VI.—*Action of the Halogens on the Salts of Trimethylsulphine.*

By LEONARD DOBBIN, Ph.D., and ORME MASSON, M.A., D.Sc., Chemical Laboratory of the University of Edinburgh.

I. *Action of Iodine on the Haloid Salts.*

WHEN dry trimethylsulphine iodide is shaken up with an ethereal solution of iodine, it becomes converted into a heavy black tarry liquid, which smells strongly of iodine; this is easily soluble in alcohol, and it reappears unchanged when the solution is evaporated. It decomposes slowly when warmed with water, iodine being evolved. It was not found possible to obtain the substance in a state fit for analysis, but there is no doubt that it is of the order of the so-called polyiodides. Jürgensen (*J. pr. Chem.*, **3**, 338) obtained a similar compound of triethylsulphine, which gave a crystalline double salt with mercuric iodide.

The bromide and the chloride of trimethylsulphine behave in a similar manner; but, if the tarry product is washed with ether and dissolved in alcohol, large reddish-black crystals are obtained when the solution is evaporated over sulphuric acid. These crystals smell of iodine and are not stable in the air. In these circumstances, it was not thought worth while to analyse them, but their general resemblance to the more stable compounds described below leaves no doubt in our minds that they consist respectively of the *bromo-diiodide* and the *chloro-diiodide* of trimethylsulphine,— Me_3SBrI_2 and Me_3SClI_2 . A compound in all respects similar to, and probably identical with, the second of these, is obtained by acting on trimethylsulphine iodide with iodine monochloride.

II. *Action of Bromine on the Iodide.*

When bromine vapour is poured over dry trimethylsulphine iodide, much heat is developed and the colourless crystals melt to a dark red liquid. The reaction goes more quickly, and, in fact, with violence, if the bromine is added in the liquid state. When addition of bromine produces no further action, the heavy red oil is exposed for a short time to the air, whereby it loses most of the excess of bromine and becomes solid. The mass is then broken up, shaken two or three times with a little ether, to remove the last traces of bromine, and dissolved in sufficient hot alcohol; as the solution cools, an abundant crop of brilliant orange-red crystals is deposited. The mother-liquor

gives a further but smaller yield when allowed to evaporate in a vacuum; these crystals are of a somewhat darker shade in colour than the others, although of the same composition. The total yield approaches very nearly to that indicated by theory.

Analysis shows the compound to be *trimethylsulphine dibromiodide*, Me_3SIBr_2 . The sulphur was estimated by combustion with a mixture of five parts of potassium carbonate to one of potassium chlorate,—a method we would recommend for those cases where the sulphur is combined directly with methyl, &c. The halogens were estimated in solutions obtained by decomposing the salt with dilute sulphurous acid: in one, the bromine was determined after removing the iodine with cupric sulphate; in the other, the total halogen was determined as silver salt.

- I. 0.2625 gram gave 0.0946 gram CO_2 and 0.0623 gram H_2O .
 II. 0.2564 „ 0.0944 gram CO_2 and 0.0605 gram H_2O .
 III. 0.2329 „ 0.1421 gram BaSO_4 .
 IV. 0.2258 „ 0.2330 gram AgBr .
 V. 0.1073 „ 0.1797 gram mixed AgBr and AgI .

	Calculated.	Found.				
		I.	II.	III.	IV.	V.
C_3	9.87	9.83	10.04	—	—	—
H_9	2.47	2.63	2.62	—	—	—
S	8.79	—	—	8.38	—	—
I	34.89	—	—	—	—	34.74
Br_2	43.96	—	—	—	43.90	—
	100.0	—	—	—	—	—

Properties of Trimethylsulphine Dibromiodide.—The orange-red crystals are not deliquescent, and are perfectly stable in air. When heated, they melt at 94 – 95° , with partial decomposition. A brown oily distillate passes over at higher temperatures and, finally, at about 180° , methyl sulphide and iodine vapour. The crystals are somewhat soluble in cold alcohol or ether, and much more so in hot alcohol. The alcoholic solution seems to undergo slight decomposition on long standing. The reaction with *water* is very characteristic; for the crystals, when shaken with it, with or without the application of heat, quickly melt to a black oil, which resembles the periodide in appearance. On long boiling, it dissolves in the water, iodine being evolved. *Platinic chloride*, added to the alcoholic solution, produces a bulky flesh-coloured precipitate.

