CCIV.—*The Synthesis of Hydrocarbons at High Temperatures.*

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IN a previous investigation by one of us (Trans., 1910, **97**, 489) the synthesis of methane was investigated between the temperatures 1200° and 1500°. The yield of methane diminished somewhat with progressive use of the same carbon, but finally attained a constant value. This decrease in the methane formation was probably due to graphitisation of the carbon, the minimum values being obtained from the first when graphite was used.

The formation of ethylene was observed at 1800° and at higher temperatures. In experiments carried out at 1200—1500°, the final quantity of methane obtained appeared to be increased by using platinum as a catalyst in contact with the carbon. No satisfactory explanation could be given of this, nor of the fact that the amount of methane, which, of course, diminishes with the temperature, began to increase at 1550°, although the formation of acetylene could not be detected below about 1800°.

The points which still remain to be cleared up are whether the quantities of methane obtained in these earlier experiments between 1200° and 1500° are the true equilibrium values, or is the yield affected by the intermediate formation of traces of acetylene or some other hydrocarbon which it has not yet been found possible to detect, or is it affected by any other cause.

Gautier and Clausmann (*Compt. rend.*, 1910, **151**, 355) have shown that by the action of oxides of iron on mixtures of carbon monoxide and dioxide at 1250°, an amount of methane is formed which is equal to 0·20 per cent. of the hydrogen present. This is probably a rough measure of the equilibrium value, but the conditions of the experiment were not sufficiently precise for an exact evaluation.

In order to elucidate the remaining points of uncertainty, the following series of experiments were carried out in the present research.

Part I.—The influence of different catalysts on the final quantity of methane obtained.

Part II.—The surrounding of the heated carbon rod by an electric field of high potential in order to influence any ionisation effect from the heated carbon.

Part III.—The detection of any hydrocarbons formed in very small quantity, or as intermediate compounds, by rapid continuous circulation of the gas through the apparatus, and then through charcoal, cooled by liquid air, in order to condense and retain any hydrocarbons as soon as possible after their formation.

Part IV.—Measurements were made of the rate at which acetylene and ethylene react with hydrogen at different temperatures, and the nature of the products obtained was ascertained.

Part I.—Effect of Catalysts.

The form of apparatus used was the same as that described in the earlier work (Trans., 1910, **97**, 500). The hydrogen was purified by filtering through a palladium tube (*loc. cit.*, p. 502). The only part of the apparatus to be subjected to a high temperature was the carbon. Temperature readings were made, as before, by means of the Wanner optical pyrometer, which was first carefully calibrated.

Analysis of Gas.—In the samples in which acetylene was absent, the gas was withdrawn from the apparatus, stored over glycerol and water, and analysed by taking from 1000 to 1500 c.c. and removing the excess of hydrogen with palladium foil, until the volume was reduced to 35—50 c.c.

After removal of the carbon monoxide, a fractional combustion of the hydrogen was brought about by mixing the gas with an excess of oxygen, and passing through a U-tube containing palladium black, and maintained at 80—100° in a small water-bath (compare Hempel, *Gas Analysis*, 1906, p. 178). After complete removal of the hydrogen in this way, the remaining mixture was ignited by a spark, and the contraction measured. The carbon dioxide formed was then removed by potassium hydroxide. By noticing the ratio between the contraction after ignition and the carbon dioxide formed, the saturated hydrocarbon was always identified as methane, for which the above ratio was always found to be 2 : 1 (with ethane this would be $2\frac{1}{2}:2$, and with propane 1 : 1).

For a satisfactory analysis of the gases obtained in experiments where unsaturated hydrocarbons were present, it was found necessary to make an examination of the methods available for the separation of acetylene and ethylene.

Use of Ammoniacal Silver Nitrate.—By taking a mixture of acetylene and hydrogen it was found that, provided the reagent was fresh, the whole of the former was absorbed by a concentrated solution of ammoniacal silver nitrate, after shaking for three minutes.

