PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXXVII.—*Researches on the Action of the Copper-Zinc Couple on Organic Bodies.*Part III. *On Normal and Iso-Propyl Iodides.*

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

As the iodides of ethyl and of amyl are decomposed by our copper-zinc couple at a temperature below their respective boiling points, we anticipated that the same would be the case with the intermediate iodides of propyl and butyl. As these bodies offer to us isomeric modifications, an additional point of interest was included in their investigation.

In the present paper we confine ourselves to the propyl compounds, but hope at some future time to describe the reactions with all the butyl iodides, if we are fortunate enough to procure specimens of them.

Action of the Dry Couple on Isopropyl Iodide.

The isopropyl compound, being the more accessible body, was the first examined. Our specimen had a constant boiling point, and seemed perfectly pure.

If it be heated to 50° with a dry copper-zinc couple a faint cloud appears in the flask after the lapse of some minutes, and gases are evolved. The action proceeds rapidly, and no further change takes place even at a boiling temperature.

In one experiment 5 c.c. (8·73 grms.) showed signs of action in fifteen minutes, and during the next four minutes 453 c.c. of gas were collected and the action ceased, leaving in the flask a body liquid at the ordinary temperature and a solid (probably iodide of zinc) which it held mainly in solution. When air was admitted to the flask white fumes formed in the neighbourhood of the liquid. When this was gently heated over a gas flame 424 c.c. of gas were quickly evolved and a small quantity of a liquid distilled. This liquid fumed in the air, and on decomposition by water gave 0·068 zinc oxide, which would be equivalent to 0·127 grm. of zinc-propyl.

In another experiment with the same quantity of isopropyl iodide at 50° the action commenced in twelve minutes, lasted six minutes, and yielded 425 c.c. of gas. The flask was then heated to 100° and kept at that temperature for twenty minutes, but no gas was evolved. It was then raised 132° and maintained at 132°—138° for two hours

During the whole of this time gas was slowly evolved, amounting to 283·2 c.c., while a little liquid distilled. The temperature was then increased, and 81·6 c.c. of gas and a further trace of liquid were obtained. The total gas collected was therefore 789·8 c.c. The amount of zinc-oxide formed by the decomposition of the two small portions of liquid in the tubes and receivers was ·018. The amount of liquid in the receiver was certainly more than ·033 grm., leading us to the belief that a little dipropyl (C_6H_{14}) is formed, as there was no iodide.

As in the course of our experiments on amylic iodide (p. 678 of this volume) we found more zinc-amyl produced when the contents of the flask were heated *in vacuo*, we adopted the same plan in this instance also.

Another preparation was made at 50° and it was then heated to 132° while the gas was constantly being pumped out. A good deal was given off, but also a much larger quantity of the liquid body than in the previous experiments. On the admission of air to the receiver this liquid was suddenly changed into a light brown solid, with evolution of much heat. On addition of water it was decomposed with a crackling noise. The oxide of zinc was ·544, which, if the liquid were zinc-propyl, would indicate 1·01 grm. of that body prepared from 8·7 grms. of the iodide.

The gas given off during the reaction at 50° was analysed by Bunsen's method, after it had been passed through a set of bulbs containing respectively alcohol and water. When it was treated with Nordhausen sulphuric acid the following data were obtained from two different preparations:—

	Volume observed.	Tempera- ture.	Difference of Hg. level.	Baro- meter.	Vol. at 0° C. and 1 m.
I. Gas used (dry)	65·57	18·2	95	750·06	40·51
After treatment (dry) ..	34·85	13·5	101·8	758·19	22·11
11. Gas used (dry)	165·1	8·8	98	756·66	118·14
After treatment (dry) ..	95·7	9·3	82·8	756·66	62·69

It appears therefore that the gas capable of being absorbed was per 100 volumes—

Expt. I.	Expt. II.	Mean.
45·43 vols.	44·55 vols.	44·99 vols.

