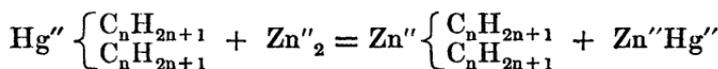


III.—*On a new Reaction for the production of the Zinc-compounds of the Alcohol-radicles.*

By Prof. E. FRANKLAND, F.R.S., and B. F. DUPPA, Esq.

IN a former communication\* we described a new process, by which the mercury-compounds of the alcohol-radicles can be produced in large quantity and with great facility. Having these substances thus at command, it became interesting to ascertain the possibility of transforming them into the corresponding zinc-compounds, by the following reaction:—



Some preliminary experiments completely established the feasibility of the transformation expressed in this equation. It was found that an excess of zinc added to the mercurial compound, readily reacted at a temperature which varied from 100° C. to 130°, eliminating the whole of the mercury, and producing the corresponding zinc compound. This reaction becomes of considerable interest when it is remembered that the processes hitherto devised for the production of organo-zinc compounds in a state of purity, are, as regards those containing amyl and methyl, attended with formidable difficulties, so much so, that the amyl compound has never hitherto been isolated, whilst the methyl body has only been prepared pure in very small quantity, and by processes which are either uncertain or tedious.

\* Journal of the Chem. Soc. [2], i, p. 415.

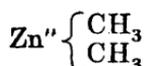
*Action of Zinc upon Mercuric methide.*

Finely granulated and dry zinc is placed in a glass tube strong enough to resist a pressure of about 5 atmospheres, and enough of the mercuric-methide added, to take up about half of the space occupied by the zinc. The tube is next drawn out to a point and laid nearly horizontally in an oil-bath heated to a temperature of 120° C. The object of placing the tube in this position, is to offer a larger surface of contact, so as to hasten the completion of the reaction. After digestion has continued for about 24 hours, the action may be regarded as complete, and the zinc-methide in the tube distilled off. It is, however, advisable to test the liquid from time to time, to ascertain whether the whole of the mercury has been precipitated or not.

On rectification, the zinc-methyl thus obtained boiled constantly at 46° C., and possessed a specific gravity in the liquid state of 1.386 at 10.5° C. An estimation of zinc yielded the following result:—

·2131 grm. was volatilised in a current of carbonic acid, and passed into dilute hydrochloric acid; the chloride of zinc was then precipitated boiling by carbonate of soda, washed, dried, and ignited. It yielded ·1830 grm. oxide of zinc.

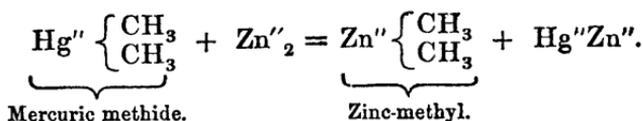
These numbers agree closely with the formula—



as seen from the following comparison:—

	Calculated.		Found.
C <sub>2</sub> . . . . .	24	25.25	—
H <sub>6</sub> . . . . .	6	6.31	—
Zn . . . . .	65	68.44	68.13
	95	100.00	

The production of zinc-methyl from mercuric methide by zinc may be represented as follows:—



The low boiling point of zinc-methyl naturally precludes the use

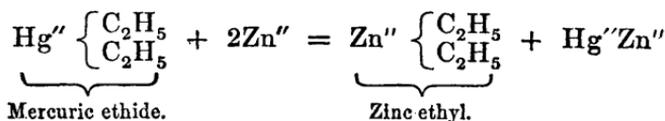
of glass vessels for its production in large quantities, and it is therefore necessary to resort to the use of an iron digester, similar in construction to the copper one previously described by one of us,\* when more than a few ounces of the body are required.

*Action of Zinc upon Mercuric ethide.*

Mercuric ethide is much more readily acted upon by zinc than the corresponding methyl-compound, a temperature of 100° C. continued for 36 hours being amply sufficient to transform the whole of the mercuric ethide into zinc-ethyl. The reaction is best conducted in the following manner:—The body of a non-tubulated retort being filled with finely granulated zinc, mercuric ethide is then introduced in sufficient quantity to occupy rather more than half the space taken up by the zinc. The neck of the retort may now be closed with a cork; but in order to avoid oxidation during the digestion, it is advisable to draw the neck out in the blow-pipe flame; it is then placed in a steam-bath until the included air is sufficiently expanded, and the point is sealed up. The retort is allowed to remain in the bath, with its neck inclining upwards, for a sufficient length of time. No pressure is generated in this operation; on the contrary, rarefaction, to a small extent, takes place, owing to the oxygen of the contained air being absorbed.

It is easy to judge how the reaction is progressing, by the amount of fluid amalgam which collects at the bottom of the retort; but it is also necessary, as in the process for zinc-methyl, to open the retort once or twice, and to test for mercury in the ethereal liquid, which is readily done by placing a drop of the latter on a watch-glass and breathing upon it, when, after a few moments, the peculiar odour of the mercury-compound will become manifest, if traces of it are still present. As soon as the whole has been decomposed, it is only necessary to submit the contents of the retort to distillation. The distillate boils constantly at 118° C., and exhibits all the properties of pure zinc-ethyl.

