Dec. 16, 1850.

WILLIAM ALLAN MILLER, M.D., V.P., in the Chair.

Henry Medlock, Esq., and James Simpson, Esq., were elected Fellows of the Society.

The following Presents were announced :

“Journal of the Franklin Institute,” Vol. XX. No. 4, October 1850; from the Society.

“Proceedings of the Philosophical Society of Glasgow,” Vol. III. No. 4; from the Society.

“Recueil des Actes des Séances Publiques de l'Académie Impériale des Sciences de St. Pétersbourg, tenues le 28 Décembre, 1847, et le 19 Décembre, 1848.”

XXXIII.—*Observations on the Constitution of the Alcohol-Radicals, and on the formation of Ethyl.*

By B. C. BRODIE, F.R.S.

(SECRETARY OF THE CHEMICAL SOCIETY.)

On the occasion of the remarks of Dr. Hofmann on Dr. Frankland's second paper on the Organic Radicals, I made to the Society some observations on the theoretical constitution of those bodies. New facts have since been brought to light which strongly confirm the view which I then gave; and as the concluding remarks of Dr. Frankland's last paper have again brought this question before the Society, I take the opportunity of here making a memorandum of them.

Dr. Frankland pointed out various and, in my opinion, indisputable analogies between these hydrocarbons and hydrogen; and representing hydrochloric acid by the symbol HCl, the chloride of ethyl as $C_4 H_5 Cl$, and the isolated element hydrogen as H, he con-

sistently gave the formula $C_4 H_5$ as that of the isolated ethyl. This formula, however, involved the singular anomaly that the atom of the gaseous ethyl occupied only half the space of the atom of all other hydrocarbons.

Gerhardt, with whose chemical ideas this anomaly was inconsistent, gave a theory of these bodies which doubled their formula.* On his view, methyl was a homologue of marsh-gas. The constitution of the two substances being thus expressed :

This view, however, not only doubled the formula of these bodies, but entirely set aside all their importance as radicals from the point of view of Frankland. Gerhardt considered himself further as justified in this by the absence of any remarkable chemical properties, by which these bodies were to be distinguished from other hydrocarbons.

Hofmann, in an elaborate, and indeed, most convincing argument, confirmed the necessity of doubling these formulæ; but at the same time he considered that the mode of the formation of the bodies appeared to be certainly in favour of the lower formula.† “Hydriodic acid and zinc,” says he, “yield iodide of zinc and hydrogen; in the same manner it would appear the iodide of an alcohol radical gives rise to the formation of iodide of zinc and the alcohol-radical.”

The perfect analogy of these reactions I admit; but I deny the inference as to the formula. If we represent the formation of the hydrogen $Zn + IH = ZnI + H$, we must, it is true, in consistency represent the formation of the radical ethyl in a similar manner, $Zn + IC_4 H_5 = ZnI + C_4 H_5$; but the formation of the hydrogen may also be represented thus :

in which case the analogous formation of the ethyl is given by the expression :

That this or some other similar expression which equally involves

* Compt. Rend. Trav. Chim. 1849, 19, and 1850, 12.

† Chem. Soc. Qu. J. III, 128.

the hypothesis that the formation of the isolated element is a chemical synthesis of the particles of the combined element, is the only rational expression of this reaction, is not an arbitrary assumption to meet the present case, but proved by a great variety of phenomena. I have elsewhere* fully discussed that general law of chemical action, of which this is, I believe, but a particular example, and I shall confine my remarks now to the present instance.

When zinc acts on the iodide of ethyl in the presence of water, the reaction, according to Frankland, is thus expressed :

this may be taken as the type of the other changes ; for substituting in the change, iodide of ethyl for water, we have the formation of ethyl

or substituting water for the iodide of ethyl, we have the formation of the hydrogen thus :

a reaction which truly takes place at high temperatures.

The view which I have given shows the relation between these phenomena, and that they are all expressions of one and the same law of chemical action, whereas, otherwise, at least two hypotheses and two different forms of chemical change are required to explain them. It is to me truly remarkable that Frankland, who maintains so strongly the analogy between the iodide of ethyl and water and the ethyl and hydrogen, yet denies the possibility of the substitution of these bodies for each other in this series of chemical changes.