A portion of the gas not absorbed by sulphuric acid was exploded in the usual way, and the following are the results:—

	Volume observed.	Tempera- ture.	Difference of Hg. level.	Baro- meter.	Vol. at 0° C. and 1 m.
I. Gas used (moist)	27·15	14	422	763·78	8·68
After adding air and O (moist)	284·39	14	165·8	763·78	158·83
After combustion (moist)	251·47	14·5	199	763·78	132·19
After absorption of CO ₂ (dry)	213·14	16·7	220·5	749·81	106·57

This gives the following results, which are compared with those calculated for hydride of propyl:—

	Found.	C ₃ H ₈ .
Gas burnt	8·68	—
Contraction	26·64	26·04
Carbonic anhydride	25·62	26·04

Another combustion gave nearly the calculated amount of carbonic anhydride, but the first contraction exceeded still more what was expected. The interior of the eudiometer, however, after the explosion presented an appearance which led us to think that some combination of oxygen with nitrogen had taken place. This of course would account for an excess of contraction.

Some of the gas which had not been treated with sulphuric acid was burnt.

	Volume observed.	Tempera- ture.	Difference of Hg. level.	Baro- meter.	Vol. at 0° C. and 1 m.
Gas used (moist)	22·57	11	416·2	746·76	7·11
After adding air and O (moist)	284·49	10	157·7	746·51	159·36
After combustion (moist)	258·82	9·2	180·8	745·1	139·61
After absorption of CO ₂ (dry)	225·04	9·3	217	756·66	117·67

Now if we assume that 100 volumes of this gas contain 45 volumes of propylene, as we are warranted to do by previous experiments, the 7·11 vols. may be supposed to be made up of 3·2 vols. of propylene, C₃H₆, and 3·91 vols. of hydride of propyl, C₃H₈. Calculating from this, we obtain numbers very similar to those found—

	Found.	Calculated.
Gas employed	7·11	—
Contraction	19·75	19·73
Carbonic anhydride	21·94	21·33
		3 v 2

It may therefore be concluded that the gas evolved at 50° is a mixture consisting of nearly equal volumes of C_3H_6 and C_3H_8 .

The gas evolved in the second part of the operation was also examined. The amount collected when the contents of the flask were submitted to dry distillation was rather less, as already shown, than that collected during the reaction at 50° , and when treated with Nordhausen sulphuric acid it was found to contain about half its volume of an olefine. It would appear therefore that the gas given off in the two parts of the reaction is of essentially the same composition, and the probable reaction is as follows:—

The two reactions go on simultaneously in about equal proportions at 50° .

Action of the Couple on Isopropyl Iodide and Water.

It was found that this iodide, like those previously examined, is decomposed at the ordinary temperature by the couple wet with water. The action commences at once.

In the first experiment with 5 c.c. of the iodide, gas was slowly evolved for 48 hours, the temperature varying from 7° to 11° . The amount collected was 820 c.c.

In another experiment, where the temperature was 13° — 16° , 831 c.c. were collected in 40 hours.

The gas thus produced was found to be readily soluble in alcohol and to burn with a luminous flame. Two portions treated with Nordhausen sulphuric acid gave an absorption amounting respectively to 7.93 and 9.73 per cent.

After removal of the residuary gas of one of these portions to the endiometer the following data were obtained:—

	Volume observed.	Tempera- ture.	Difference of Hg. level.	Baro- meter.	Vol. at 0° and 1 m.
Gas used (moist)	27.85	12	413	773.43	9.5
After adding air and O (moist)	416.6	6.2	28	754.07	293.3
After combustion (moist) ..	388.3	6.2	50.6	754.38	264.65
After absorption of CO_2 (dry)	368.6	9	74.6	735.84	236.28

which gives the following results, agreeing very closely with those calculated for propyl hydride:—

	Found.	C_3H_8 .
Gas used	9.5	—
Contraction	28.65	28.5
Carbonic anhydride	28.37	28.5

Action of the Couple on Isopropyl Iodide and Alcohol.

