XII.—*On the Stibethyls and Stibmethylys.*

BY G. B. BUCKTON, Esq., F.R.S.

CHEMISTS are already aware, through the researches of Dr. Hofmann, that zinc-ethyl reacts on terchloride of antimony in a manner similar to that shown by terchloride of phosphorus;—in the former case, triethylstibine is formed, in the latter case, triethylphosphine. The same successful labourer in this field of chemical inquiry, in his profound and complete history of ammonia, lately communicated to the Chemical Society, groups these bodies as primary triamines, or ammonias in which antimony and phosphorus severally play the parts of nitrogen, and three equivalents of ethyl those of hydrogen.

The following experiments were undertaken with the intention of testing how far the compounds of antimony with methyl and ethyl, were limited to the ammonia-type, and more particularly to determine whether, by assimilating more than three molecules of methyl, &c., bodies might arise referable to the types of antimonious and antimonic acids.

Triethylstibine is known to combine with two equivalents of chlorine or iodine to form its haloïd salts. If substitution could be effected, through zinc-ethyl, in these substances, a pentethylated radical would arise, showing the antimony in a complete condition of saturation.

Coarsely powdered antimony attacks iodide of ethyl readily, when sealed in tubes, and exposed to a temperature of about 140° C. An oily liquid is formed, composed of biniodide of triethylstibine, with probably a little teriodide of antimony. This biniodide, $\text{Sb}(\text{C}_4\text{H}_9)_3\text{I}_2$, produces considerable heat when mixed with zinc-ethyl, a pasty mass being formed, upon the surface of which a yellowish liquid floats. Distillation is attended by an abundant evolution of inflammable gas, which is charged with the vapour of triethylstibine. To remove as far as possible the inconvenience of these dense white antimonial fumes, the first distillation is best performed in a quilled receiver, the tube of which is plunged into water.

The yellowish heavy liquid, obtained as above, was rectified in an atmosphere of coal gas.

The first portion contained a little ether, which was separated, after which the temperature rose to 150° , between which and 170° C. all the liquid products passed over.

The fraction boiling below 160° C. had the properties of triethylstibine, but gave numbers slightly higher than those required by theory.

	Theory.		Experiment.	
Sb	129	59·73	—	—
C_{12}	72	33·33	33·51	33·97
H_{15}	15	6·94	7·17	7·39
	<hr/> 216	<hr/> 100·00		

Triethylstibine, when pure, is a colourless and limpid fluid, having a faint odour, which can scarcely be styled alliaceous. An unpleasant and very persistent taste is left in the mouth when a small portion only of its vapour has been inhaled. It is spontaneously inflammable in air, but may be kept unchanged under a layer of water. It mixes with bromine, under water, without disengaging any noticeable quantity of gas, and the oily bibromide of triethylstibine is formed. With hydrochloric acid hydrogen gas is liberated, and the corresponding non-fuming bichloride is produced.

Triethylstibine is a very stable body, and distils without

change. Here it differs from Stanethyl, which, as Dr. Frankland has shown, deposits when heated, half its quantity of tin, and passes into stannic diethyl.

Lowig and Schweitzer found the boiling point of triethylstibine to be 159° C.

'A combustion of the samples boiling between 160° and 170° C., showed a considerable increase in the percentage of both carbon and hydrogen.

Although the numbers obtained, approach more nearly the composition of tetrethylstibine than that of pentethylstibine, it is thought more probable that the latter substance is really contained in the mixture. The percentage of carbon and hydrogen was not increased by another rectification of the sample, and it soon became evident that the body was broken up by heat. This observation furnishes an explanation of the copious liberation of gas noticed during the distillation of biniodide of triethylstibine with zinc-ethyl.