35·5 C.c. of pure ethylene were shaken with the same reagent. The absorption after three minutes amounted to 7·63 c.c., and after another three minutes' treatment a further 2·5 c.c. was absorbed.

Bromine water containing an excess of bromine was found completely to absorb acetylene and ethylene, if shaken, after three minutes. No means of absorbing acetylene without affecting the ethylene was found. Ammoniacal silver nitrate was used, with which the absorption of the acetylene was complete, and that of the ethylene assumed to amount to one-quarter to one-fifth of the total quantity present. The remainder of the ethylene was absorbed by treating the gas with bromine water, followed by potassium hydroxide solution. The hydrogen and methane were then estimated as described above.

Purification of Carbon.—The carbon, in the form of a rod, usually 4 mm. in diameter and about 8 cm. long, was purified by heating in chlorine to about 1400° for one to two hours in a vessel similar to the reaction vessel, but in which the brass water-cooled holders were previously coated with shellac. This form of apparatus is specially suited for this purification, as the chlorides formed from the impurities distil rapidly away, and condense in the cold parts of the apparatus. The vessel was always evacuated, and refilled with chlorine several times while the heating was continued. The carbon was then heated in hydrogen in the same manner for the same time, the apparatus being frequently exhausted to a low pressure. After transferring to the reaction vessel (*loc. cit.*, p. 501), the carbon was heated for two to three hours, to about 1200°, at the low pressure of about 0·01 mm. In this way, the ash content of the carbon was usually reduced to below 0·1 per cent., and the hydrogen below 0·01 per cent. In the case of the carbon rods which were used in presence of platinum or palladium as a catalyst, these metals, to the amount of about 0·2 gram, were coated on the carbon, by electrodeposition, after the treatment in chlorine. The order of the experiments has been carefully noted in the results below to show in some cases the effect of continued use of the same carbon.

Use of Platinum as a Catalyst.

Carbon coated with Platinum. 4 mm. × 11 cm.

			Product.	
Order of experiment.	Duration.	Temp. (approx.)*	CO. Per cent.	CH$_4$.
1.	1¾ hrs.	1250°	0·09	0·522
2.	3½ ,,	1150	0·11	0·702
Carbon coated with Palladium. No. 1. 5 mm. × 11·2 cm.				
1.	1¼ hrs.	1175°	0·08	0·630
2.	½ hr.	1400	0·22	0·328
Carbon coated with Palladium. No. 2. 5 mm. × 5·5 cm.				
1.	1¼ hrs.	1320°	0·08	0·498
2.	3 ,,	1450	0·56	0·212

Carbon coated with Silicon.—The rod (5 mm. × 9 cm.) was coated with an even deposit of silicon by heating in an atmosphere of hydrogen and silicon tetrachloride, at about 1700°, for twenty minutes under conditions which have been determined by one of us, in conjunction with W. Fielding (Trans., 1909, **95**, 1497).

			Product.			
Order of experiment.	Duration.	Temp. (approx.)*	CO.	CH$_4$. Per cent.	C$_2$H$_2$.	C$_2$H$_4$.
1.	1¼ hrs.	1225°	0·004	0·218	—	—
2.	1 hr.	1600	0·56	0·286	0·0016†	—
3.	35 mins.	1710	0·02	0·467	0·95	?

The above results show that there is no appreciable difference between platinum and palladium in their influence as catalysts in assisting the reaction, and that silicon has no appreciable catalytic effect. The results obtained with platinum are in complete agreement with those found in the earlier work (*loc. cit.*, p. 510).

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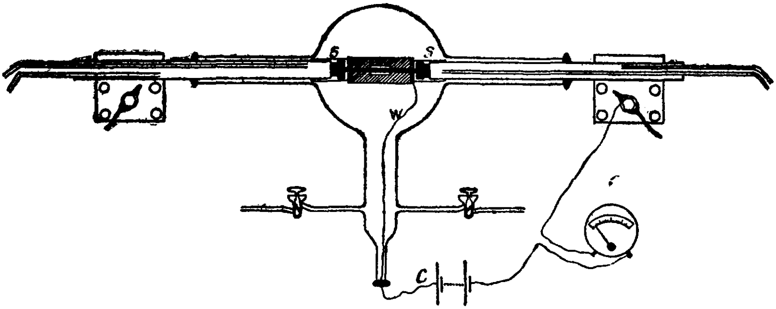
* Not corrected for departure from "black body" radiation from the coated surface.

