XXIII.—*Researches on the Action of the Copper-Zinc Couple on Organic Bodies.*—Part VIII. *On Chloroform, Bromoform, and Iodoform.*

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IN our earliest description of the power of the copper-zinc couple we stated that it was capable of decomposing chloroform. We have lately examined its action upon this body, and the analogous bromine and iodine compounds.

CHLOROFORM.

The dry couple was found to have no action upon this substance either when alone or in presence of pure ether.

In presence of *absolute alcohol* no action was observed at the ordinary temperature. At about 50° C., however, action takes place, and in a few minutes proceeds rapidly.

In one experiment 5 c.c. of chloroform (7·5 grams) were mixed with 20 c.c. of absolute alcohol, and the mixture added to twice the usual quantity of couple. No action was observable in one hour (temp. 12° C.). The temperature was now raised to 60°. In five minutes 20 c.c. of gas had collected, and in the next three minutes 50 c.c. (The action had now become so rapid, and the temperature had risen so considerably in consequence, that it was necessary to agitate the flask in cold water.) In the next five minutes 680 c.c., and in the next two minutes 180 c.c., had collected; in another four minutes the action was practically over. The quantity of gas collected during the 19 minutes amounted to 984 c.c. (corrected).

The chlorine in combination with zinc was determined in the usual way, and found to be equivalent to 5·92 grams of CHCl_3 , which would

1,109 c.c. of marsh-gas, assuming the three atoms of chlorine to have been replaced by hydrogen.

In another similar experiment, with equal quantities of material, the contents of the flask were heated to 20° C. for 15 minutes. No action took place. At 50° action commenced and quickly became very violent. In 15 minutes action was practically over, 967 c.c. having been collected.

The gas, after being washed with alcohol and water, possessed the general properties of methyl hydride.

The product remaining in the flask was very viscid, and very soluble in alcohol. Water added to the alcoholic solution produced a copious precipitate of ZnH_2O_2 . The atomic ratio of zinc to chlorine was determined and found to be 1 : 1·08.

The product, after the removal of alcohol by distillation, behaved just as the chloro-ethylate of zinc which we obtained by the reaction—

and described by us in the Society's Journal for May, 1874.

Subsequent experiments upon bromoform and iodoform induced us to suspect the formation of some acetylene during the action of the couple upon chloroform in presence of alcohol. Another experiment was therefore made similar to those already described, the gas being passed through a solution of cuprous chloride in ammonia. Some of the red acetylene compound which on analysis gave ·0689 Cu, equal to 12 c.c. acetylene or ·1296 gram chloroform.

Taking the above facts into consideration, we may conclude that about 92 *per cent.* of the action may be represented by the equation—

and a small percentage by the equation—

We tried the action of the couple in the presence of water. 5 c.c. were added to the usual quantity of couple wet with water, temperature 12° C. Gas was at once slowly evolved. The temperature of the contents of the flask rose somewhat in the first 20 minutes, and the action became more rapid. In the first hour 170 c.c. of gas had collected; in the second, 60 c.c.; in the third, 35 c.c.; and so on, in a diminishing ratio. At the end of four days the action was no longer going on. The total gas collected measured 626 c.c.

The couple remaining in the flask was coated with a white substance, which was found to be oxychloride of zinc, the formation of

which in all probability prevented the completion of the reaction, and accounts for its rapid falling off. The gas burnt with a flame like marsh-gas.

The reaction may therefore be represented thus—

From these results it might be expected that with aqueous alcohol the reaction would take place at a lower temperature than when absolute alcohol is employed. Such was found to be the case. An experiment was made with 5 c.c. of chloroform mixed with 15 c.c. of absolute alcohol and 5 c.c. of water, added to twice the usual quantity of the dry couple. Evolution of gas commenced immediately, and in a few minutes the contents of the flask had sensibly risen in temperature. 150 c.c. of gas collected during the first ten minutes, and the action continued in a diminishing ratio for about 24 hours, when it was found that 438 c.c. had collected.

Oxychloride of zinc was found adhering to the remaining couple, which probably stopped the action, as on the addition of more water the action did not recommence.