Tetrethylstibine.		Sample 1.		Sample 2.	
Sb	129	52·65	—	—	—
C ₁₆	96	39·19	37·51	37·44	35·96
H ₂₀	20	8·16	7·90	8·01	7·43
	245	100·00			7·39

The decomposition of such a body by heat is analogous to that of pentachloride of antimony, which is thus known to yield chlorine gas and the terchloride. In the same manner,

The existence of a stibium compound, containing more than three molecules of ethyl, was confirmed by the deportment of the sample under examination towards bromine. A portion of the fuming liquid was thrown up into the head of an eudiometer tube standing over mercury, and small quantities of bromine were introduced from time to time. The mixture was attended with a violent action, and a bulk of permanent gas was formed. As the neutral point was approached, all visible action ceased, but when the bromine was in slight excess, a partial absorption of gas was noticed.

As triethylstibine unites with bromine to form the bibromide without liberation of gas, the appearance of ethylene and hydride of ethyl can only be explained by the presence of a more complex ethylated radical than triethylstibine.

The absorption of gas also would thus be easily explained.

Triethylstibine passes into the non-fuming bichloride also more readily with concentrated hydrochloric acid than the substance here described, which loses its character of spontaneous inflammability only after long boiling.

It is remarkable that zinc-ethyl is not attacked by bichloride of triethylstibine, even when the mixture is raised to its boiling point.

The most characteristic salt of triethylstibine is the bisulphide, which is easily formed by heating the radical with alcohol and sulphur. It crystallises in long silky needles, which are readily soluble in water. This salt is rapidly decomposed by boiling in excess of aqueous cyanide of potassium. The cyanide is in this manner converted into sulphocyanide of potassium, and triethylstibine is liberated in white fumes.

If the mixture containing the higher stibium-radical be boiled with alcohol and sulphur, there is formed, together with bisulphide of triethylstibine, a considerable quantity of bisulphide of ethyl. This substance becomes immediately evident by its powerful and repulsive odour.

Although triethylstibine is remarkably persistent in itself, its salts are in general easily reduced.

The most convenient method of obtaining the radical triethylstibine is by distilling its salts with granulated zinc. As the biniodide is easily formed, it is well suited for such an operation. The action is set up with some energy, and the products are most conveniently received under water.

I have failed in forming substitution-products by bringing together triethylstibine and bisulphide of carbon. The same failure also has happened in my attempts to cause a reaction between triethylstibine and dibromide of ethylene. An interesting body from triethylphosphine, homologous to sulphocarbamate of ammonium, has been obtained by Hofmann :

With triethylstibine the tubes invariably burst at a temperature of 140°C ., and below this point no change appeared in the materials.

Having some quantity of triethylstibine at my disposal, a few experiments in confirmation of those of M. Löwig were made.

On the Salts of Tetrethylstibine.

Triethylstibine was mixed with a slight excess of iodide of ethyl. In the course of a few hours, a mass of fine crystals of iodide of tetrethylstibine was obtained.

Iodide of tetrethylstibine, when mixed with zinc-ethyl and distilled, yields the same results as if biniodide of triethylstibine had been employed. Iodide of zinc, fixed gases, and a mixture of two radicals incapable of separation by heat were obtained.

Oxide of Tetrethylstibine is very soluble in water, and is uncrystallizable. When heated above 100° C. it undergoes decomposition, with liberation of white fumes of triethylstibine.

Sulphate and nitrate of tetrethylstibine are crystalline salts.

Chloride of Tetrethylstibine is also crystalline. When dissolved in water, and mixed with bichloride of platinum, it yielded a fine yellow crystalline salt, which was but little soluble in alcohol.

When ignited and separated from the antimony, the following analytical result was obtained.

0.7856 grm. of salt, gave 0.1752 grm. of platinum, which accords most nearly to the formula,

$\text{Sb}(\text{C}_4\text{H}_5)_4\text{Cl.PtCl}_2$			
Theory requires.			Found.
Sb . .	129.0	28.63	—
C_{16} . .	96.0	21.30	—
H_{20} . .	20.0	4.44	—
Cl_3 . .	106.5	23.65	—
Pt . .	99.0	21.98	22.31
	<hr/> 450.5	<hr/> 100.00	

Löwig obtained a salt much richer in platinum, to which he assigns the composition,

Action of Zinc-methyl on Biniodide of Trimethylstibine.