The action of this iodide with alcohol was more rapid than with water, as was also the case with the iodides previously examined.

5 c.c. mixed with 10 c.c. of absolute alcohol were poured upon the dry couple, at a temperature of 9° . In four minutes there was an evolution of gas, which proceeded so rapidly that the flask had to be immersed in cold water, at 7° . Nevertheless in four more minutes the action was complete, and 823 c.c. of gas had been collected. In another experiment 5 c.c. of the iodide were poured upon a couple which had been washed with absolute alcohol, but not dried. The temperature was 17° . Evolution of gas commenced in two minutes, when the flask was at once immersed in water at 13° . In ten minutes, 885 c.c. had been collected. The whole gas evolved in this experiment was 913 c.c.

If the propyl contained in 5 c.c. of the iodide were wholly converted into C_3H_8 , it should yield 1150 c.c. of gas. The actual yield, therefore, whether in the case of water or alcohol, is considerably less than the theoretical, but this probably arises from its solubility in the water over which it was collected, and the carrying over of some vapour of the iodide.

Action of Zinc alone.

As isopropyl iodide is so easily decomposed by the copper-zinc couple, it occurred to us that it might be attacked by zinc alone. On trying the experiment with clean zinc foil it was found that no action whatever took place at 50° , though the heat was continued for an hour, but that on immersing the flask in boiling water, evolution of gas commenced in eight minutes, and proceeded so rapidly, that in twelve minutes more it was complete, and 605 c.c. of gas had been collected. The residue in the flask fumed slightly in the air, and when heated gently over a flame, it gave off 177 c.c. of gas, and a small quantity of the volatile zinc compound decomposable by water.

For the purpose of comparison, a flask containing 5 c.c. of the iodide, and the ordinary copper zinc couple was similarly immersed in boiling water. Evolution of gas commenced at once, and in five minutes the action was complete, 490 c.c. of gas being collected.

This illustrates the fact that even when zinc alone is capable of effecting a decomposition, the copper-zinc does it at a lower temperature, or with greater rapidity; also that the decomposition is not

identical in the two cases, for the more elevated temperature causes a larger proportion of the organic compound to be resolved into hydride and olefine.

On repeating the above experiment with pure zinc, finely granulated, we found that with it also the reaction took place at the boiling temperature.*

The reaction with isopropyl iodide and water and clean zinc takes place exceedingly slowly at 20°; when the usual quantities were employed, only 35 c.c. of gas were collected in 24 hours. When the temperature is raised, the production of gas is greatly increased.

The reaction with the iodide and alcohol with clean zinc foil at 20°, commenced in a few minutes, and the action proceeded rapidly, but not so violently as with the couple. With pure zinc granulated, we obtained the same result.

Propyl hydride has been prepared by Schorlemmer (*Proc. Roy. Soc.*, 1869, p. 373) by the mutual action of isopropyl iodide, zinc, hydrochloric acid and water, but the reaction with zinc alone in presence of alcohol, seems to offer a better method of preparing this gas; better, in fact, than when the couple is employed, as it is more manageable.

Action of the Dry Couple on Normal Propyl Iodide.

We procured a specimen of the normal propyl iodide, which boiled almost constantly at 101°, and we found that it was attacked very slowly by clean zinc foil, or pure zinc, even at its boiling point, and that it was acted on by the couple very differently from the iso-compound.

In the first place 5 c.c. (8·81 grms.) were heated in contact with the dry couple for an hour at 50°, the temperature at which the iso-compound is attacked, but no action whatever took place. A similar portion was afterwards heated with the couple, at 80°, in the manner described in a previous paper (*Chem. Soc. Journal*, May, 1873, p. 445). In forty minutes dense white fumes were observed in the flask, but they were not accompanied by any appreciable evolution of gas. The heating was continued for twenty minutes, when the flask was allowed to cool, and its contents were washed out with ether. When water was added to this solution, a brisk effervescence ensued, and hydrated oxide of zinc was thrown down. The amount of zinc-oxide was 1·414, which would be equivalent to 2·636 grms. of zinc-propyl, and that would be 67·4 per cent. of the amount theoretically obtainable from 5 c.c. of the iodide.

