CVII.—*The Direct Union of Carbon and Hydrogen. Synthesis of Methane. Part II.*

By William Arthur Bone and Hubert Frank Coward.

In our previous paper on this subject (Trans., 1908, **93**, 1975), experiments were described in which 73 per cent. of the theoretical yield of methane was obtained by heating less than 0·1 gram of highly purified sugar charcoal to a temperature of about 1150° in a current of pure and thoroughly dried hydrogen, thus establishing beyond all doubt the direct synthesis of methane as originally reported by Bone and Jerdan in 1897 (Trans., **71**, 41), the validity of which had been questioned by Berthelot (*Compt rend.*, 1905, **40**, 905; *Ann. Chim. Phys.*, 1905, [viii], **6**, 183), by Pring and Hutton (Trans., 1906, **89**, 1591), and also by Mayer and Altmayer (*Ber.*, 1907, **40**, 2134).*

Our failure to achieve an absolutely quantitative conversion of carbon into methane was ascribed to the reducing action of the gas on the inner surface of the porcelain tube used in the experiments referred to, and in a footnote (*loc. cit.*, p. 1988) it was reported that, subsequent to the writing of the paper, Dr. Ernest Feilmann had, as a result of a careful microchemical analysis, discovered unmistakable signs of lead in the glaze of the porcelain tube, a circumstance which would sufficiently explain the partial loss of methane during the experiments.

* We may refer the reader to pp. 1976—1978 of our previous paper (*loc. cit.*) for a detailed criticism of the inconclusive experiments of all these authors.

Correspondence was at once entered into with the authorities of the Royal Berlin Factory, where the porcelain tubes had been manufactured, and as the result of a careful inquiry we were informed that whereas "die Glasure, welche für unser Hartporzellan verwendet wird, vollkommen bleifrei ist," the batch of tubes in question had been fired in a kiln which had been accidentally fouled by certain lead glazes and enamels. The factory authorities very kindly undertook specially to prepare a new batch of tubes for our further experiments; these were carefully tested for us by Dr. Feilmann, and although he was unable to report their absolute freedom from lead, the amount of contamination was very much smaller than in the tubes previously used. On repeating our experiments with these new tubes, we have succeeded in obtaining as nearly as possible quantitative yields of methane (certainly exceeding 95 per cent.) from less than 0·03 gram of highly purified carbon.

Before describing these further experiments, however, we desire to refer to certain points raised in Mr. Pring's recent paper on this subject (this vol., p. 498). It is satisfactory to note that this author, now that he has adopted the method for estimating small percentages of methane previously devised by us, acknowledges the probability (p. 500) "that the conclusions of Bone and Jerdan and Bone and Coward, that carbon unites directly with hydrogen to form methane, will be upheld," but later on (p. 503) he quite unjustifiably casts an aspersion on the method employed by us, in common with Bone and Jerdan, for purifying the carbon. Thus, he remarks, "The method . . . for purifying the carbon consisted in igniting the finely divided substance for several days in a stream of chlorine, followed by hydrogen, at a temperature of 1100—1200°. The disadvantage of this method lies in the improbability of ever being able to remove the last traces of combined hydrogen, and the serious contamination which must result from contact with the containing vessel during the long period necessary for the treatment."

In our previous paper analyses of the carbon purified according to our method were given (*loc. cit.*, p. 198), showing that it contained no more than 0·06 per cent. of hydrogen, of which at least part was undoubtedly present in an "occluded" form. We are also happily in a position to refute Mr. Pring's unwarranted suggestion of "serious contamination" from contact with the walls of the containing vessel, seeing that the ash content of our purified carbon has never exceeded 0·06 per cent. As Mr. Pring states in his last paper (p. 504) that his highly purified rods contained "less than 0·10 per cent. of hydrogen and 0·05 per cent. of ash," he is

not entitled to infer that he used a purer form of carbon than previous workers.

Shortly after the appearance of our previous paper, E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1588) claimed to have synthesised ethylene by passing a mixture of approximately equal volumes of carbon monoxide and hydrogen over pieces of coke impregnated with reduced nickel and palladium, and maintained at 95° to 100° only. The exit gas, he said, contained in one experiment 6·6, and in another 8·3 per cent. of "ethylene," which, however, *could not be absorbed by means of either bromine or bromine water*, although it was rapidly taken up by a concentrated solution of potassium mercuric iodide in sodium hydroxide. This supposed synthesis of ethylene was also quoted with approval in the "Annual Reports" for 1909 (p. 77). According to our experience, however, whereas ethylene, diluted with carbon monoxide and hydrogen in the proportion reported by Orloff, is rapidly and completely absorbed by bromine, it is practically untouched by the reagent employed by him for its removal.

