–sulphur dioxide addition compounds have the structure $[(R_3N)_2SO]^{++}[SO_3]^{--}$ Our knowledge of the mechanisms available in substitution processes suffices to show that argument (*a*) does not necessitate the theory; and the chemistry on which argument (*b*) is based is incorrect. For instance, Jander has mistaken triethylammonium hydrogen sulphite for the triethylamine–sulphur dioxide addition compound, and his various supposed demonstrations of exchange or oxidation of the sulphite ion, without disturbance to the SO group presumed to be contained in the cation, are all quite illusory. The real addition compound of triethylamine and sulphur dioxide is deeply coloured in the liquid state and in solution. It is a weak electrolyte in sulphur dioxide. Its molecular weight in sulphur dioxide, as determined by elevation of the boiling point of the solvent, corresponds to the simple formula R_3NSO_2. It reacts easily with water and oxygen to form colourless triethylammonium salts, chiefly the hydrogen sulphite, hydrogen sulphate, and normal sulphate. Its constitution is discussed, particularly in relation to Weiss's electron-transfer theory of certain types of molecular compound.

Jander and his collaborators have advanced a comprehensive theory of reactions in liquid sulphur dioxide (Jander and Wickert, *Z. physikal. Chem.*, 1936, *A*, **178**, 57; *Ber.*, 1937, **70**, 251; Jander and Ullmann, *Z anorg. Chem.*, 1937, **230**, 405; Jander, Knoll, and Immig, *ibid.*, **232**, 229; Jander and Immig, *ibid.* **233**, 295; Jander and Ruppolt, *Z. physikal. Chem.*, 1937, *A*, **179**, 43). The theory appears to have gained at least a limited degree of acceptance; Emeléus, for example, characterises it as " convincing " (*Ann. Reports*, 1939, **36**, 141; cf. Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry," p. 482). According to this theory, ions are created in liquid sulphur dioxide by the transference of an oxide ion (O^{--}), much as they are created in water by the transference of a proton. There is the difference that the ions formed by oxide-ion transfer are bivalent, but, this being understood, the ionic equilibrium assumed for sulphur dioxide, $2SO_2 \rightleftharpoons SO^{++} + SO_3^{--}$, is compared with the fundamental ionic equilibrium of aqueous solution: $2H_2O \rightleftharpoons H_3O^+ + OH^-$. It is implied that, for reactions in sulphur dioxide, ionised sulphites are " analogous to bases," *i.e.*, that they play a role which is similar, apart from the valency difference, to that of ionised hydroxides in aqueous reactions. Likewise, the assumed cation SO^{++} is supposed to function, except as to its valency, similarly to the hydrogen ion of aqueous solutions.

The arguments by which Jander seeks to establish this concept are of two general kinds, which it is convenient to distinguish since they are to be criticised on different grounds.

Argument (1) has reference to the reactions of thionyl chloride with inorganic anions. The central example is the reaction with sulphites, *e.g.*, $Cs_2SO_3 + SOCl_2 \longrightarrow 2SO_2 + 2CsCl$, which Jander regards as a process " analogous to neutralisation "—essentially a combination of SO^{++} with SO_3^{--} to form undissociated solvent.

Argument (2) consists in the claim that amines take up SO^{++} from sulphur dioxide, just as they take up protons from water, to form ammonium ions—diammonium ions in sulphur dioxide, because of the bivalency of SO^{++}. The most fully discussed example is that of triethylamine. Analytical support is claimed for the conclusion that this base exists in sulphur dioxide essentially in the form of the ion-pair (I); that this form can be isolated by evaporation of the solvent as a colourless crystalline salt; and that it can be made to undergo anion exchange without disturbance to the SO group in the cation. Jander compares the formation of ion-pair (I) to the formation of ammonium hydroxides in aqueous solutions of amines.

$$[(NEt_3)_2SO]^{++}[SO_3]^{--} \quad (I.)$$

The obvious comment on argument (1) is that it does not necessitate the theory. Thionyl chloride reacts generally with weakly acidic hydroxyl compounds or their anions to liberate, ultimately, both its chlorine atoms as chloride ions, as well as a molecule of sulphur dioxide. We should certainly expect thionyl chloride to show the same type of reactivity towards the anion of so weak an oxy-acid as the bisulphite ion, the special nature of which provides an evident reason for the formation of the second molecule of sulphur dioxide. It is difficult to see what else could happen.