This is soluble in hot water, from which it crystallises in the golden cubes and octahedra characteristic of trimethylsulphine platino-chloride. Estimations of the platinum confirmed its identity.

- I. 0.2377 gram of the salt gave 0.0824 gram of platinum.
 II. 0.2436 " " 0.0843 " "

Pt per cent.	Calculated for (Me ₃ S) ₂ PtCl ₆ .	Found.	
		I.	II.
.....	34.94	34.66	34.60

Freshly precipitated *silver oxide*, when shaken with the alcoholic solution, is converted into haloïd salt, the liquid at the same time losing its orange colour and acquiring an alkaline reaction. This is due to the formation of trimethylsulphine hydroxide. On evaporation, some crystals of iodoform are obtained. *Silver nitrate* and *silver sulphate* also decolorise the alcoholic solution, rendering it strongly acid. The corresponding salts of trimethylsulphine are probably produced, but the reactions have not been fully investigated. *Alcoholic potash*, added to the alcoholic solution till the colour is gone, gives a yellow precipitate which increases on the addition of water, and is proved to be iodoform by its smell and general properties. The filtrate from this contains haloïd salts of potassium and trimethylsulphine. The final action of *aqueous potash* on the crystals themselves is the same, except that no iodoform is produced; but there seems to be at first an unstable product formed which imparts an opalescent green colour to the solution. *Ammonia solution* at once converts the crystals of the dibromiodide into a black solid matter which, after careful washing and drying, has the appearance and properties of iodide of nitrogen, exploding with great violence and extreme readiness. The filtrate contains haloïd salts of ammonium and trimethylsulphine.

Ammonia gas acts quite differently. If the gas be blown from the mouth of a bottle of ammonia solution over the orange-red crystals, these at once acquire a dark green colour which, however, the warmth of the hand is sufficient to dispel. But if the crystals be submitted to a current of dry ammonia, this initial green colour quickly gives place to black, which is in turn succeeded, in the course of two hours or more, by a uniform light apple-green. These phenomena are due to the formation of a direct addition product of the composition Me₃SIBr₂.2NH₃. It is an amorphous, non-explosive, light-green solid body, stable only in an atmosphere of ammonia. In a current of dry air, it loses ammonia and reverts to the intermediate black condition, the loss being very rapid at first, then slower and slower,

though it probably becomes complete in the course of time. At a temperature of $75-80^{\circ}$ the compound melts, ammonia is rapidly evolved, and the original dibromiodide is left. Mere solution in alcohol effects a similar decomposition. Water dissolves it with liberation of iodine, which explains the formation of iodide of nitrogen by the action of excess of ammonia solution on the dibromiodide.

The composition of this very unstable compound could be determined only synthetically. It was done in the following manner. The powdered dibromiodide was placed in a porcelain boat inside a short glass-stoppered tube, the weight of the tube and boat together being known, as well as that of the substance taken. The tube was then clamped in a horizontal position, and closed with a cork through which passed two tubes—one for outlet and the other, reaching to the far end, for inlet of the ammonia. The gas, dried by passing through U-tubes containing solid potash, was then allowed to act for a quarter of an hour, at the end of which time it was displaced for a few seconds by dry air, and, the cork having been quickly exchanged for the glass stopper, the tube was weighed.

This operation was repeated several times, until the weight became constant. While weighing—though this was done as quickly as possible—the light green colour became tarnished with black at the edges.

0.7172 gram of the dibromiodide became 0.7841 gram by absorption of ammonia.