Experimental.

The apparatus and experimental procedure adopted by us in the following experiments was in all important respects identical with that already described in detail in our previous paper (pp. 1982 to 1992), with the exception that the arrangement of two coaxial tubes containing the carbon was heated electrically instead of in a gas furnace. In each of the three following experiments we succeeded in almost quantitatively converting about 0·03 gram of highly purified sugar charcoal into methane by maintaining it at about 1150° in a steady current of thoroughly dried hydrogen prepared by the electrolysis of a solution of recrystallised barium hydroxide. The rate of flow of the gas through the heated tube was about 1000 to 1100 c.c. per hour, and each experiment extended over an unbroken period of from seventeen to twenty-five hours. In order to accelerate the methane formation, and thus complete each experiment within a period which would not overtax either the capability of the apparatus for withstanding the fierce temperature, or the physical endurance of the operators, the purified carbon was previously intimately mixed with about 4 per cent. of its weight of finely divided platinum.

At the outset of each experiment a weighed quantity of the carbon was introduced into the inner of the two coaxial porcelain tubes, which in all but one experiment was protected by a loose quartz lining; the carbon was not (as in some of our previous experiments) contained in a platinum boat, but was in immediate

contact with either the porcelain tube or its quartz lining. As soon as all the air in the apparatus and its connexions had been thoroughly displaced by dry hydrogen, the coaxial porcelain tubes were as rapidly as possible raised to the experimental temperature, the current of hydrogen being suspended until the full heat of the furnace had been attained. After re-starting the current of hydrogen, the whole of the exit gas was collected, during several successive periods of about five hours each throughout the experiment, in a series of graduated glass holders over a mixture of equal volumes of water and glycerol.

At the end of each experiment the gas current was stopped, and after the porcelain tubes had cooled down to the room temperature, any small quantity of unchanged carbon remaining in the inner tube was carefully withdrawn and estimated, its weight being deducted from that of the carbon originally taken.

The gaseous contents of the various gas-holders, having attained the laboratory temperature, were measured, and a litre sample withdrawn from each for subsequent concentration over palladium foil to about 25 c.c., as described on p. 1979 of our previous paper. Each concentrate was finally carefully measured in a graduated burette over mercury, and thereafter submitted to an accurate analysis for oxides of carbon (if any), methane, and hydrogen. In this way a very accurate determination of the methane content of the gas collected during each successive period of the experiment was effected, and we regard the figures recorded for methane as significant to certainly the second, and possibly even the third, decimal place.

There was never any carbon dioxide in the products, and very rarely any carbon monoxide; even when the latter could be detected, it rarely exceeded 0·01 per cent. in the gases issuing from the heated tube. The nitrogen content of these gases was usually well below 0·1 per cent.

Purification and Analysis of the Carbon Used.

The sugar charcoal employed had been previously purified by being heated (1) in a constantly maintained vacuum at 600° for twenty-four hours, (2) in dry chlorine at 1150° for twenty-four hours, followed by (3) in pure dry hydrogen at 1150° for forty-eight hours. Analysis showed that it contained not more than 0·06 per cent. of ash and less than 0·1 per cent. of hydrogen, mainly in an "occluded" form. Before being used in the experiments, it was intimately mixed with 4 per cent. of its weight of finely divided platinum.

Purity of the Hydrogen.—A litre of the hydrogen used was

collected in a holder over the mixture of equal parts of glycerol and water, and subsequently concentrated over palladium foil at 100° to 25·3 c.c. Analysis of this concentrate showed that the original gas had contained: Hydrogen = 99·98; methane = 0·007; and nitrogen = 0·013 per cent. This is probably an exaggerated estimate of the hydrocarbon impurity present, and must be considered as a *maximum* figure.

Experiment I.

November 28-29th, 1908. Temperature = 1150°.

The inner porcelain tube was fitted with a quartz lining.

Carbon taken (after allowing for 4 per cent. of platinum added)...	0·0327 gram
Carbon remaining over at the end of the experiment	0·0028 ,,
Carbon used	0·0299 ,,

Methane corresponding with 0·0299 gram carbon = 55·8 c.c. at 0° and 760 mm.