In some reactions of thionyl chloride with organic hydroxyl compounds it is possible to distinguish a first stage, in which only one chlorine atom of the two in thionyl chloride has become liberated as a chloride ion; the other product is then an organic chlorosulphinate, $R{\cdot}O{\cdot}SOCl$. We still do not know, however, whether, or in what circumstances, this first stage is a single process, or is itself composite. The chlorosulphinate might be formed by a bimolecular reaction between the molecule $SOCl_2$ and the hydroxyl compound or its anion; alternatively, it might arise from a unimolecular reaction in which, first, the thionyl chloride ionises to $SOCl^+$ and Cl^-, and then, in a subsequent fast stage, the cation $SOCl^+$ decomposes the hydroxyl compound or associates with the anion. We are familiar with this type of problem in connexion with the substitution reactions of alkyl and acyl halides *: no one would dogmatise nowadays as to the mechanism of such a reaction simply on the basis of a knowledge of the products.

Although the reaction of thionyl chloride with sulphite ion has not yet been separated into stages, it is natural to suppose that two stages exist corresponding to the liberation as chloride ion of the two chlorine atoms. This being assumed, the entity with which the sulphite ion interacts in the first stage may, as shown above, be $SOCl_2$ in a bimolecular displacement of one chloride ion; or it may be $SOCl^+$, the displacement being of a unimolecular nature; it cannot be SO^{++} as in Jander's theory. Even if the assumption of stages be rejected, it remains true that the nature of the ultimate product of the sulphite reaction is not determinative with respect to mechanism.†

Jander's argument (2) is much more to the point; indeed, our opinion is that it would prove his thesis if the alleged facts were true. However, we consider them erroneous for reasons to be shown.

We became interested in this subject because, at the time of the appearance of Jander's papers, we were planning a study of the kinetics of the reaction between tertiary amines and alkyl halides in sulphur dioxide solution—a study which we subsequently carried a certain distance (cf. J., 1940, 1011). It was, however, necessary as a preliminary measure to ascertain whether, for instance, in sulphur dioxide solution, there really are *two* molecules of amine in each kinetically separate particle containing amine, as formula (I) would represent in the case of triethylamine. The internal evidence in Jander's papers, as well as the previous literature of sulphur dioxide–amine systems, seemed to make it very probable that Jander's conclusions were in error, and this was confirmed as soon as we began to study sulphur dioxide solutions of triethylamine. Our results bear on the general question of the nature of molecular compounds and are published in view of the interest recently evinced by other workers in this subject.

The compound to which formula (I) is assigned by Jander and Wickert was obtained by dissolving triethyl-

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* Unimolecular and bimolecular substitutions of *acid* halides have been studied in these laboratories, but the results are not yet published.

† No discussion is included in the text of Jander's reactions between thionyl chloride and other anions, because for these even the nature of the ultimate substitution products is hypothetical.

amine in sulphur dioxide and evaporating the solvent. They describe it as a colourless, crystalline substance of m. p. 73°. The composition $(NEt_3 + SO_2)_n$ is stated to have been established by analysis, but an independent appraisal of the only analysis which is even partially quoted, an estimation of the SO_2 content, is precluded by the omission of an essential figure, *viz.*, the weight of substance which gave the stated *weight* of sulphur dioxide (the percentage content is not given). No evidence of molecular complexity is presented, the value $n = 2$ being assumed without proof.

Our finding is that no colourless, crystalline solid compound having a melting point above the room temperature is formed by the combination of triethylamine and sulphur dioxide alone, although various saline substances can be obtained from mixtures of triethylamine and sulphur dioxide by permitting the absorption of moisture and oxygen. Such absorption, however, naturally alters the composition as found by analysis.

In the absence of moisture and oxygen, triethylamine and sulphur dioxide combine, with considerable evolution of heat, to form an orange-red liquid. On cooling to $-80°$, this sets to a colourless crystalline solid, which, at a temperature well below 0°, melts to the same strongly coloured liquid. This substance appears to have a small but appreciable vapour pressure at room temperature, possibly an indication of dissociation. Either triethylamine or sulphur dioxide can be gradually withdrawn at low pressure with the aid of a chemical absorbent; and, if the absorbent is selective for one of the volatile components, the other accumulates in the gas space. The composition of the residual orange-red liquid is, however, definite, and corresponds to the formula $(NEt_3 + SO_2)_n$, as determined by estimation of its triethylamine and sulphur dioxide content (p. 247). Its molecular complexity has been determined in sulphur dioxide, in which the compound forms a bright orange-yellow solution. It was first demonstrated that, although this solution has a finite electrical conductivity, this is of such an order of magnitude as to indicate that only a quite small proportion of the solute exists in the form of dissociated ions (p. 247). Next, the apparent molecular weight of triethylamine (weighed as such) in sulphur dioxide was found to be normal (p. 247) by measurement of the elevation of the boiling point of the solvent. Since there is no extensive electrolytic dissociation to be taken into account, this result shows that only one triethylamine molecule is contained in each kinetically independent particle of the coloured compound which constitutes the solute. Finally, the molecular weight in sulphur dioxide of the isolated coloured compound (weighed as such) was determined by the same method : it also was normal to within the error of measurement (p. 247). This established the essentially monomeric character ($n = 1$) of the coloured compound $(NEt_3 + SO_2)$ in sulphur dioxide solution.

