XX.—*Researches on the Action of the Copper-Zinc Couple on Organic Bodies.*—Part VI. *On Ethyl Bromide.*

By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S.

AN examination of the action of our couple on ethyl bromide appeared desirable for two very different reasons. In the first place we should learn whether the behaviour of the bromide was analogous to that of the iodide, and might be able to prepare bromine analogues of zinc ethiodide and of the zinc iodo-ethylate which we described in Part I of these researches (*Journ. Chem. Soc.*, 1873, pp. 445—452). In the second place, as the bromide is much cheaper than the iodide of ethyl, and contains more of the organic radical, we hoped it might afford a method of preparing zinc-ethyl at a smaller cost.

According to Pierre, the boiling point of ethyl bromide is $40\cdot7^{\circ}$ when the barometer stands at 757 mm., and the specific gravity is $1\cdot4733$ at 0° . Our experience has been somewhat different. We examined three specimens.

Specimen I, made by Hopkin and Williams by the action of phosphorus bromide, after rectification and drying, boiled at 38° — 39° , bar. 760 mm. Its specific gravity was $1\cdot385$ at 15° .

Specimen II, made by Hopkin and Williams by acting on pure alcohol with strong hydrobromic acid, boiled at $38\cdot5^{\circ}$ — $39\cdot5^{\circ}$. Its specific gravity was $1\cdot47$ at 15° .

Specimen III, made by ourselves by acting on alcohol with phosphorus and bromine, boiled also at $38\cdot5^{\circ}$ — $39\cdot5^{\circ}$.

Action of the Dry Couple on the Bromide.

The action between the copper-zinc couple and the bromide appears to depend on small differences of condition, the nature of which we have not been able satisfactorily to determine.

In one experiment 5 c.c. (about 7·3 grams) of the specimen prepared by means of bromide of phosphorus, were boiled with a dry couple in

the usual way, and in 14 hours the return flow had ceased, and the action appeared complete. In the flask, mixed of course with the copper and remaining zinc, was a white crystalline body, which effervesced on addition of alcohol, and was violently decomposed by water with formation of zinc bromide and oxide. This crystalline body yields zinc-ethyl when heated. It dissolves readily in ether, but the ether separates only imperfectly from it by evaporation *in vacuo* over sulphuric acid, leaving a viscid mass. In a portion of this the atomic ratio of bromine and zinc was determined, and found to be 1 : 0.983. There can be no doubt, therefore, that the crystalline body produced was zinc ethylobromide, $\left. \begin{matrix} \text{C}_2\text{H}_5 \\ \text{Br} \end{matrix} \right\} \text{Zn}$, the analogue of Frankland's ethiodide.

In Part I we showed that the iodine-compound could be prepared by gently heating zinc-ethyl and zinc iodide together. We found that this bromine-compound could also be formed in a similar way. It melts at 62°, and crystallises on cooling in white pearly scales.

In another experiment 5 c.c. of the same specimen of bromide were heated with a couple in a water-bath at 55°. In 36 hours the return flow ceased. The flask was gently heated over a gas-flame, and the zinc-ethyl produced was distilled over in a current of carbonic acid gas into water. The zinc oxide obtained amounted to 0.606 gram, which, however, is equivalent only to 1.63 gram of ethyl bromide. This small yield led us to determine the amount of bromine which had combined with zinc during the experiment, and we found it to indicate the decomposition of 4.4 grams of the ethyl compound. It is evident, therefore, that the bulk of the product is lost through the conversion of the ethylic element into permanent gases.

In an experiment similar to the last in every respect, as far as we know, no action whatever took place in 36 hours.

In two other experiments, performed simultaneously and in a perfectly similar manner, the return flow ceased in about 40 hours. Ethylobromide of zinc was produced in each case, but in different quantity; for on decomposing the one with water and the other with alcohol, 400 c.c. of ethyl hydride were evolved in one case, and 750 c.c. in the other. This shows that in the first about one-fourth of the possible amount of ethylobromide had been produced, in the second nearly a half.

Another pair of experiments was made with specimens II and III of the ethyl bromide. No action in 36 hours in either case.

These contradictory results led us to inquire whether the action had been started by the presence of some moisture or a trace of alcohol. Two simultaneous experiments were therefore made with two portions of 5 c.c. each of specimen II, the one portion being saturated with

water, the other mixed with 0·5 gram of absolute alcohol. In 20 hours there was no action in the first, while in the second the return flow had greatly diminished. On opening the flask, fumes were produced, and on heating it over a lamp, zinc-ethyl mixed with some ethyl bromide distilled. The zinc-ethyl gave 0·058 gram of zinc oxide, equivalent to '013 gram of the original bromide, but the amount of bromine in combination with zinc in the flask showed that 3·4 gram of the original substance had been acted upon. The alcohol present was sufficient to destroy the ethylobromide produced from 1·18 gram, and if it really started the action, it is evident that the action was continued afterwards without its intervention.

Action of the Couple upon Ethyl Bromide mixed with a small quantity of Ethyl Iodide.