* This reaction is the more remarkable, as Schorlemmer finds that isopropyl iodide is not decomposed by sodium, even at the boiling-point. See *Proc. Roy. Soc.*, 1867, p. 34.

In a subsequent experiment the same quantity of iodide was heated in contact with the dry couple, by means of a chloride of calcium bath at 109° . At the end of ten minutes the return flow of the liquid appeared to have ceased, while very little gas—not more than 50 c.c.—had been evolved. When cool, the organic compound in the flask did not crystallise, but seemed, as in the case of the iso-compound, to be a liquid body, holding a solid in solution. It was distilled in a current of carbonic gas, in the same way as the ethyl compound had been distilled, and a liquid came over, which, when decomposed by water, yielded 1.32 gram of ZnO , equivalent to 2.46 grams of zinc-propyl, or 62.9 per cent. of the possible amount. Yet the distillate contained some undecomposed propyl iodide.

The experiment was repeated with this difference, that after the return flow had ceased, which required nine minutes, the flask was exposed for another nine minutes to the heat of a bath at 117° . The product was liquid, as before, but the distillate contained no iodide, and yielded 1.578 ZnO , equivalent to 2.94 grams of zinc-propyl, or 75.2 per cent. of the possible quantity—a larger yield than we ever obtained in the case of zinc-ethyl.

A third experiment was made with a specimen of the normal propyl iodide obtained from another source. The result was as before; but the liquid product was distilled into a weighed receiver, previously filled with carbonic acid, and was found to weigh 2.712 grams, or 69.3 per cent. of the theoretical amount of zinc-propyl, obtainable from 5 c.c. of iodide employed. On re-distillation, the great bulk came over between 146° and 148° .

A preparation was then made on a larger scale, 15 c.c. of the iodide were taken, and three times the usual amount of couple, a two-ounce flask being still employed.* When it was heated in a bath at 109° , the return flow ceased in thirteen minutes, but a temperature of 117° was maintained for twenty minutes more, in order to insure complete conversion. There was some gas evolved during the whole period, but the production diminished considerably towards the end. The quantity collected was 290 c.c. When the bath was heated at 149° distillation commenced, but it was finished off at 182° . The flask then contained some reduced zinc, partly in a crystalline form. The liquid in the receiver weighed 8.563 grams, or 73 per cent. of the possible amount of zinc-propyl. On re-distillation in a bath, the whole passed over between 142° — 148° , leaving a small residue of metallic zinc.

Zinc-propyl thus produced is probably the same body as that which Cahours obtained by double decomposition, though that chemist has

* Two-thirds of the couple was transferred from another flask in which it had been prepared, dried, and annealed.

not yet published a description of it. Our compound is a colourless mobile and volatile liquid, of specific gravity 1.098 at 15° C., and boiling at about 146°. When exposed to the air it takes fire spontaneously,* burning with a bluish white flame. If dry air be allowed gradual access to it, it is converted into a white solid, which does not fume in contact with air, but is decomposed by water, with a crackling noise and effervescence.

1.0885 grm. of the liquid yielded on decomposition with water, 0.583 grm. ZnO, giving the following percentages:—

	Found.	Calculated for Zn $\left\{ \begin{array}{l} \text{C}_3\text{H}_7 \\ \text{C}_3\text{H}_7. \end{array} \right.$
Zinc.	42.98	43.04

Action of the Couple on Normal Propyl Iodide and Water, or Alcohol.

When 5 c.c. of the normal iodide were poured upon the couple wet with water at 13°, gas was almost immediately evolved, but the action proceeded very slowly. In about 84 hours it ceased, when 884 c.c. were found in the receiver. The temperature had varied from 13° to 19°. This gas was not diminished in volume by treatment with Nordhausen sulphuric acid; it dissolved readily in alcohol, and burnt with a very luminous flame.