When this compound is exposed to atmospheric air it absorbs water rapidly, and oxygen more slowly. The first visible effect is due essentially to the absorption of water, which converts the original orange-red liquid into a mass of colourless crystals, having m. p. 74—75°. This appears to be a single compound. It has the composition $(NEt_3 + SO_2 + H_2O)$ as we have proved by estimating the triethylamine content as usual, and the sulphur dioxide content both by quantitative oxidation with bromine and by precipitation as barium sulphate after oxidation with excess of bromine. The last two estimations distinguish water absorption, which does not destroy the reducing power of the sulphur dioxide, from oxygen absorption, which does (p. 247). On account of the agreement in melting point and general physical character, we suppose this compound to be the substance for which Jander claimed to have obtained analyses agreeing with the composition $(NEt_3 + SO_2)$. Obviously it is *triethylammonium hydrogen sulphite*, $[NEt_3H]^+[HSO_3]^-$.

This salt is hygroscopic, but even if kept in dry air it undergoes further change, the melting point at first dropping to 55° or lower and then rising to above 115°. Using the same method of analysis, we showed that these changes are due to absorption of oxygen, the bisulphite radical becoming progressively replaced by bisulphate (p. 247). Specimens melting above 115° were found to consist mainly of triethylammonium hydrogen sulphate $[NEt_3H]^+[HSO_4]^-$, though they still contained appreciable amounts of the hydrogen sulphite.

Specimens which had become oxidised also contained a proportion of normal triethylammonium salts : the triethylamine content was slightly higher than corresponded to the sulphite plus sulphate. This can be readily explained if we assume the contaminant to be normal triethylammonium sulphate, though the analyses do not distinguish the presence of this from that of the corresponding normal sulphite. The conversion of triethylammonium hydrogen sulphite by oxidation into triethylammonium hydrogen sulphate produces a considerably stronger acid, and we may well suppose that this would remove a certain amount of triethylamine from the still unoxidised hydrogen sulphite to form normal triethylammonium sulphate, in addition to sulphurous acid which would become lost Such a loss of sulphur dioxide, over and above the loss by oxidation, appears clearly in the analytical figures (p. 247).

Jander and Wickert claim to have demonstrated anion exchange in compound (I), without disturbance to the structure of its cation, by the isolation of a salt of structure (II) after double decomposition with potassium bromide :

$$\text{(I.)}\quad [(NEt_3)_2SO]^{++}[SO_3]^{--} \xrightarrow[KBr]{} [(NEt_3)_2SO]^{++}Br_2^{-}\quad \text{(II.)}$$

The salt is said to have been obtained as a residue on evaporation of the sulphur dioxide solvent after filtration from precipitated potassium sulphite. It is described as a white solid of m. p. 230°.

This claim is clearly untenable in the light of the evidence given above : neither the real addition compound of trithylamine and sulphur dioxide, nor the triethylammonium hydrogen sulphite which Jander mistook for it, could have yielded such a substance. As a matter of fact the claim is just as clearly untenable on the evidence which Jander and Wickert themselves provide. Amplifying a general statement to the effect that their salt was pure and its analysis satisfactory, the authors refer to two estimations. One was of the sulphur content : it gave the result that a quantity of salt corresponding to a content of 0·2968 g. of triethylamine contained 0·0128 g. of sulphur, a figure which, the authors say, is to be compared with a theoretically calculated sulphur content of 0·0129 g. The theoretical sulphur content has, however, been incorrectly calculated, and should be 0·0470 g. The second estimation was of the bromine content, but any independent appraisal of this is excluded by the omission, once again, of an essential figure. There is no evidence at all that the solid analysed was not impure triethylamine hydrobromide, containing a minor proportion of either triethylammonium hydrogen sulphite or (more probably) the hydrogen sulphate. The melting point of pure triethylamine hydrobromide is given in the literature as 248—250°, and hence the melting point of the residue which Jander and Wickert claimed to be salt (II) is not inconsistent with the interpretation suggested.