Our earliest experiments on ethyl bromide were made with a specimen that boiled at 40°—42°,—the boiling point given in the books being 40·7°,—but which we afterwards found to contain 3·1 per cent. of ethyl iodide. The reaction always took place with this specimen, and with comparative rapidity. We can scarcely be wrong in supposing that the ethiodide was first formed, which facilitated the formation of the ethylobromide. In three experiments the following quantities of zinc-ethyl were obtained:—

	C ₂ H ₅ Br used.	Duration of first heating.	ZnO obtained.	Equivalent to C ₄ H ₁₀ Zn.
No. 1....	7·4 grams.	11 hours.	0·908	1·39 gram.
" 2....	"	10·5 "	0·875	1·33 "
" 3....	"	10 "	—	1·48 "

As the amount of zinc-ethyl theoretically obtainable from 7·4 grams of the bromide is 4·17 grams, it is evident that the loss amounts to two-thirds of the whole. In order to see where this occurs, the third experiment was carried out with great care. The ethylobromide was heated in a paraffin bath at 240°, and the gas evolved in each operation was collected. This gas burnt with a very bright flame and formed an oily body with bromine. Fuming sulphuric acid absorbed 48 per cent. of its volume, leaving a gas which also burnt luminously.

We concluded, as in the case of the ethyl iodide, that this gas consisted of ethylene and ethyl hydride in equal volumes.

The 7·4 gram of ethyl bromide may be thus accounted for:—

Vapour carried over with the gas	
during the first heating	= 1.08 grams.
100 c.c. of gas during first heating	= 0.48 „
515 c.c. of gas during the heating	
of the ethylbromide	= 2.50 „
1.48 gram of zinc ethyl	= 2.60 „
Gas dissolved in water, and other	
loss	= 0.74 „
	<hr/>
	7.4 „

It is evident that in this experiment the ethylbromide split up by heat according to the two following equations in about equal proportions :—

It is probable that the greater destruction of the bromine-zinc compound by heat than in the case of the analogous iodine-zinc compound is caused by the higher temperature at which the reaction takes place.

As a method of preparing zinc-ethyl, it is evident that bromide mixed with a little iodide may be employed, but it can be economically employed only in those cases where the zinc salt produced is thrown away. For manufacturing purposes it would be less advantageous than the process we formerly described.

Action of the Couple on Ethyl Bromide and Water or Alcohol.

The action in presence of water or alcohol, at the ordinary temperature is very slow.

5 c.c. of the bromide were added to a copper-zinc couple wet with water at 11°. Evolution of gas soon commenced, but in 24 hours only 100 c.c. had collected. The gas had the properties of ethyl hydride; and the flask contained bromide and oxide of zinc.

5 c.c. of the bromide were added to a couple wet with absolute alcohol at 11°C. Evolution of gas did not commence for three hours, and then it proceeded at the rate of about 5 c.c. per hour.

5 c.c. (7.3 grams) of the bromide were mixed with 10 c.c. of absolute alcohol, and added to twice the usual quantity of couple. The flask was heated by immersion in water at 55° for six hours, and at 75° for two hours more, when evolution of gas ceased: 955 c.c. had been collected, and it had the properties of hydride of ethyl. The product in the flask was semi-fluid; and the addition of water to it

produced bromide of zinc with a copious precipitate of zinc oxide. The amount of bromine in combination with zinc showed that 5.07 grams of the ethyl-compound had been decomposed, which would be equivalent to 1041 c.c. of gas.

In order to study this new product more fully, another portion was prepared in the same way and separated from the metals in the flask by solution in alcohol and filtration. This alcoholic extract was colourless. A portion was used for determination of the atomic ratio between the zinc and bromine, which was found to be—

$$1 : 1.025.$$

Another portion was heated at 100° in a distilling flask, but this temperature was found insufficient to drive off all the alcohol, though it was becoming yellowish and viscid. It was then kept at 200° for an hour, which did free it from the alcohol, but at the same time turned it brownish yellow. It was semi-solid at 200°, and quite solid at the ordinary temperature. A determination of the bromine in a portion of this indicated 45.55 per cent., which is somewhat higher than pure

$\left. \begin{array}{c} \text{C}_2\text{H}_5\text{O} \\ \text{Br} \end{array} \right\} \text{Zn}$ would give, viz., 42.1 per cent. On heating another portion gently over a flame, it blackened, with separation of metallic zinc, and gave off a little combustible gas, and the odour of ether.

From the close analogy of these properties to those of the iodo-ethylate of zinc, which is produced in a precisely similar way from the iodide of ethyl, there can be no reasonable doubt that this body is the brom-ethylate of zinc, $\left. \begin{array}{c} \text{C}_2\text{H}_5\text{O} \\ \text{Br} \end{array} \right\} \text{Zn}$.

The action of water is easily understood—

If it is really ether that is produced from it by the action of heat, that may arise simply from the reaction of two molecules :—

Conclusion.

These results are perfectly analogous to those we obtained when studying the action of the couple on the iodide of ethyl. They are moreover in perfect accordance with the ordinary belief that a bromide is a more stable compound than an iodide.

The view we are disposed to take of the reactions is as follows :—The bromide of ethyl attacking the metal gives rise in all cases to the

ethylobromide of zinc, $\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{Br} \end{smallmatrix} \right\} \text{Zn}$. When this is heated by itself, two molecules react on one another or redistribute their elements with production of zinc bromide and zinc-ethyl, or the ethyl molecules may also redistribute their elements, with formation of the gases C_2H_6 and C_2H_4 . When, however, water is present at the moment of formation of the ethylobromide of zinc, or is added afterwards, it suffers the simple decomposition:—

while alcohol under similar circumstances effects a similar change—

This explanation is applicable to all the analogous reactions formerly described where the copper-zinc couple attacks the iodides of ethyl, methyl, amyl or propyl; and we believe it to be the true explanation, since it disposes of the difficulty why alcohol should give up its hydrogen to the organic radical, though it is not itself capable of being decomposed by the couple.