† Estimated colorimetrically.

Part II.—Influence of an Electric Field Surrounding the Heated Carbon.

At the suggestion of Mr. R. E. Slade, a number of experiments were carried out to ascertain if any influence is exerted by ionisation from the carbon on the formation of methane. A cylinder of fine platinum gauze, 8 cm. long and 2 cm. in diameter, was taken (Fig. 1). A rectangular opening in the middle 1 cm. × 0·6 cm. was made to allow an uninterrupted view of the rod by the pyrometer. Thin tubes of fused silica were inserted at *S S* to prevent contact of the platinum with the brass tubes. A wire at *W* enabled electrical contact to be made with the cylinder *S*. The whole of this was then mounted in the reaction vessel by sliding through the side-tubes, and the wire *W* allowed to emerge through the neck at the bottom, where an air-tight joint was made by means of wax. In this way, a difference of potential could be applied between the heated rod and the surrounding cylinder by means of a circuit *C*, which is independent of the one used for heating the rod. A difference of potential of from 200 to 400 volts in either direction could thus be maintained, and the ionisation current measured by using a milliammeter in the circuit.

FIG. 1.



With a carbon rod 9 cm. long and 5 mm. in diameter, heated in an atmosphere of hydrogen, the following values were found for the ionisation current:

	Ionisation current when field on gauze was	
Temp.	+200 to 300 milliamps.	−200 to −300 milliamps.
1200°	0·02	—
1550	0·88	0·07
1625	1·20	0·08
1720	—	0·11
1845	5·0	—

The current produced when the platinum was negatively charged must have arisen from the negative ionisation of this metal, which became heated by radiation from the carbon, as subsequent work on the ionisation from carbon at high temperatures has shown that no measurable amount of positive ions are produced at any temperature below 2000°.

Rod No. 1.—Amorphous carbon, 9 cm. × 5 mm., purified as described above (p. 1800.)

Order of experiment.	Duration.	Temp.	Charge on platinum cylinder.	Product.			
				CO.	CH_4.	C_2H_2.	C_2H_4.
					Per cent.		
1.	3 hrs.	1330°	+210	0·5	0·212	—	—
2.	2½ ,,	1330	−375	0·14	0·200	—	—
3.	1 hr.	1560	+360	0·62	0·260	—	—

Rod No. 2.—Partly purified by heating in a high vacuum for three hours at 1200°.

1.	8 mins.	1850°	+210	1·6	1·46	0·43	0·90

The rod was afterwards analysed, and found to contain 0·32 per cent. of ash.

Rod No. 3.—Partly purified by heating electrically in chlorine for fifteen minutes at about 1200°, and then in hydrogen, and, after mounting in reaction vessel, heating in a high vacuum for four hours to about 1200°.

1.	12 mins.	1850°	−200	2·5	1·01	0·60	0·50

Rod No. 4.—Not purified. 5 mm. × 8 cm.

1.	12 mins.	1850°	+210	2·1	0·57	0·40	0·32

Rod No. 5.—Not purified. 4 mm. × 8 cm.

1.	7½ mins.	1825°	−220	5·0	0·69	0·50	?

Rod No. 6.—4 mm. × 7 cm. Purified by heating in chlorine for fifteen minutes, then in hydrogen for the same time, and finally in a vacuum for an hour.

1.	5 mins.	1900°	+220	4·2	0·50	1·05	?

Rod No. 7.—5 mm. × 7 cm. Purified by heating electrically in hydrogen at 1600—1700° for three hours with occasional exhaustions.