Similarly untenable is Jander and Immig's claim to have oxidised compound (I) by means of iodine in sulphur dioxide with the result that the sulphite anion was converted into sulphate or exchanged for iodide, all without affecting the SO group in the cation :

$$I_2 + 2[(NEt_3)_2SO]^{++}[SO_3]^{--} \longrightarrow [(NEt_3)_2SO]^{++}[SO_4]^{--} + [(NEt_3)_2SO]^{++}I_2^{--} + SO_2$$

How much iodine will be absorbed by a solution of triethylamine in sulphur dioxide simply depends on how much water, and how much oxygen, have previously been absorbed from the atmosphere, in fact, on how much hydrogen sulphite ion has been formed by hydration and not destroyed by oxidation.*

The compounds of amines with sulphur dioxide are the subject of a considerable previous literature, which is in general agreement with the preceding conclusions. Prior to Jander's publications, numerous aliphatic, aromatic, and heterocyclic amines had been shown to form coloured, easily dissociable, sulphur dioxide addition compounds, having the two components in 1 : 1 molecular ratio (Michaelis, *Ber.*, 1891, **24**, 745; *Annalen*, 1892, **274**, 192, 208; André, *Compt. rend.*, 1900, **130**, 1714; Korezynski and Glebocka, *Gazzetta*, 1920, **50**, I, 378; Hill, *J. Amer. Chem. Soc.*, 1931, **53**, 2598; Foote and Fleischer, *ibid.*, 1934, **56**, 870; Hill and Fitzgerald, *ibid.*, 1935, **57**, 250). With the addition compounds of the less volatile amines a general tendency had been noted towards the loss of sulphur dioxide preferentially; and also, on exposure to air, towards a concurrent loss of colour. In a more detailed study of these phenomena in the case of the aniline addition compound, ($NH_2Ph + SO_2$), Hill showed that, on exposure to the atmosphere, this substance loses some of its sulphur dioxide, and simultaneously absorbs moisture, forming a mixture of colourless salts, which he identified as the hydrogen sulphite and normal sulphite of aniline. The more recent investigators have concentrated on measurements of the physical properties and phase-equilibria of amine–sulphur dioxide systems (cf. Foote and Fleischer, Hill and Fitzgerald, *locc. cit.*; also Bright and Jasper, *J. Amer. Chem. Soc.*, 1941, **63**, 2486; Bright and Frobenius, *ibid.*, 1943, **65**, 637; Burg, *ibid.*, p. 1629). Burg concluded from a study of the vapour pressure of the trimethylamine–sulphur dioxide system that the simple formulation $Me_3N \rightarrow SO_2$ for the addition compound is to be preferred to Jander's.

The difficulty we have with the simple, covalent formulation of the addition compounds is that it does not seem easy to account on this basis for their strong colour—for instance, that of the triethylamine–sulphur dioxide compound in the liquid state or in solution in sulphur dioxide. The simple formula $R_3N \rightarrow SO_2$, or its equivalent $R_3\overset{+}{N}-\overset{-}{S}O_2$, depicts a zwitterion : it is an internal ammonium sulphinate, in the same sense as that in which an amine oxide is an internal ammonium oxide. The electronic frequencies both of ammonium ions and of sulphinate ion groups are sufficiently far out in the ultra-violet to make it appear improbable that a zwitterion composed from these two groups should show strong visible colour. The coloured compounds are, moreover, weak, though not very weak, electrolytes in sulphur dioxide. Thus the conductivity of triethylamine–sulphur dioxide in, say, 0·025M-solution at −10·75° is of the order ($10^5\kappa = 3$) of 1% of that of a typical strong electrolyte such as tetraethylammonium chloride at the same concentration and temperature ($10^5\kappa = 216$). The suggestion we would make is that the coloured compounds may exemplify the process to which Weiss in particular has called attention, namely, the formation of molecular compounds by partial or complete electron transfer (Weiss, *Nature*, 1941, **147**, 512; *Trans. Faraday Soc.*, 1941, **37**, 780; J., 1942, 245; J., 1943, 462). It is not, of course, a consequence of this hypothesis that the ions $(NR_3)^+(SO_2)^-$, even when fully formed, must become completely dissociated in any particular solvent, since they may (to put it crudely) attract each other more strongly than the solvent attracts each of them : a necessity for a free-energy increase on dissociation will limit the extent of the process. The ions are, of course, also free radicals, and therefore it should be possible to test this suggestion by means of magnetic measurements or the catalysis of ortho–para-hydrogen conversion. The reason we have not done this is that the work here described was performed only to guide our interpretation of another investigation, and was not intended itself to lead to a publication.