	Gain per cent.
Calculated for $\text{Me}_3\text{SIBr}_2, 2\text{NH}_3$	9.34
Found	9.32

III. *Action of Chlorine on the Iodide.*

Chlorine, well washed and dried, is passed into a flask containing dry powdered trimethylsulphine iodide. This at once melts, much heat being developed, and a pasty black substance is formed, which quickly changes to a light yellow solid body. If the flask be surrounded with cold water, the product will remain of a dark colour, for the reaction is checked at the first stage; but it may be completed by afterwards substituting warm water for the cold and continuing the passage of the chlorine. The final product consists of *trimethylsulphine dichloriodide*, Me_3SICl_2 . It is readily purified in the same manner as the dibromiodide, and separates from the hot alcoholic solution in an abundant crop of canary-yellow crystals, which closely resemble the dibromiodide in general properties. The mother-liquor, when evaporated in a vacuum, yields a smaller crop of crystals, of a darker shade, but identical composition. On long standing, the alco-

holic solution undergoes some decomposition, distinctly more than in the case of the dibromiodide.

Analysis.—I. 0.1953 gram of the substance gave 0.0931 gram CO_2 and 0.0582 gram H_2O .

II. 0.1847 gram gave 0.0892 gram CO_2 and 0.0565 gram H_2O .

III. 0.2321 „ 0.1959 „ BaSO_4 .

	Calculated.	Found.		
		I.	II.	III.
C_3	13.09	13.05	13.17	—
H_9	3.27	3.31	3.40	—
S	11.63	—	—	11.59
I	46.18	—	—	—
Cl_2	25.83	—	—	—
	100.00	—	—	—

Properties.—The yellow crystals of the dichloriodide are stable in air at ordinary temperatures. They melt at $103\text{--}104^\circ$ with partial decomposition, evolve a brown oily distillate when further heated, and the vapours of methyl sulphide and iodine above 170° . *Platinic chloride*, added to the alcoholic solution, gives a bulky precipitate, shown to consist of trimethylsulphine platinochloride by its general properties and by the following analyses:—

I. 0.1176 gram gave 0.0404 gram of platinum.

II. 0.1621 „ 0.2458 „ AgCl .

	Calculated for $(\text{Me}_3\text{S})_2\text{PtCl}_6$.	Found.
Pt	34.94	(I.) 34.35
Cl	37.71	(II.) 37.51

With *silver salts* and with *caustic potash*, the dichloriodide acts in a manner precisely similar to the dibromiodide. *Ammonia solution* decomposes it with formation of iodide of nitrogen. With perfectly dry *ammonia gas*, it forms the compound $\text{Me}_3\text{SiCl}_2 \cdot 2\text{NH}_3$, the various stages in the reaction being hardly distinguishable from those in the formation of the corresponding dibromiodide derivative. The final product, however, is not so light in colour; and, when exposed to the atmosphere, it not only loses ammonia but absorbs moisture, and becomes converted into a wet black paste, which is not the case with its analogue. In other respects it resembles it closely. The composition was determined synthetically in the manner already described.

0.2738 gram of the dichloriodide became 0.3067 gram by absorption of ammonia :—

	Gain per cent.
Calculated for $\text{Me}_3\text{SiCl}_2, 2\text{NH}_3$	12.36
Found.....	12.02

IV. Action of Iodine Monochloride on the Chloride.

This results, as might be expected, in the formation of *trimethylsulphine dichloriodide*. The reaction which takes place when the iodine monochloride is poured gradually over the dry chloride closely resembles that produced by the action of bromine on the iodide. Much heat is developed, and the salt melts to a black pasty mass. This, however, assumes a light yellow colour and dry consistency when purified by a few washings with ether. The crystals obtained by cooling the hot alcoholic solution are identical in appearance and properties with those of the dichloriodide obtained by the method already described. The yield is large.

V. Action of Iodine Monochloride on the Bromide.

This action produces a body which, after washing with ether, separates from hot alcohol in the form of crystals, which are intermediate in colour between the light yellow dichloriodide and the orange-red dibromiodide, both of which it otherwise closely resembles. It melts at 87° with partial decomposition, which becomes complete at 180 — 190° .

Combustions of the substance gave the following results, showing that it consists of *trimethylsulphine chlorobromiodide*, Me_3SiBrCl .