As the methyl-molecule is simpler in structure than that of ethyl, it was thought that a penta-methylated body might possibly resist decomposition during distillation. The biniodide of trimethylstibine may be obtained in beautiful crystals, by acting on

metallic antimony with iodide of methyl, at a temperature of 140° C. As these crystals were found to decompose zinc-methyl energetically, an appeal was again made to experiment.

The materials were mixed slowly in a retort, and after the first action had subsided, the mass was submitted to a temperature of 100° in a water-bath, which removed the excess of zinc-methyl and ether. Subsequently, the distillation of the solid mass was completed over the sand bath.

In this way, a heavy pale-coloured liquid was obtained, which, after agitation with water and weak acid, was rectified in an atmosphere of coal gas, heat being applied by a water-bath.

Fractions were taken between 80° — 86° , 86° — 96° , 96° — 100° C.

All these samples had the following properties:

They were oily bodies with faint odours, heavier than water, with which they did not mix. When exposed to the air, they were not spontaneously inflammable, neither did they, at ordinary temperatures, give off white fumes. When dropped on a warm surface, however, they ignited and burnt with a luminous flame, accompanied by a dense antimonial cloud.

The following numbers were obtained by analysis of these samples:—

	80° — 86°		86° — 96°	96° — 100°	
Carbon . .	21.99	21.20	26.90	30.18	31.64
Hydrogen .	5.08	5.23	5.92	6.83	6.98

For comparison, the numbers required by theory for antimony with three, four, and five equivalents of methyl, are appended.

Sb Me ₃		Sb Me ₄		Sb Me ₅	
Sb	74.25	Sb	68.37	Sb	63.19
C ₆	20.69	C ₈	25.39	C ₁₀	29.46
H ₉	5.16	H ₁₂	6.34	H ₁₅	7.35
<hr/>		<hr/>		<hr/>	
100.00		100.00		100.00	

Notwithstanding the circumstance that the above samples are not spontaneously inflammable (a character pre-eminently shewn by trimethylstibine), the composition of No. 1, seems to indicate its identity with that body. Before being confident with reference to the composition of Nos. 2 and 3, some weight must be given to an observation here made, viz., that in the decomposition of zinc-methyl by a high temperature, instead of gases being eliminated, as is known to be the case with zinc-ethyl, hydro-carbons are pro-

duced which burn with a smoky flame. These substances I have not yet been able to examine, but it would appear that the methyl-molecules undergo duplication, and thus give rise to bodies possessing high boiling points.

It is therefore possible, that pentamethylstibine may be resolved by heat into trimethylstibine and such a hydrocarbon. This would account also for the excess in the carbon and hydrogen given by analysis of sample No. 3.

In conclusion, it is thought that a reviewal of these experiments, in both the ethyl and methyl series, will justify the conclusion that the higher stibium organo-radicals exist. A better method for their isolation however, is still a desideratum.

Apparatus for general fractional Distillation in Carbonic Acid Gas.

A. Inverted bell glass with open neck.

B. Stand with thick vulcanized indian rubber collar E.

C. Circular table with sockets for holding bottles 1, 2, 3, &c.

D. Thick glass rod, sliding air-tight through collar and stand, by which the table and bottles may be raised, lowered, or rotated at pleasure.

F. Quilled receiver and retort.

I. and K. Tubes for entrance and exit of carbonic acid or other gas.

G. Clamp with forked arm, to secure the bell to the stand, and permit the table

to rotate eccentrically, if required. The tube of the receiver may thus be introduced into any one of the bottles.

H. Slate cover, which may be ground to fit the lip of the bell, or simply luted to it with linseed.