EXPERIMENTAL.

Purification of Materials.—A sample of triethylamine from the British Drug Houses was kept for several days over successive fresh samples of solid potassium hydroxide ("AnalaR"). When the latter no longer became moist or brown,

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* It seems obvious that a similar series of criticisms will be found applicable to Jander, Knoll, and Immig's findings, which we have not directly reinvestigated, concerning the compound of unsubstituted ammonia with sulphur dioxide. For this they claim to have established the structure $[(NH_3)_2SO]^{++}SO_3^{--}$ by means of a series of reactions, closely similar to those attributed to the corresponding triethylamine derivative.

the amine was boiled for some hours under reflux with fused barium oxide and fractionated. The part having b. p. 89·3—89·7°/758 mm. was kept for one day over sodium, then boiled under reflux over a fresh sample of sodium, and again fractionated. The centre fraction had b. p. 89·6—89·7°/758 mm. Sulphur dioxide, from a fresh, full syphon, was distilled into the first bulb of an all-glass apparatus, where it was dried by means of phosphoric oxide, and distilled through a column of this reagent.

Triethylamine–Sulphur Dioxide.—A well-dried apparatus filled with nitrogen being used, triethylamine (*ca.* 14 c.c.) and sulphur dioxide (*ca.* 5 c.c.) were brought together in a bulb cooled with solid carbon dioxide and alcohol. The temperature was then allowed to rise, and the apparatus was pumped out for some hours with a rotary oil pump. The pressure was increased to atmospheric by the admission of dry nitrogen in order to facilitate the removal of samples. The ***molecular compound*** is an orange-red, rather viscous liquid at the ordinary temperature; dilute solutions of it in sulphur dioxide are bright orange-yellow, and they may, of course, be prepared either by adding triethylamine to excess of liquid sulphur dioxide or by first preparing the molecular compound as described above [Found : $\mathrm{NEt_3}$, 60·9; $\mathrm{SO_2}$ (by oxidation), 39·1; $\mathrm{SO_2}$ (as $\mathrm{BaSO_4}$), 39·5. $\mathrm{NEt_3SO_2}$ requires $\mathrm{NEt_3}$, 61·2; $\mathrm{SO_2}$, 38·8%].

A number of measurements were made of the conductivity of the compound in sulphur dioxide at −10·75°. For this purpose the sulphur dioxide, purified as described above, was subjected to an additional distillation from a little triethylamine; the distillate, which was quite colourless, was then distilled into the conductivity cell. All distillations were non-ebullient, and were carried out in a good vacuum, and in well-dried apparatus. Triethylamine was added directly to the sulphur dioxide in the cell by using a weight pipette. The temperature was maintained by means of a thermostat fitted with an " Electrolux " refrigerating unit, a small heating bulb, and the usual regulating devices. It was found that the conductivity of the sulphur dioxide solvent was too low to be measured with our apparatus, whereas the solutions had small, but quite appreciable, conductivities, which, however, increased slowly with time. The following experiment is typical : Molarity = 0·0237; conductivity readings :

Time after mixing	3 mins.	1·75 hrs.	19·0 hrs.
$10^5 \kappa$ (with κ in ohm^{-1}cm.$^{-1}$)	2·9	3·4	4·0

In spite of many attempts we have failed to trace the cause of this slow increase of conductivity. However, since the design of our conductivity cell was not such as to exclude rigorously all air and moisture (in order to facilitate cleaning and charging, the cell was " loose " and merely stoppered, not sealed on to a vacuum line), we are not disposed to attach any special significance to the effect, for which a minute amount of hydration and oxidation could be held responsible. Thus we regard the earliest reading as the best approximation to the true conductivity of the molecular compound. It seems to be too closely reproducible to be ascribed to an adventitious impurity, although we cannot be dogmatic with regard to the significance of a conductivity of this small order.