I. 0.3071 gram substance gave 0.1314 gram CO_2 and 0.0832 gram H_2O .

II. 0.3228 gram substance gave 0.1378 gram CO_2 and 0.0894 gram H_2O .

	Calculated for Me_3SiBrCl .	Found.	
		I.	II.
C	11.27	11.67	11.64
H	2.82	3.01	3.07

VI. Action of Bromine on the Bromide.

This action resembles that of bromine on the iodide, but the properties of the products of the two reactions are quite different. Heat is evolved, and the crystals melt to a dark-red heavy liquid, which does not solidify when washed with ether ; nor can it be crystallised

from alcohol, as it separates unchanged in appearance when the solution is evaporated. When surrounded with a freezing mixture of snow and salt, it becomes more viscous but does not solidify. It smells of bromine; and it is slowly decomposed on exposure to the atmosphere, drops of a solution of trimethylsulphine bromide (which is deliquescent) making their appearance on the surface of the liquid after a day or two. It is decomposed much more quickly when heated on the water-bath, and the bromide is then obtained in the crystalline state. Even when the substance is kept in a desiccator containing sulphuric acid, there is continuous, though slow, loss of bromine. When shaken with water, it is slowly decomposed and passes into solution.

As such a body could not be obtained in a state fit for analysis, it was thought desirable to make some quantitative synthetic experiments with perfectly dry materials. The purity of the trimethylsulphine bromide was first ascertained by an estimation of its bromine. 0.2260 gram of the salt gave 0.2695 gram AgBr.

	Calculated.	Found.
Br.	50.95	50.74

In this and subsequent experiments with the bromide and chloride, which are both extremely deliquescent, special precautions were employed to obtain the salt in a perfectly dry state. It was placed in a small porcelain boat inside a glass tube, the boat and tube, with a ground glass stopper, being previously weighed. The tube was then placed horizontally, without its stopper, in a larger tube surrounded with boiling water, and closed by a doubly perforated cork. The salt being thus kept at 100°, dry air was led over its surface for from two to three hours. The tube was then quickly stoppered and weighed with its contents. By replacing the glass stopper by a cork provided with inlet and outlet tubes, it was possible afterwards to operate on the weighed salt with a stream of chlorine, or of air charged with bromine vapour, and to weigh the product (after clearing the tube out with dry air) without more than a momentary exposure to the atmosphere.

0.2441 gram of the dry bromide was exposed for two hours to a perfectly dry current of air charged with bromine vapour. The red oil, which was rapidly formed, continued during that time to increase in volume, in depth of colour, and in mobility. The increase in weight was 1.3208 gram, which is equivalent to a gain of from ten to eleven atoms of bromine by one molecule of the bromide; and there is no reason to suppose that the absorption would have stopped there. Dry air was then passed over the surface of the liquid for several hours, and weighings were made at intervals; after which the tube

and its contents were left for three days in a desiccator containing solid potash and then again weighed. The following table shows the results of this experiment:—

	Air passed.	Weight.	Weight gained.	Gain per cent.	Mols. of Br gained by 1 mol. of Me_3SBr .
Taken, 0.2441 gram of Me_3SBr , and bromine passed over it for two hours.	—	1.5649	1.3208	541	5.30
	2 hours ...	0.7510	0.5069	207	2.03
	4 „ ...	0.5483	0.3042	124	1.22
	6 „ ...	0.5031	0.2590	106	1.04
	8 „ ...	0.4777	0.2336	95	0.93
	9 „ ...	0.4689	0.2248	92	0.90
	11 „ ...	0.4613	0.2172	89	0.87
	After 3 days over KOH	0.4467	0.2026	83	0.81

Now, the calculated percentage gain, for the formation of Me_3SBr_3 , is 101.9, so that it is obvious that this compound, if formed at all, tends, on the one hand, to absorb a large excess of bromine when in an atmosphere containing it, and, on the other, to decompose steadily when in air free from bromine. As it is impossible, however, to isolate this or any other definite compound, all we can assert is that bromine does combine with trimethylsulphine bromide with development of heat, and that the analogy of the dibromiodide is in favour of the supposition that the tribromide is formed.

