XVII.—*Action of Sodium upon Iodide of Methyl mixed with Ether.*

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PURE methyl has not yet been obtained. Kolbe's method, viz., electrolysis of an acetate, yields methyl always contaminated by some foreign body, probably oxide of methyl, which cannot be completely removed.

Frankland's method, viz., decomposition of iodide of methyl by zinc, also gives a mixture, which, in this case, consists of hydride of methyl and free methyl. This hydride of methyl, Frankland regards as a secondary product, formed after the gas has left the production tube, and due to decomposition of moisture by some zinc-methyl, with which the gas, as it issues forth, is invariably accompanied.

Bearing this circumstance in mind, we determined to try the action of sodium upon iodide of methyl. Since sodium-methyl cannot be prepared by such a process, we expected to obtain pure methyl. Our expectation was not realized, as will appear in the course of the paper.

The iodide of methyl used in our experiments, boiled constantly at 43° C.

We enclosed in a glass tube some sodium along with a few grammes of iodide of methyl and ether. In order to insure the absence of moisture, we next made a short preliminary digestion in the water-bath. Then we let out the first portion of gas, which was no doubt contaminated with products due to traces of water adhering to the materials employed in the experiment. Afterwards we resealed the tube, heated again to 100° C., and collected the gas over boiling water. After having stood in contact with water during a night, the gas was analysed according to the method employed by Bunsen.

We give the particulars of the analyses:—

The gas was divided into two portions, one of which was placed in the combustion eudiometer, and the other in the absorption tube.

I.—*In the Eudiometer.*

	Volume	Temperature	Pressure	Volume reduced to 0°C. and 1 meter pressure
Volume of gas taken	72.00	26.9°C.	meter 0.15085	9.8876
Volume after addition of oxygen ..	180.96	27.1°	0.25844	42.547
Volume after addition of air	340.90	26.2°	0.41561	129.28
Volume after explosion	308.54	26.7°	0.38336	107.74
Volume after absorption of CO ₂ ..	275.42	25.5°	0.378	95.221
Volume after addition of Hydrogen ..	375.0	26.7°	0.4717	161.13
Volume after explosion	252.98	27.3°	0.3575	82.23

II.—*In the absorption tube.*

	Volume	Temperature	Pressure	Volume reduced to 0°C. and 1 meter pressure
Volume of gas taken	93.70	26.9°	meter 0.65305	55.706
Volume after the action of potash } and pyrogallie acid }	90.63	26.6°	0.6781	55.591
Volume after the absorption of olefines	82.8	25.5°	0.6675	50.551

Some gas after the removal of CO₂, oxygen and olefines, was transferred from the absorption tube to the eudiometer. Its analysis gave the numbers following:—

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III.—*In the Eudiometer.*

	Volume	Temperature	Pressure	Volume reduced to 0°C. and 1 meter pressure
Volume taken	84·32	26·7°C.	meter 0·16676	12·809
Volume after the addition of oxygen ..	399·36	26·7°	0·48686	177·12
Volume after explosion	364·95	27·8°	0·45242	150·11
Volume after the absorption of carbonic acid }	330·25	25·1°	0·4463	134·99

Another analysis of the same gas yielded :—

IV.—*In the Eudiometer.*

Corrected at 0° C. and one meter pressure								
Volume taken	..	..	..	..	..	..	..	10·365
Volume after the addition of oxygen	..	..	..	..	..	..	..	160·75
Volume after explosion	..	..	..	..	..	..	..	138·40
Volume after absorption of CO ₂	..	..	..	..	..	..	..	125·60

A third analysis of the same gas gave :—

V.—*In the Eudiometer.*

Corrected at 0° C. and one meter pressure								
Volume taken	..	..	..	..	..	..	..	18·037
Volume after the addition of oxygen	..	..	..	..	..	..	..	85·611
Volume after the addition of air	..	..	..	..	..	..	..	198·04
Volume after explosion and absorption of CO ₂	..	..	..	..	..	..	..	137·05
Volume after addition of hydrogen	..	..	..	..	..	..	..	258·67
Volume after explosion	..	..	..	..	..	..	..	114·73

Analysis II. shows that the gas was free from carbonic acid and oxygen. It also shows that 55·706 volumes of the gas contained 5·155 vol. of olefines.