Order of experiment.	Duration.	Temp.	Charge on platinum cylinder.	Product.			
				CO.	CH_4.	C_2H_2.	C_2H_4.
				Per cent.			
1.	30 mins.	1560°	−200	0·24	0·243	—	—
2.	30 ,,	1680	−200	0·50	?	trace (0·001%)	?
3.	30 ,,	1650	+200	0·05	0·220	trace (0·001%)	?
4.	30 ,,	1550	+200	$<$0·005	0·180	—	?
5.	30 ,,	1580	−190	$<$0·003	0·182	—	?
6.	70 ,,	1525	−195	$<$0·003	0·180	—	?
7.	3¼ hrs.	1215	−220	$<$0·003	0·188	—	—
8.	3 ,,	1230	+340	0·01	0·201	—	—

At the end of this series the carbon rod was analysed, and found to contain 0·05 per cent. of ash.

The formation of acetylene at 1650° and 1680° was detected by passing a large quantity of the gas through a small washing spiral containing ammoniacal cuprous chloride, by which method the presence of 0·001 per cent. of acetylene can be shown. In this way it was possible to detect the acetylene formed at a temperature about 100° below that previously found.

The above experiments, in which long-continued use was made of the same carbon, show clearly that ionisation by the carbon makes no difference to the yield of methane. The quantity of methane obtained at 1525—1550°, namely, 0·180 per cent., is in agreement with the results obtained in earlier work (Trans., 1910, **97**, 510).

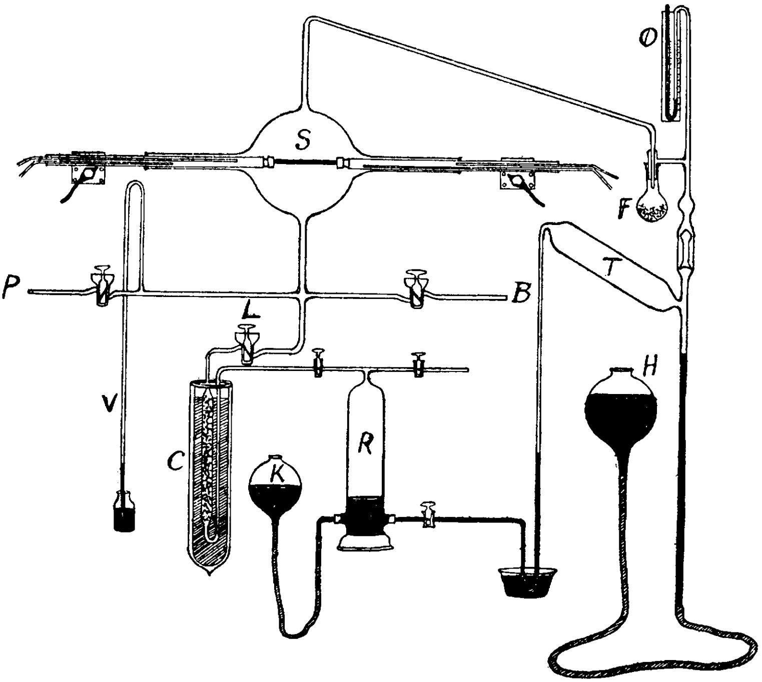
At the lower temperatures, 1215—1330°, where the reaction has been found to be so slow, sufficient time was not allowed for the formation of methane to reach its maximum value, but the above experiments prove that the ionisation of carbon has no effect on the rate at which methane is formed.

Part III.—Detection of Hydrocarbons formed as Intermediate Compounds, or in very small quantities, by continuously circulating the gas through the reaction vessel at different pressures, and then at atmospheric pressure through charcoal at −180°.

The reaction vessel was similar to the one previously used, but of smaller capacity. The globe *S* (Fig. 2) was 13 cm., and the side-tubes 1·3 cm. in diameter. The water-cooled brass tubes fitting into these were 1 cm. in diameter. Graphite plugs were inserted in the sealed brass tubes as usual, and an amorphous carbon rod of 3 or 4 mm. diameter and 7 to 8 cm. long was fitted.