VII. *Action of Bromine on the Chloride.*

This action is precisely similar in character and appearance to that of bromine on the bromide. A dark-red oil is rapidly formed, which goes on absorbing bromine as long as it is exposed to air charged with the vapour of that substance, but gives it up again, at a progressively decreasing rate, in a current of dry air or in a desiccator containing solid potash. It is unnecessary to give the details of the experiments, as they were similar to the one described in the last paragraph: they afforded no evidence in favour of the existence of the chlorodibromide, $\text{Me}_3\text{SBr}_2\text{Cl}$, or of that of any other definite compound.

VIII. *Action of Chlorine on the Bromide.*

At the first touch of chlorine, the colourless crystals of trimethylsulphine bromide assume an orange tinge; and then they gradually melt to a clear yellow viscous liquid, in which, at first, solid orange-coloured pieces may be seen floating. The final product smells of chlorine, which it evolves when exposed over solid potash or subjected to a current of dry air. Water acts on it, causing the liberation of minute bubbles of chlorine. The following quantitative experiment was made.

0.2746 gram of the dry bromide was subjected to the action of dry chlorine for one hour, at the end of which time it was found to weigh 0.4100 gram. A second hour's chlorination increased this to 0.4169 gram; and it did not increase further. This is equivalent to a gain of 51.8 per cent., or 1.146 molecules of chlorine by one molecule of the bromide, the formation of $\text{Me}_3\text{SBrCl}_2$ requiring a percentage gain of 45.2. The product was then allowed to stand for two days over solid potash, after which the weight was found to be 0.3873 gram, which corresponds to a gain of 41.0 per cent., or 0.907 molecule of chlorine by one molecule of the bromide. On further exposure it continued to lose weight, though slowly.

The experimental evidence in this case, therefore, decidedly favours the belief that *trimethylsulphine dichlorobromide*, $\text{Me}_3\text{SBrCl}_2$, is formed, which is what one would expect from the analogy of the dichloriodide. No doubt, the very different physical properties of chlorine and bromine may account for the fact that trimethylsulphine bromide (and, as will be seen, chloride) absorbs but a small excess of the former, though an apparently unlimited excess of the latter.

IX. *Action of Chlorine on the Chloride.*

In order to observe this action properly, it is necessary to have both the chlorine and the chloride absolutely dry. If this precaution be taken, the crystals will turn yellow and begin to melt the instant the chlorine touches them. There is no sensible development of heat. After a few minutes the whole mass becomes converted into a clear pale yellow liquid, which undergoes no further change of appearance, though it goes on absorbing chlorine for some few minutes longer. This product has some characteristic properties. When exposed to the air for a very brief period, it suddenly solidifies; and when once this (apparently physical) change has taken place, the substance is not in the least affected by subsequent exposure to a chlorine current, however prolonged. Thus, in one experiment, the current of chlorine was stopped as soon as the product appeared to be uniformly liquid (five minutes from commencement), and dry air was then

passed through to sweep out the tube. This caused the substance to solidify. It was weighed and then again exposed to chlorine for half an hour; but the weight was found to be unchanged, though the quantity of chlorine taken up was not nearly so large as in other experiments. In another case, after nearly the maximum amount had been absorbed (twenty minutes from commencement), some accidental cause produced sudden solidification; and the rapid escape of dissolved chlorine caused the formation of a number of small crater-like excrescences on the surface. The action of a drop of water on the solid compound is particularly striking, for it causes a violent effervescence of chlorine. At the same time trimethylsulphine chloride passes into solution. Absolute alcohol and ether both decompose it in a similar manner; but the chlorine is, of course, not liberated as such. The chlorinated chloride is decomposed more rapidly in dry air than any of the other compounds already described.

The purity of the chloride employed in the experiments tabulated below was tested by means of a chlorine estimation. 0·3100 gram of the salt gave 0·3899 gram of AgCl.

	Calculated for Me_3SCl .	Found.
Cl	31·55	31·11

In every experiment, the salt was dried for from two to three hours in the manner already described. In experiment I the tube was swept out with a current of dry air before weighing, so that the product assumed the solid state. In the other cases, this was avoided by weighing the tube full of chlorine (with its cork, and tubes closed by caoutchouc caps); and the weight to be deducted for this extra chlorine was determined as accurately as possible by preliminary experiments. In experiment IV it was proved that the maximum weight had been gained.