There is a remarkable case of the formation of hydrogen to which I have referred in the paper before alluded to,† which I believe can only be accounted for on the view I have given. This is the decomposition of the hydruret of copper $\text{Cu}_2 \text{H}$ by hydrochloric acid. The substance itself and the reaction were discovered by Wurtz. Hydrochloric acid, which does not act upon copper, decomposes this body, thus :

This I regard as (what is called) a simple case of double decompo-

* Phil. Trans. 1850, II, 789.

† Phil. Trans. 1850, II, 798.

sition. The formation of the hydrogen being the correlative fact to the formation of protochloride of copper. The oxidation of alcohols by hydrate of potash is likewise a case in point. The hydrogen in this experiment comes partly from the alcohol, and partly from the hydrate of the alkali, thus :

I regard the formation of the hydrogen as a chemical synthesis as truly as that of the acetic acid. The decomposition of water by the zinc-methyl is perfectly analogous to the formation of hydrogen by the decomposition of the hydruret of copper. Thus $\text{Zn C}_2 \text{ H}_3 + \text{HO} = \text{ZnO} + \text{C}_2 \text{ H}_3 \text{ H}$, and in the oxidation of acetic acid by the hydrate of potash and the formation of marsh-gas or the hydride of methyl, the methyl combines with the hydrogen of the hydrate of potash in the same way as the hydrogen of the alcohol in the other experiment, thus :

we can therefore with one of these bodies effect the same kind of chemical changes as with the other.

These considerations induced me to try the experiment, whether the zinc-ethyl would not decompose the iodide of ethyl, with the formation of iodide of zinc and ethyl :

as the copper-hydrogen decomposes the hydrochloric acid with the formation of protochloride of copper and hydrogen. This experiment was wanting to complete the series of analogies, for, although Frankland* had shown the presence of zinc-ethyl, or some body containing this compound, among the products of the reaction of zinc upon the iodide of ethyl, yet he had not shown that it took any part in the change ; and, indeed, as it was a constant product of the decomposition, as also was olefiant gas and hydride of ethyl, when once formed, it might never be decomposed. With this view, I prepared a tube according to the directions of Frankland, containing

* Chem. Soc. Q^u. J. II, 298.

iodide of ethyl, with a great excess of zinc, and exposed it for some hours to a temperature of 140° to 150° C., at which temperature I had ascertained that a considerable proportion of zinc-ethyl was formed. I broke the end of the tube, allowed the gas formed to escape, and then introduced a fresh portion of iodide of ethyl, and re-sealed the capillary opening. The zinc was still in excess. The tube was now exposed for some hours to a temperature of 100° C. in a water-bath. On re-opening the tube, a certain quantity, although small, of gas was evolved, showing that action had evidently taken place. This might be the result of the action of the zinc-ethyl on the iodide of ethyl, but it was also possible that even at 100° the excess of zinc had acted on the iodide, for the residue still contained a large portion of zinc-ethyl, effervescing strongly with water; I now repeated this experiment, with the difference only that I at once placed the tube in the water bath. After several hours' action, the iodide of ethyl had disappeared, the zinc was covered with a crystalline crust, and on opening the tube under water, a small quantity of gas was given off, and the residue contained a large quantity of zinc-ethyl. Hence it is plain, that even at 100° zinc acts upon the iodide of ethyl. The question now was, whether the zinc-ethyl thus formed could be decomposed by the iodide at a higher temperature. My first experiments were quite unsuccessful: I took a small quantity of zinc and a very large quantity of the iodide of ethyl, and exposed the sealed tube for several hours to a temperature of 100° . It was then transferred unopened to an oil bath, and kept for several hours at a temperature of about 160° C. At the end of this time a much larger quantity of gas was given off than at 100° ; but the residue still effervesced strongly with water, nor could I at all succeed, even when very small portions of zinc were used, in entirely getting rid of the zinc-ethyl. The substance, however, which had been exposed to the higher temperature had undergone a great alteration in appearance, the tube being full of white crystals. The zinc-ethyl also, from the quantity of gas evolved, had been undoubtedly acted upon, although partially. It occurred to me that the reason of the cessation of the action, was that the zinc-ethyl, or other substance formed in the experiment, was not sufficiently soluble in the surrounding fluid, and that the action would be different in a different medium. Frankland* had already found that the zinc-ethyl was soluble in ether; ether therefore appeared to be a suitable solvent. I therefore repeated these experiments, still with a great excess of the iodide of ethyl, but with the addition of