The pressure of gas inside the apparatus was indicated by the mercury gauge *V* and the vacuum gauge *O*. The vessel was exhausted to a fraction of a millimetre by means of a Sprengel automatic mercury pump connected to *P*. The vessel was filled with pure hydrogen, which entered at *B*, after passing through a heated palladium tube. The large Töpler pump *T*, fitted with a drying bulb *F*, enabled gas to be quickly removed from the reaction vessel at any pressure, and passed into the reservoir *R*, where, by regulating the height of the mercury *K*, the pressure was usually adjusted to be a little above atmospheric. By then turning and carefully regulating the tap *L*, the hydrogen could be slowly re-admitted into the reaction vessel, after passing through the tube *C* containing cocoanut charcoal, which was kept immersed in liquid air. It was, of course, first necessary to saturate the charcoal with

FIG. 2.



hydrogen, a large quantity of which is absorbed at atmospheric pressure. A very rapid circulation of gas and removal of absorbable constituents could thus be carried out at different gaseous pressures in *S*. However, since this absorption is probably not complete, the method cannot be applied for precise quantitative results.

In many of the experiments, the operation of the Töpler pump was made mechanical by the use of a motor and pulley for raising and lowering the reservoir *H*. In this way a steady and known rate of circulation could be kept up for several hours.

Fractional Separation of Hydrocarbons by Absorption with Charcoal at Low Temperatures.

It was found that if methane and acetylene, together with a large excess of hydrogen, are absorbed in charcoal cooled by liquid air (−190° to −180°), and if the liquid air is then replaced by a mixture of ether and carbon dioxide (−80°) and the gas withdrawn from the charcoal until the pressure is reduced to 3 mm., then nearly all the hydrogen is given off, about one-third of the methane (b. p. −160°), and only a trace of the acetylene (b. p. −85°). On removing the ether and carbon dioxide, the remaining gases, consisting of hydrogen, methane, acetylene, ethylene, carbon monoxide, and dioxide, could then be removed by the Sprengel pump. The last traces of acetylene and ethylene could only be removed, however, by warming the charcoal for some time in a high vacuum.

Reaction between Unsaturated Hydrocarbons and Hydrogen when Absorbed in Charcoal.

It is well known that charcoal, by condensing, has the power of bringing about reactions between gases which do not take place under ordinary conditions, and it became consequently necessary to ascertain if any influence of this kind is exerted on acetylene or ethylene when in presence of hydrogen.

In the use of charcoal for dealing with gaseous carbon compounds, an obstacle which is encountered is due to the difficulty of entirely removing such compounds as carbon dioxide, water vapour, and other readily condensable gases from the charcoal, small quantities of such gases constantly reappearing during future use of the charcoal. The charcoal used in these experiments was prepared by carefully carbonising cocoanut shell, which was then granulated, and a small quantity placed in a glass tube. This was exhausted for four or five days with a Sprengel pump, and the charcoal heated from time to time with a Bunsen flame. Hydrogen was then admitted several times, in some cases after cooling the charcoal by liquid air, and then pumped off until a high vacuum was obtained. After treating in this manner, some hydrogen was admitted, withdrawn after warming the charcoal, and, on analysis, still found to contain 1 c.c. of carbon dioxide.

A number of experiments were carried out, in which mixtures of acetylene or ethylene and hydrogen were left in contact with cocoanut charcoal at different temperatures. The reaction between these unsaturated hydrocarbons and oxygen was investigated in a similar manner. The results showed that the reaction between acetylene and hydrogen, when occluded in charcoal and heated at

100—200°, leads to the formation of ethylene in quantities not exceeding about 2 per cent., and an amount of methane which is smaller than this.

In presence of oxygen, acetylene and ethylene are partly oxidised at about 200°, but only slightly, if at all, at room temperatures. Exact measurements of the amount of carbon dioxide present when only in small quantities was prevented by the difficulty of completely removing this gas from the charcoal after each experiment. The results show that carefully purified cocoanut charcoal can, without appreciable error, be used for the fractional separation of hydrocarbons in presence of hydrogen.