The molecular weight of triethylamine in sulphur dioxide was determined ebullioscopically. A Walker–Lumsden apparatus, adapted on obvious lines for use with solvents boiling below room temperature, was employed for the purpose. With 0·54 g. of triethylamine, the following elevations were recorded :

Vol. of solution (c.c.)	7·25	8·30	9·25	12·35
Elevation of b. p.	0·80°	0·60°	0·50°	0·35°

From the graph of the results we find $M = 111$ (calc. for $\mathrm{NEt_3}$: $M = 101$).

The same method being used, a determination was made of the molecular weight of triethylamine–sulphur dioxide (weighed as such, with precautions against access of air and moisture) in sulphur dioxide solution. With 1·27 g. of triethylamine–sulphur dioxide, the following elevations were obtained :

Vol. of solution (c.c.)	10·20	11·50	12·75	16·50	18·15
Elevation of b. p.	0·92°	0·77°	0·70°	0·50°	0·45°

From the graph of these data we find $M = 151$ (Calc. for $\mathrm{NEt_3SO_2}$: $M = 165$). The ebullioscopic method, as used by us, was not very precise : we assess the possible error as about 15%.

Hydration and Oxidation of Triethylamine–Sulphur Dioxide.—A sample of the liquid molecular compound was exposed to ordinary air and stirred until the colour just vanished. The dry solid so formed had m. p. 74—75°, and appeared from its analysis to consist of fairly pure ***triethylammonium hydrogen sulphite*** [Found : $\mathrm{NEt_3}$, 54·9; $\mathrm{SO_2}$ (by oxidation), 35·3; $\mathrm{SO_2}$ (as $\mathrm{BaSO_4}$), 36·5. $\mathrm{NEt_3H_2SO_3}$ requires $\mathrm{NEt_3}$, 55·2; $\mathrm{SO_2}$, 35·0]. This material was exposed over phosphoric oxide in the vacuum of a good oil pump for 45 minutes. It then had m. p. 68—70° [Found : $\mathrm{SO_2}$ (by oxidation), 34·3%]. The salt is hygroscopic.

The same substance was kept overnight in air at atmospheric pressure over phosphoric oxide. It then had m. p. 55—60°, and according to its analysis contained a considerable quantity of triethylammonium hydrogen sulphate as well as a small proportion of normal triethylammonium salts [Found : $\mathrm{NEt_3}$, 56·7; $\mathrm{SO_2}$ (by oxidation), 23·2; $\mathrm{SO_2}$ (as $\mathrm{BaSO_4}$), 36·0%]. After several weeks' keeping in dry air, these processes had gone further. The material now had m. p. 117—120°, and according to its analysis consisted mainly of triethylammonium hydrogen sulphate with minor proportions of the hydrogen sulphite and of normal triethylammonium salts [Found : $\mathrm{NEt_3}$, 53·9; $\mathrm{SO_2}$ (by oxidation), 6·0; $\mathrm{SO_2}$ (as $\mathrm{BaSO_4}$), 31·0. Calc. for $\mathrm{NEt_3H_2SO_4}$: $\mathrm{NEt_3}$, 50·8; $\mathrm{SO_2}$ (by oxidation), 0·0; $\mathrm{SO_2}$ (as $\mathrm{BaSO_4}$), 32·2%].

Some further analyses are quoted for samples of oxidised salts obtained in other experiments, the conditions of preparation varying slightly from case to case. A sample obtained by exposure of the molecular compound in a desiccator over potassium hydroxide with occasional admission of ordinary moist air had m. p. 55–59° and was unusually rich in normal triethylammonium salts, a circumstance which may be correlated with the observation that an odour of triethylamine is produced when the molecular compound is left in an evacuated desiccator over potassium hydroxide [Found : $\mathrm{NEt_3}$, 57·7; $\mathrm{SO_2}$ (by oxidation), 20·2; $\mathrm{SO_2}$ (as $\mathrm{BaSO_4}$), 28·5%]. A crust of solid salts skimmed off from the surface of the liquid molecular compound had m. p. 64—67° [Found : $\mathrm{NEt_3}$, 55·3; $\mathrm{SO_2}$ (as $\mathrm{BaSO_4}$), 31·4%]. Material taken directly from excess of the liquid molecular compound by diluting it with ether and acetone, filtering off the substance, and washing it with these solvents, was left for some days in a desiccator. It then had m. p. 115—118° [Found : $\mathrm{NEt_3}$, 54·4, 54·3; $\mathrm{SO_2}$ (as $\mathrm{BaSO_4}$), 32·0%].

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[*Received, February 21st,* 1944.]