The formation of zinc-ethyl by the action of zinc upon mercuric ethide may be thus expressed:—



\* Phil. Trans., 1855, pp. 260 and 261.

In forming an opinion of the comparative value of this and the previously known processes for the production of zinc-ethyl, it must be borne in mind that mercuric ethide is most readily obtained in nearly the quantity indicated by theory, and that this body, in its turn, is completely transformed without loss into zinc-ethyl. On the other hand, the production of the latter by the action of zinc upon iodide of ethyl, involves considerable loss, owing to the intermediate formation of ethiodide of zinc,  $Zn \left\{ \begin{array}{l} C_2H_5 \\ I \end{array} \right.$ . This compound not only requires a very high temperature for its decomposition, but also deposits, at the expense of the resulting zinc-ethyl, a considerable quantity of metallic zinc. Nevertheless, we are of opinion that the process we are now proposing is only to be recommended in the absence of the apparatus necessary for the production of zinc-ethyl by the method first described by one of us.\* In our hands the processes devised by Pebal† and by Rieth and Beilstein‡ have not given satisfactory results. That of the latter chemists, which appears to be by far the better of the two, yielded us only 40 per cent. of the theoretical quantity, which is greatly below the amount obtained by the use of a metallic digester.

#### *Action of Zinc upon Mercuric Amylide.*

Mercuric amylyde, treated with zinc in the same manner as mercuric ethide, and exposed in an oil-bath to a temperature of 130°C. for 36 hours, is completely converted into zinc-amyl, which then only requires to be separated from the zinc-amalgam by distillation. On rectification, the distillate began to boil at about 50°C., when a very small quantity of a mixture of amylene and hydride of amyl distilled, whilst the thermometer was rapidly rising to 220°C., between which temperature and 222°C. the remainder of the product passed over.

Submitted to analysis this liquid gave the following results:—

I. ·3214 grm. burnt with oxide of copper, gave ·6834 grm. carbonic acid and ·3112 grm. water.

II. ·3898 grm. gave ·8251 grm. carbonic acid and ·3770 grm. water.

III. ·4815 grm., decomposed by dilute hydrochloric acid, and

\* Phil. Trans., 1855, p. 259.

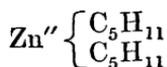
† Ann. Ch. Pharm. cxviii, 22.

‡ Ann. Ch. Pharm. cxxvi, 2, 48.

precipitated with carbonate of soda, gave 1840 grm. oxide of zinc.

IV. 6770 grm., decomposed by alcoholic solution of hydrochloric acid, and precipitated as before, gave 2664 grm. oxide of zinc.

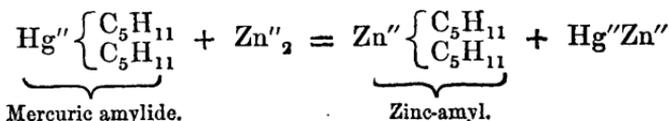
These numbers correspond closely with the formula



as seen from the following calculation :—

	I.	II.	III.	IV.	Mean.
C <sub>10</sub> .. 120 ..	57·97 ..	57·99 ..	57·77 ..	..	.. 57·88
H <sub>22</sub> .. 22 ..	10·63 ..	10·76 ..	10·75 ..	..	.. 10·76
Zn .. 65 ..	31·40 ..	..	.. 30·67 ..	31·34 ..	31·01
	207	100·00			99·65

The action of zinc upon mercuric amyliide may therefore be thus represented :—



Zinc-amyli is a colourless, transparent and mobile liquid, possessing an amylic odour, and having a specific gravity of 1·022 at 0°C. It boils at 220°C., and distils unchanged. A determination of the vapour-density by Gay Lussac's method gave the following numbers :—

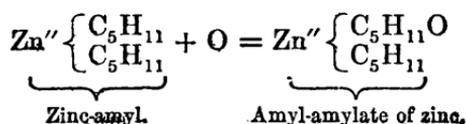
Weight of zinc-amyli used .....	3197 grm.
Observed volume of vapour .....	68·19 c. c.
Temperature .....	235°C.
Height of column of oil .....	75·5 mm.
Height of inner column of mercury .....	142·5 mm.
Height of barometer .....	755·0 mm.
Corrected volume of vapour at 0° C. and 760 mm. pressure .....	35·5 c. c.
Specific gravity of vapour .....	6·95

Zinc-amyl vapour, therefore, consists of one volume of zinc vapour united with two volumes of amyl, the whole being condensed to two volumes :—

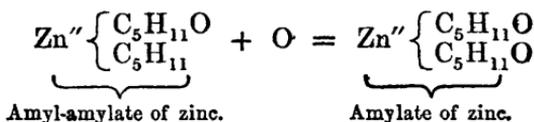
2 volumes of amyl vapour.....	9·8124
1 volume of zinc vapour .....	4·4942
	2   14·3066
	7·1533
Found by experiment.....	6·95

At about 240°C. zinc-amyl slowly decomposes ; a vapour-density taken at this temperature gave the number 6·64, and when the apparatus cooled, it was found that a notable quantity of amylene and hydride of amyl had been formed.