Zinc-foil was found not to have an action on chloroform mixed with absolute alcohol at 60° C., but at the boiling-point of the mixture there is a slow action, CH_4 and $\text{C}_2\text{H}_5\text{O} \left. \vphantom{\text{C}_2\text{H}_5\text{O}} \right\} \text{Zn}$ (chloroethylate of zinc) being produced.

Zinc-foil was also found slowly to act upon chloroform mixed with alcohol diluted with one-fourth of its volume of water at 50° C., zinc oxychloride and CH_4 being the principal products.

It is evident that the reactions described above afford a ready method of preparing marsh-gas.

BROMOFORM.

Action of the Couple in presence of Alcohol.

If the couple be in a finely divided condition, this reaction takes place after a minute or two with almost explosive violence. It was found necessary, therefore, in order to study the reaction, to employ a coarse couple.

It was found that the gas produced by the reaction burnt with a very luminous flame. This led us to suspect the presence of some olefiant gas or acetylene, and accordingly the gas was passed through an ammoniacal solution of cuprous chloride. A quantity of a red precipitate formed which when washed and dried detonated upon heating, and had all the other properties of copper acetylide.

In one experiment 2.5 c.c. (7 grams) were added to 20 c.c. of absolute alcohol, and the mixture was added to the usual quantity of dry

couple. Action commenced at once at the ordinary temperature, and the liquid soon becoming hot, it proceeded very rapidly. The flask was kept agitated in cold water. In seven minutes the evolution of gas had ceased.

The gas produced in the reaction, after passing through a solution of ammoniacal cuprous chloride, measured 190 c.c. It did not combine with bromine, and burnt with an almost non-luminous flame, yielding carbonic anhydride. Determination of copper in the red precipitate gave .334 gram of copper.

The product of the reaction left in the flask possessed the general properties of the bromoethylate of zinc previously described by us, and gave on determining the atomic ratio of zinc to bromine 1 of the former to 1.5 of the latter. The total zinc found in combination with bromine was equivalent to 6.5 grams of bromoform.

In another experiment 203 c.c. of non-absorbable gas were obtained, and .333 gram of copper in the copper acetylide precipitate. The ratio of zinc to bromine was 1 : 1.48.

Now, taking the mean of the above results, we have—

	Grams.
Gas possessing the properties of marsh-gas, equivalent to	2.21 of bromoform.
Gas forming a red precipitate with ammoniacal cuprous chloride, calculated as acetylene....	1.33 ,,
Total accounted for by gaseous products.....	3.54 ,,

That nearly the whole of the bromoform undergoes decomposition is evident from the amount of bromine found in combination with zinc in the flask. But what becomes of the CH of the CHBr_3 , corresponding to nearly 3 grams?

Thinking that benzene a polymeride of acetylene (C_6H_6), might have been produced and retained in the flask, that substance was sought for, but only with a negative result. In fact till recently the whereabouts of this CH remained a mystery, but it was explained when we came to experiment with iodoform.

The ratio of zinc to bromine would point to the reactions—

as having taken place in about equal proportions, but the ratio of acetylene to marsh-gas would seem to show that nearly two-thirds of the bromoform was decomposed according to the reaction (a), the other third being according to reaction (b).

Zinc-foil.—2.5 c.c. (7 grams) of bromoform were mixed with 20 c.c.

of alcohol and added to the usual quantity of zinc-foil in small pieces. No apparent action was observable in 30 minutes at a temperature of 40° C., only a slight action at 50° , but after a few minutes' heating at 60° the evolution of gas became very rapid, and the action ceased in about 30 minutes.

Examination of the products gave—

	Grams.
Gas non-absorbable by ammoniacal cuprous chloride 521 c.c., equivalent to	5.88 of bromoform.
Gas absorbable by the same, equivalent to ..	0.13 ,,
Bromine combined with zinc, equivalent to ..	6.67 ,,

The ratio of zinc to bromine was found to be as 1 to 1.17.