* Chem. Soc. Qu. J. III, 293.

about twice its bulk of pure ether. The experiment succeeded perfectly. At 100° C., the zinc disappears, with the formation of only a trace of gas, and a large quantity of the zinc-ethyl. A small quantity of solid matter remains in the tube, but no zinc. A tube which had thus been exposed for several hours to 100° was now heated to 170° in an oil-bath. A large quantity of white crystals were deposited, and on opening the tube under water, a considerable quantity of gas was evolved, and the residue contained not a trace of zinc-ethyl, neither the fluid nor the solid matter effervescing with water. On ether alone, at this temperature, zinc has not the slightest action.

In the experiments of Frankland, there are two ways in which zinc decomposes the iodide of ethyl: the one in which the two particles of ethyl combine and ethyl is formed, the other in which one of these particles decomposes the other, with the formation of hydride of ethyl, C_4H_5H , and olefiant gas or the hydride of acetylene, C_4H_3H . This latter decomposition we may conceive to take place by the division of the hydrogen within the body, thus:

Frankland had indeed already ascertained the presence of ethyl in the gas produced by the action of zinc upon the iodide of ethyl and ether at a high temperature; but yet it seemed to me of importance to prove that the decomposition had not taken place entirely in this latter manner. For it was possible that the reaction of the zinc-ethyl on the iodide of ethyl might differ from that of the zinc, and that the constant formation of the hydride of ethyl and olefiant gas might be owing to this very reaction. I therefore dried the gas, and treated it with anhydrous sulphuric acid and manganese, after the method of Frankland, and conducted the experiment with the precautions which he recommends. After the necessary corrections for temperature and pressure, an experiment of this nature gave the following results: Total bulk of the gas, 39.78; gas after the absorption by SO_3 , 33.54; gas after the absorption by alcohol, 4.53. This gives as the constitution of the gas, allowing the gas unabsorbed by sulphuric acid to be a mixture of ethyl and the hydride of ethyl:

Ethyl	.	.	.	.	.	6.24
Ethyl and hydride of ethyl	.	.	.	.	.	29.01
Nitrogen	.	.	.	.	.	4.53
						<hr/>
						39.78

It was plain, therefore, that only a very small portion of the iodide of ethyl had been decomposed in this other manner. In Frankland's experiment (without ether), the ratio of the gas absorbed by alcohol to the ethyl was as 100:28.6; in this experiment it is as 100:21.5. Circumstances have as yet prevented me from completing the analysis of this gas; but this experiment, together with those of Frankland, I consider conclusive as to the nature of the reaction.

The next step in these experiments should be the decomposition of the iodide of methyl or of amyl by the zinc-ethyl, in which case, the formation of a compound hydrocarbon might be anticipated of the formula C_2H_3 , C_4H_5 , or C_5H_6 . C_4H_5 , ethyl-methyl and ethyl-amyl.* Ethyl stands to hydride of ethyl in the same relation as ether to alcohol, and would be to these hydrocarbons as ordinary ether to the compound ethers discovered by Williamson.† The parallel series being complete, thus:

H	H	Hydrogen	.	.	.	$\frac{H}{H}$	} O ₂ Water.
C_4H_5	H	Hydride of ethyl	.	.	.	$C_4\frac{H_5}{H}$	} O ₂ Alcohol.
C_4H_5	C_4H_5	Ethyl	.	.	.	$C_4\frac{H_5}{C_4H_5}$	} O ₂ Ether
C_4H_5	C_2H_3	Ethyl-methyl (unknown)				$C_4\frac{H_5}{C_2H_3}$	} O ₂ Ethylate of methyl.
C_4H_5	$C_{10}H_{11}$	Ethyl-amyl (unknown)				$C_4\frac{H_5}{C_{10}H_{11}}$	} O ₂ Amylate of ethyl.

* Dr. Hofmann has communicated to me that he has actually tried this experiment with the iodide of amyl, but without success. The same causes, however, which prevent the reaction with iodide of ethyl, would here doubtless operate with yet greater force, the iodide of amyl being decomposed by zinc only with very great difficulty. It is probable that if the iodide of amyl were mixed with ether, the decomposition would be greatly facilitated. I can hardly doubt that, at any rate, the methyl-compound would be readily obtained.

† Phil. Mag. XXXVII, 350.