No. of experiment.	Weight of chloride taken.	Weight of product.	Gain per cent.	Molecules of Cl gained by Me_3SCl .	Time allowed.
I	0·2770	0·3874	39·85	0·631	5 minutes
II	0·3110	0·5170	66·23	1·049	20 „
III	0·2377	0·4068	71·14	1·127	30 „
IV	0·2344	0·4036	72·18	1·144 (maximum)	45 „

In order to prove beyond doubt that the reaction consists in the simple addition of chlorine, and that there is no substitution of that

element for hydrogen, a combustion of the product of experiment I was made, the results of which may be compared with those obtained from the unacted-on chloride.

I. 0.2634 gram of the unacted-on chloride gave 0.3045 gram CO_2 and 0.1918 gram H_2O .

II. 0.2770 gram of the chloride, after it had been acted on by chlorine, gave 0.3217 gram CO_2 and 0.2020 gram H_2O .

		Found.	
		I.	II.
		Before	After
		chlorination.	chlorination.
C	Calculated for Me_3SCL . 32.00	31.72	31.67
H	8.00	8.14	8.10

From these experiments, it seems fair to conclude that *trimethylsulphine trichloride*, Me_3SCL_3 , is formed—a peculiar and unstable compound possessed of a limited power of dissolving chlorine when placed in an atmosphere of that gas.

X. Action of Halogens on the Sulphate.

We have not yet fully investigated the reactions of trimethylsulphine sulphate with the halogens; but we have ascertained by experiments the following facts. (1.) Iodine does not combine with it in the same way as it does with the haloïd salts. (2.) Bromine combines with it to form a red solid body, which resembles the dibromiodide rather than the products obtained by bromination of the bromide and chloride, but is less stable than the former. (3.) Chlorine acts on it to form a product which closely resembles the trichloride in its general properties, and particularly in the rapid effervescence of chlorine which occurs when water is dropped on it. We are pursuing the investigation of these reactions and of those of the halogens with other salts of trimethylsulphine.

XI. Summary and Theoretical Considerations.

It has been shown that all the haloïd salts of trimethylsulphine combine directly with chlorine, bromine, iodine, and iodine monochloride. In no case does there occur a replacement of one halogen by the other. The product of each reaction may be formulated as Me_3SX_3 (if we understand X to represent Cl, Br, or I, indiscriminately), this being proved with certainty in some cases, and fairly inferred in those where proof is wanting. In the following table, which shows the ten possible variations of the general formula, a query (?)

indicates that the substance has not been proved by quantitative experiments to have the formula attributed to it. This proof might be obtained in the cases of Nos. II and III; in those of I, VII, and VIII, this is rendered impossible by the readiness with which the compounds dissolve excess of the halogen, and by their unstable nature.

No.	Formula.	Appearance.	Behaviour in dry air.	How produced.
I	$\text{Me}_3\text{SI}_3 ?$..	Black tarry matter.....	—	$\text{Me}_3\text{SI} + \text{I}_2$
II	$\text{Me}_3\text{SI}_2\text{Br} ?$..	Dark crystals	—	$\text{Me}_3\text{SBr} + \text{I}_2$
III	$\text{Me}_3\text{SI}_2\text{Cl} ?$..	Dark crystals	—	$\text{Me}_3\text{SCl} + \text{I}_2$, or $\text{Me}_3\text{SI} + \text{ICl}$
IV	Me_3SIBr_2 ..	Orange-red crystals	Perfectly stable..	$\text{Me}_3\text{SI} + \text{Br}_2$
V	Me_3SIBrCl ..	Orange crystals	Perfectly stable..	$\text{Me}_3\text{SBr} + \text{ICl}$
VI	Me_3SICl_2 ..	Yellow crystals	Stable.....	$\text{Me}_3\text{SI} + \text{Cl}_2$, or $\text{Me}_3\text{SCl} + \text{ICl}$
VII	$\text{Me}_3\text{SBr}_3 ?$..	Orange-red viscous liquid	Loses Br slowly..	$\text{Me}_3\text{SBr} + \text{Br}_2$
VIII	$\text{Me}_3\text{SBr}_2\text{Cl} ?$..	Orange-red viscous liquid	Loses Br slowly..	$\text{Me}_3\text{SCl} + \text{Br}_2$
IX	$\text{Me}_3\text{SBrCl}_2$..	Yellow viscous liquid...	Loses Cl (and Br?)	$\text{Me}_3\text{SBr} + \text{Cl}_2$
X	Me_3SCl_3 ..	Yellow liquid (or solid) ..	Loses Cl.....	$\text{Me}_3\text{SCl} + \text{Cl}_2$