In percentage C_nH_n	.	.	9·3
Gas freed from C_nH_n	.	.	90·7
			<hr/>
			100·0

Analysis I. shows that 9·8876 vols. of gas contain 0·368 vol. of nitrogen. In percentage nitrogen = 3·7.

Analysis V. of the gas free from C_nH_n shows that 18·037 vols. contain 0·21 vol. of nitrogen, or 90·7 vols. contain 1·05 vols. of nitrogen. But 100 vols. of the original gas contain 90·7 vols. of gas free from C_nH_n . Therefore, 100 vols. of the original gas contain 1·05 vols. of nitrogen.

The determination of nitrogen at the end of a hydro-carbon gas analysis is subject to a little irregularity, inasmuch as the small quantities of air introduced in the course of the analysis, tell in the aggregate upon the final nitrogen determination.

Adopting the mean of our two results, we have 2·4 for the percentage of nitrogen.

From Analysis I. we obtain :—

		In percentage.
Original gas	9·8876	100·0
Nitrogen	0·237	2·4
Combustible gas	9·6506	97·6
Oxygen consumed	24·4084	246·9
Carbonic acid formed	12·519	126·6

Analyses III., IV., and V., all of the residual gas after removal of C_nH_n give :—

	III.	IV.	V.	Mean.
Combustible gas	12·507	10·091	17·560	88·3
Oxygen burnt	29·623	25·059	43·430	215·7
Carbonic acid formed	15·120	12·80	—	109·1

To arrive at the condensation of the olefines we make use of the following data :—

100 vols. of the original gas are composed of,

9·3 vols. of C_nH_n .

2·4 vols. of nitrogen.

88·3 vols. of residual hydro-carbon.

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And on combustion furnish,

246·9 vols. oxygen consumed.

126·6 vols. carbonic acid.

88·3 vols. of the residual hydro-carbon gas furnish

215·7 vols. oxygen consumed.

109·1 vols. carbonic acid.

Hence the 9·3 vols. of C_nH_n furnish

31·2 vols. oxygen consumed.

17·5 vols. carbonic acid.

The C_nH_n , therefore, has the condensation of ethylene, which requires,

Vol. taken . . . 1·0

Oxygen burnt . . . 3·0

Carbonic acid . . . 2·0

With so low a percentage of C_nH_n as is present in the gas under examination, great accuracy in the determination of its condensation is not to be expected; the very indirect manner of arriving at the result having the effect of concentrating the errors of the whole analysis upon the small percentage of olefine.

The 88·3 vols. of hydro-carbon must consist, for the most part, of marsh gas. Some other more complex hydro-carbon is also present; but what other, cannot be revealed by a mere combustion analysis. If the hydro-carbon be very complex, then the percentage of marsh gas must be high; if less complex, then the percentage of marsh gas falls.

Assuming that the accompanying hydro-carbon is methyl, in which case the proportion of marsh gas reaches its lowest, we have for the composition of the gas

C_4H_4	.	.	.	9·3
Nitrogen	.	.	.	2·4
Hydride of methyl	.	.	.	65·0
Methyl	.	.	.	23·3
				<hr/>
				100·0

As is well known, a combustion cannot distinguish marsh gas from a mixture in equivalent quantities of methyl and hydrogen.

That our marsh gas was such a mixture, was highly improbable. Direct proof we have nevertheless sought in another experiment.

We made a fresh quantity of gas, collected it over strong alcohol (previously boiled) and shook it up therewith. Since methyl is very much more soluble in alcohol than is hydrogen, the gas discharged from this alcohol by boiling, should have been very rich in methyl. After washing with water, however, it yielded on combustion numbers agreeing with the composition of hydride of methyl, viz. :—

Contraction		Carbonic Acid.
10·31	:	5·27

Hydride of methyl requires contraction to carbonic acid in the ratio of 2 : 1.

This gas also contained hardly any olefine, viz., only 2·7 per cent.

We have thus established the following conclusions :—

At 100° C. sodium decomposes iodide of methyl in presence of dry ether, yielding a large quantity of hydride of methyl.

The equation expressing the production of the hydride is neither of the following :—

because, the amount of C_nH_n is too small for the hydride of methyl.

What the product, complementary to the hydride of methyl, really consists of, we have not yet been able to determine.

In conclusion we have to add that we have repeated the experiment and obtained similar results to those which we have described in the paper. With potassium likewise the same peculiarity has been observed as with sodium.

The further investigation of the subject will be made by one of us.