When 5 c.c. of the normal iodide were poured upon the couple wet with absolute alcohol at 15°, evolution of gas commenced in twenty minutes, soon after which the temperature of the flask rose considerably. The action was complete in 45 minutes, when 766 c.c. had been collected, but some iodide had distilled over unchanged.

In another similar experiment the action commenced in 28 minutes, when the flask was at once immersed in water at 17°. Gas was evolved for about 24 hours, when 868 c.c. had been collected.

The amount of gas, as usual, falls short of the quantity possible on the supposition that the propyl passes over entirely as the hydride, C_3H_8 , viz., 1161 c. c., but it shows at least that the gas obtained corresponded to 2 volumes.

Comparison of Results.

This inquiry has added to the evidence already existing of the comparative instability of the iso-propyl compounds. We have noticed the following points of contrast:—

The iso-propyl iodide is rapidly decomposed by zinc alone at its boiling point, 89°, while the normal propyl iodide is decomposed very slowly by zinc alone at its higher boiling point 101°.

* It was found that zinc-propyl was rendered not spontaneously inflammable by admixture with a little less than 3 per cent. of propyl iodide.

The iso-compound is decomposed by the copper-zinc couple at about 50°; the normal compound at about 80°.

In this decomposition about half of the iso-compound is split up into permanent gases; little, if any, of the normal compound is so split up.

The resulting liquid in the one case (zinc-isopropyl?) is scarcely volatile; that in the other case (zinc-propyl) rises easily in vapour, notwithstanding its high boiling point. The first is decomposed at about 132°, giving mainly gases and metallic zinc: the second distils over unchanged at a higher temperature.

The reaction between the propyl iodide and water, or alcohol, with the couple, takes place much more rapidly in the case of the iso-compound than in that of the normal compound; while an olefine makes its appearance during the decomposition of the first, but not of the second.

On comparing these results with those previously obtained with the ethyl and amyl compounds, it is evident that it is the normal, and not the iso-propyliodide that is acted upon in an analogous manner. The main difference perhaps is that there seems to be no crystalline propyliodide of zinc, but that the reaction is mainly, if not wholly—

Additional Notes on the Couple.

In performing these experiments with 5 c.c. of liquid, we have employed zinc foil having a surface of about 260 square centimeters on each side and weighing about 9 grams. It is crumpled up and torn to pieces just so as to introduce it into the flask, and leave irregular spaces between the different pieces. After treatment with copper sulphate, the zinc sulphate produced should be thoroughly washed away; and particular attention should, of course, be paid to the purity of the alcohol and ether with which it is dried, for any deposit on the surface would be highly injurious. In drying the couple in a stream of carbonic acid it has been found convenient to heat it till the zinc begins to soften, not melt; on cooling, the zinc will be found to be annealed, and may be gently pressed to the bottom of the flask.

It has been suggested to us that zinc foil necessarily contains some quantity of lead, and that this may have an important bearing on the reaction. Specimens of zinc from various sources have, therefore, been examined, and have given the following percentages of lead:—

Zinc foil used for couple*	0·96 and 0·93 per cent.
Granulated zinc, commonly used in our laboratory.	1·13 per cent.

* Supplied by Messrs. Hopkin and Williams.

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Granulated zinc from Dr. Frank-	
land's laboratory	0·96 per cent.
Ordinary sheet zinc	0·89 „

It appears, therefore, that the zinc foil contains no more lead than the form of zinc which has been usually employed, and we have no evidence to show whether the presence of one per cent. of this metal is favourable or unfavourable to the action of the couple.

A comparative experiment was made with 18 grams of granulated zinc on which copper had been deposited in the same manner as before. It gave with normal propyl iodide the same reaction as the couple made of foil, but much more slowly. This superiority of the foil depends doubtless on its presenting so large an extent of surface in a given cubical space, and therefore forming so large a number of small circuits between the two metals and the liquid.