In this list, it will be seen that those compounds are the most stable which contain one iodine-atom; that those which contain more than one are difficult to purify on account of peculiarities which seem to characterise many of the known polyiodides of organic bases; and that those which contain no iodine tend to break up into their components, except in an atmosphere of chlorine or bromine, as the case may be.

As regards the constitution of these compounds, three theories are worthy of consideration. The first would regard them as examples of mere molecular combination, and would write the general formula $\text{Me}_3\text{SX}, \text{X}_2$. This, however, is not in accordance with the nature of the decomposition which the crystalline members of the series undergo when heated, nor with the fact that so high a temperature is required to effect it. The second theory is represented by the formula $\text{Me}_3\text{S}-\text{X} < \frac{\text{X}}{\text{X}}$, and assumes that the halogen-atom of the original salt becomes triad. In support of this may be quoted the general reactions of the dibromide and the dichloride, and particularly the fact that they combine with two molecules of ammonia; also the ease with which the trichloride breaks up, inasmuch as we should certainly expect the monad group Cl_3 to be very unstable if it exists at all. But this theory obviously cannot account for the combination of trimethylsulphine sulphate with bromine and with chlorine; and this fact must be regarded as affording a strong argument against

the theory; for we have already pointed out the striking similarity between the compounds so formed and some of those derived from the haloïd salts.

The third theory is capable of general application to all the bodies we have described. It assumes that they are trimethyl-sulphinic

salts, $\text{Me}_3\text{S} \begin{smallmatrix} \diagup \text{X} \\ \text{X} \\ \diagdown \text{X} \end{smallmatrix}$, in which the sulphur atom is hexad.

The analogy between these bodies and the so-called polyiodides (Weltzien, *Ann. Chem. Pharm.*, **86**, 292; **91**, 36: Tilden, this Journal, 1865, 99: Jörgensen, *Ber.*, **2**, 460; *J. pr. Chem.*, **3**, 145, 328) and polybromides (Marquart, *J. pr. Chem.*, **1**, 429) of the nitrogen bases is well marked. Moreover, Tilden (this Journal, 1866, 145) describes a dichloriodide of tetrethylammonium, which he obtained by acting on the chloride with iodine monochloride; and Weltzien (*Ann. Chem. Pharm.*, **99**, 11) also obtained some similar compounds by indirect means. Professor Crum Brown suggested to us, therefore, that we should investigate the hitherto untried action of bromine on the iodide of tetramethylammonium; and we have found that this reaction produces a red crystalline body so closely resembling the dibromiodide of trimethylsulphine as to leave no doubt of its true nature. Moreover, we have found that both bromine and chlorine unite with the sulphate of tetramethylammonium to form compounds which cannot be distinguished by their general properties from those obtained from the corresponding trimethylsulphine salt. We purpose making a complete investigation of the halogen compounds of the tetramethylammonium salts; but what we have already observed, taken together with the work of those chemists whom we have quoted, seems to justify us in saying that there is a large class of substances formed by the union of halogens with the salts of organic bases; and that any theory, to be acceptable, must be applicable equally to such examples as the "polyiodides," the dibromiodide of trimethylsulphine, the trichloride of trimethylsulphine, the product resulting from the union of bromine with tetramethylammonium iodide, and the products obtained by the union of bromine and chlorine with the sulphates of trimethylsulphine and tetramethylammonium. If, therefore, the bodies we have described are trimethylsulphinic salts, containing hexad sulphur, it would seem that nitrogen is capable of becoming heptad. Further evidence is, however, wanted on this point.

In conclusion, we desire to express our gratitude to Professor Crum Brown for having given us the great benefit of his aid and advice in this investigation.