Total duration = 17½ hours. Total hydrogen used = 18 litres at 0° and 760 mm.

Period	1	2	3	4	5
Time (hours)	0—5¼	5¼—10¼	10¼—11¼	11¼—16½	16½—17½
Total volume of gas collected (litres)	5·6	5·6	1·0	5·7	1·0
Pressure (mm.)	769	772	—	775	775
Temperature	12°	12°	—	13°	13°
Percentages in the gas collected: CO	0 020	nil	nil	0 02	nil
CH_4	0·505	0·375	0·180	0·085	0·04
N_2	0·140	0·090	0·030	0·090	0·01

Total methane in the gas collected	54·72 c.c.	at 0°	and 760	mm.
Less 0·007 per cent. (*maximum*) of methane in the 18 litres of hydrogen used.....	1·26	,,	,,	,,
Methane from carbon.....	53·46	,,	,,	,,

The yield of methane in this experiment was, therefore, not less than 95·8 per cent. of that theoretically obtainable.

Experiment II.

December 3-4th, 1908. Temperature = 1150°.

No quartz lining was used in this experiment.

Carbon taken (after allowing for 4 per cent. of platinum added)... 0·0272 gram
Carbon left at the end of the experiment..... 0·0033 ,,

Carbon used ..... 0·0239 ,,

Methane corresponding with 0·0239 gram carbon = 44·4 c.c. at 0° and 760 mm.

Total duration = 21¾ hours. Total hydrogen used = 22·4 litres at 0° and 760 mm.

Period.....	1	2	3	4	5	6
Time (hours)	0—5¼	5¼—10½	10½—15¾	15¾—16⅔	16⅔—20¾	20¾—21¾
Total volume of gas collected (litres)...	5·7	5·6	5·7	1·0	4·6	1·0
Pressure (mm.)	774	773	773	773	772	772
Temperature	12°	12°	12°	12°	14°	14°
Percentages in the gas collected CO	0·030	nil	nil	nil	nil	0·01
CH_4	0·305	0·230	0·165	0·115	0·095	0·06
N_2	0·030	0·050	0·030	0·020	0·090	0·20

Total methane in the gas collected .... 44·00 c.c. at 0° and 760 mm.
Less 0·007 per cent. (*maximum*) of methane in the 22·4 litres of hydrogen used..... 1·57 ,, ,, ,,

Methane from carbon..... 42·43 ,, ,, ,,

The yield of methane in this experiment was, therefore, not less than 95·6 per cent. of that theoretically obtainable.

Experiment III.

April 15-16th, 1909. Temperature = 1120—1150°.

The inner porcelain tube was fitted with a quartz lining.

Carbon taken (after allowing for 4 per cent. of platinum added)... 0·03283 gram
Carbon left at the end of the experiment..... 0·00420 ,,

Carbon used ..... 0·02863 ,,

Methane corresponding with 0·02863 gram of carbon = 53·4 c.c. at 0° and 760 mm.

Total duration = 25 hours. Total hydrogen used = 28·35 litres at 0° and 760 mm.

Period	1	2	3	4	5	6	7
Time (hours).....	0—5	5—9½	9½—14	14—18½	18½—19½	19½—24	24—25
Total volume of gas collected (litres)	5·75	5·75	5·75	5·60	1·00	5·60	1·00
Pressure (mm.)...	766	764	760	762	762	763	763
Temperature.....	20°	20°	22°	22°	19°	21°	21°
Percentages in the gas collected CO	nil	nil	0·010	0·010	0·010	nil	nil
Percentages in the gas collected CH_4	0·41	0·275	0·125	0·070	0·050	0·060	0·03
Percentages in the gas collected N_2	0·04	0·050	0·070	0·040	0·090	0·080	0·12

Total methane in the gas collected ..... 50·6 c.c. at 0° and 760 mm.
Less 0·007 per cent. (*maximum*) in the 28·35 litres of hydrogen used ..... 2·0 ,, ,, ,,

Methane from carbon ..... 48·6 ,, ,, ,,

The yield in this experiment was, therefore, approximately 91 per cent. of that theoretically obtainable.

In conclusion, we desire to express our indebtedness to Dr. Feilmann for his very skilful microchemical examinations of the porcelain tubes used in the above experiments, and also to the Government Grant Committee of the Royal Society for help in meeting part of the expense of the experiments.

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