Comparing the respective actions of the couple and of zinc upon bromoform and alcohol, there is noticeable not only a difference in the degree of action of the two agents, but also in the relative amounts of the two hydrocarbons produced. Thus with zinc, acetylene appears in much smaller quantity, while marsh-gas is produced in very much greater quantity. Also with zinc there is no CH unaccounted for, as as the case when the couple was employed.

Bromoform. Couple and Water.

At the ordinary temperature action takes place very slowly, CH_4 being evolved and zinc bromide and oxybromide formed. At 60° C. the action is of course more rapid, and the CH_4 is found mixed with a very little acetylene.

iodoform.

Couple in presence of Alcohol.

Action takes place at the ordinary temperature of the air, but extremely slowly. This may be due in part to the slight solubility of iodoform in alcohol. At 40° C. the action is perceptible, and with agitation quickly becomes somewhat rapid.

In one experiment 8.45 grams of iodoform and 10 c.c. of absolute alcohol were added to the couple, and the whole heated to 40° C. by immersion in water at that temperature. The evolution of gas ceased in 25 minutes. It contained a large proportion of acetylene.

The gas non-absorbable by ammoniacal cuprous chloride measured 226 c.c., which is equivalent to	3.97 grams CHI_3
The copper in the acetylene precipitate weighed 0.375 gram, equivalent to	2.32 ,,
	<hr/> 6.29 ,,

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The ratio of zinc and iodine in the semi-fluid product remaining in the flask was 1 of zinc to 1.41 of iodine.

Zinc-foil.—In one experiment 8.6 grams of iodoform mixed with 10 c.c. of alcohol were added to about 9 grams of zinc-foil crumpled and in small pieces. A very slow action was observable at 50° C., but at the boiling-point of the alcohol the action was rapid, being completed in about ten minutes.

The gas non-absorbable by cuprous solution	
measured 377 c.c., equivalent to	6.63 grams CHI_3 .
The copper in acetylene precipitate was equivalent to	1.29 ,,
	<hr/> 7.92 ,,

The ratio of zinc to iodine in the product of the reaction in the flask was 1 : 1.11, which would appear to indicate that about 89 per cent. of the substance had been decomposed according to the equation—

We remark here, as we previously remarked when speaking of bromoform, that the couple gives a greater proportion of the acetylene reaction than does zinc alone; and also, that practically the whole of the CH in the iodoform is accounted for when zinc is employed, whereas a considerable proportion of those elements apparently disappears when the couple is used.

The fact that the loss of CH occurs only when the couple is used led us to think that the CH would be found in combination with the copper of the couple. The following experiment with iodoform was consequently made:—

5 grams of iodoform and 10 c.c. of alcohol were heated with a proportional quantity of couple. After the reaction, the solid residue in the flask was washed with alcohol, then with water dried over sulphuric acid *in vacuo*, and finally burnt with copper oxide. 0.166 gram of CO_2 was obtained, which is equivalent to 1.487 gram of iodoform, a quantity closely corresponding to that which we had been unable to account for. It is to be presumed that it existed as acetylide of copper.

Thinking that a greater yield of gaseous acetylene might be obtained by using platinum, with which acetylene is not known to combine, we employed a zinc-platinum couple. We found that the reaction with iodoform and alcohol took place at a lower temperature and was more

energetic, but about the same proportion of CH_4 to C_2H_4 was obtained as with the copper-zinc couple, and also about the same amount of loss. Carbon was found in the insoluble residue, but whether as acetylide or some polymeride of acetylene it is difficult to say.

Conclusion.

In presence of alcohol the three bodies are split up in the same general manner, acetylene and marsh-gas being the hydrocarbon products in addition to the haloïd zinc-ethylates previously described by us. In the cases of chloroform and bromoform there is noticeable a marked difference in their activity, the latter being, as we might expect, the more energetic. The insolubility of iodoform in alcohol prevents us from drawing any conclusion as to its comparative activity. There is also a gradation in the proportion of acetylene. Thus 1·7 per cent. of chloroform, 19 per cent. of bromoform, and 27·4 per cent. of iodoform were converted into this body.