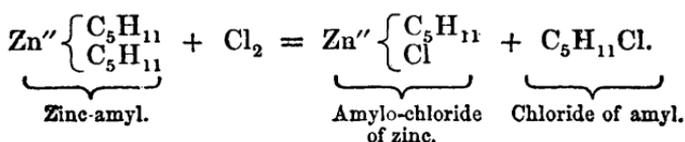
Zinc-amyl fumes strongly when exposed to the air, but it does not ignite spontaneously, as is the case with the corresponding methyl and ethyl compounds ; when dropped into pure oxygen, however, it bursts into brilliant white flame, attended with slight explosion. By slow oxidation, zinc-amyl is first converted into *amyl-amylate of zinc* :



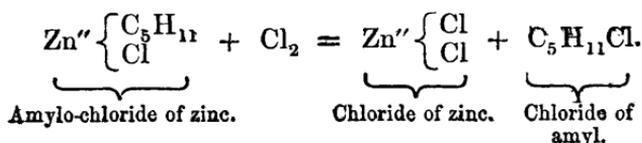
and, finally, into *amylate of zinc* :



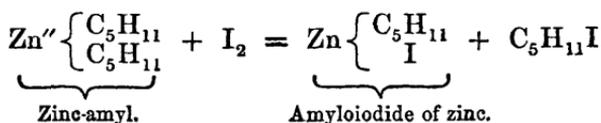
When zinc-amyl is brought into contact with chlorine, it inflames spontaneously, burning with a lurid flame, which deposits much soot. A more gradual action would doubtless be attended with the formation of *amyl-chloride of zinc* and chloride of amyl :



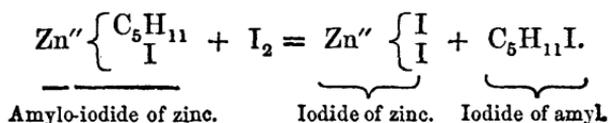
and, secondly, of chloride of zinc and chloride of amyl :



The addition of iodine to zinc-amyl is attended with considerable elevation of temperature, the materials becoming pasty, from the formation of *amylo-iodide of zinc* :



The further addition of iodine rendered the materials again fluid, and almost limpid, owing to the decomposition of the amylo-iodide of zinc :



On treating the product with water, iodide of zinc dissolved, whilst a heavy liquid, boiling at 147° C. and having the properties of iodide of amyl, subsided to the bottom of the vessel.

#### *Action of various Metals on Mercuric ethide.*

From the readiness with which the mercurial compounds of the alcohol-radicles are decomposed by zinc, we were induced to test their behaviour with other metals. For this purpose, we selected mercuric ethide, since we found this compound to be more readily acted upon by zinc than the corresponding methyl and amyl bodies.

*Iron*, reduced from the sesquioxide by hydrogen, was submitted to the action of mercuric ethide, at temperatures varying from 100° to 150° C., but with no other result than the formation of large quantities of inflammable gas, and the precipitation of mercury without amalgamation, no traces of a ferrous or ferric com-

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pound of ethyl being formed. There can be little doubt that the mercuric ethide was gradually decomposed by a lengthened exposure to a high temperature, quite independently of any action of the iron, which, indeed, appeared to be null.

*Copper*, in the state of filings, was treated with mercuric ethide for three hours at  $100^{\circ}$  C., without any effect being produced, but after exposure for five or six hours to  $150^{\circ}$  C., the metal became slightly amalgamated, and gas was evolved when the tube was opened. In this case, the precipitation of mercury appears to have arisen, rather from the decomposition of the ethide by heat, than from any action of the metallic copper upon that body.

*Cadmium* and mercuric ethide react upon each other but very slowly and imperfectly. As in the reaction with zinc, amalgam is formed, and also a considerable quantity of cadmium-ethyl; but notwithstanding long digestion at a temperature varying from  $100^{\circ}$  to  $130^{\circ}$  C., we were unable to obtain a product free from the mercury compound.

Finely powdered *bismuth* heated with mercuric ethide, was acted on to a considerable extent, bismuth-ethyl being formed in large quantity; nevertheless, though the digestion was continued for many hours, at temperatures varying from  $120^{\circ}$  to  $140^{\circ}$  C., we were unable to decompose the whole of the mercuric body. Had a larger proportion of bismuth been used, so as to present a greater surface of contact, the conversion would probably have been perfect; but as our object was merely to point out the behaviour of the various metals with mercuric ethide, we did not pursue this reaction further, although we consider that it promises to produce organo-compounds of bismuth with great facility.

*Silver* does not decompose mercuric ethide at  $100^{\circ}$  C., although at  $150^{\circ}$ , considerable action takes place, gas in large quantities being evolved; but no trace of an argentiferous organic compound is perceptible.

*Gold leaves* placed in mercuric ethide heated to  $120^{\circ}$  C., rapidly disappear, forming a perfect amalgam, accompanied by a liberation of gas. No organo-auric body is, however, formed.

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