After these preliminary experiments, use was made of the circulation apparatus described above, and shown in Fig. 2. If the intermediate formation of acetylene or any other stable hydrocarbon takes any part in the yield of methane, then by continuously circulating the gases through the reaction vessel and through the cold charcoal tube, any such compounds will be partly or entirely condensed, and after a sufficient quantity has collected, can be removed and analysed in the usual manner.

Experiments were, in this way, carried out at various pressures. If acetylene plays any part in the reaction, it follows that by working at a lower pressure the ratio of the less condensed molecule acetylene to the more condensed methane will be higher than at a higher pressure. The pressure of gas in the reservoir *R* (Fig. 2) and in the charcoal was usually higher than atmospheric, to enable more efficient condensation, and to obviate leaks through the rubber stoppers at the base of the reservoir.

Purification of Charcoal.—In order to remove the last traces of acetylene from the freshly prepared charcoal, it was found necessary to exhaust to the lowest possible pressure for a period of several days, occasionally heating and admitting hydrogen. It is probably not at all possible to remove all the water vapour and denser hydrocarbons. After the purification treatment, none of the latter were evolved, however, with the gases during subsequent experiments, so that their presence did not interfere with the measurements.

In the experiments of this series, very particular precautions were taken to obtain the carbon in the purest condition. In addition to the usual preliminary purification, only carbon was taken which had been used for a long interval in previous experiments, where it had undergone prolonged heating in hydrogen.

The experiment below is described in some detail, as it is typical of the remainder in this series.

Expt. 1.—The carbon rod (7 cm. × 4 mm.), which had been coated with platinum, was heated for five and a-half hours at 1400° in hydrogen at a pressure of 12 to 14 cm. The pressure of gas in the mercury reservoir (*R*) was kept at 74 cm. (in all subsequent experiments this was kept at 77 cm.). The speed of circulation of the gas was arranged so that the volume in the vessel was renewed every two minutes. The total volume of gas circulated through the charcoal and measured at N.T.P. was estimated at 38 litres. A quantity of hydrogen was then removed from the charcoal while still at −180°, until the pressure was reduced to 2 cm. The liquid air around the charcoal was then replaced by ether and carbon dioxide at −80°, and 720 c.c. of gas removed, which reduced the pressure to about 1 cm. Most of the hydrogen was removed from this gas by condensing with palladium foil, and the residue found to contain 6·23 c.c. of methane and 2·10 c.c. of carbon monoxide. After warming the tube to room temperature, 22·5 c.c. more gas were withdrawn (the last portions being obtained by warming to about 200°). This last sample was found to contain 1·15 c.c. of ethylene, 0·72 c.c. of carbon monoxide, and 3·95 c.c. of methane, and no other hydrocarbon. The total gas condensed therefore contained:

CH_4, 10·18 c.c., or 0·026 per cent. of whole.
C_2H_4, 1·15 c.c., „ 0·003 „ „
CO, 2·85 c.c., „ 0·007 „ „

The experiments in this series can be represented in tabular form as follows:

No. of experiment.	Temp. of carbon.	Pressure of gas (cm.).	Duration of experiment.	Total volume of gas circulated (litres N.T.P.).	Percentage composition of gas.			
					CH_4.	C_2H_4.	C_2H_2.	CO.
4.	1200°	7—30	4 hrs.	26	0·049	0·0005	nil.	0·01
2.	1225	50—60	10½ „	80	0·010	0·00014	nil.	0·04
1.	1400	12—14	5½ „	88	0·026	0·003	nil.	—
3.	1400	10—25	9 „	31	0·039	0·002	nil.	—
5.	1650	7—30	1½ „	10	0·1104	0·0025	0·012	—
6.	1800	76	7 mins.	2·5	—	0·052	0·024	0·11

Experiments 2 and 6 were conducted with pure carbon, and the others with platinum coated rods. In Nos. 3 to 5, the same carbon rod was used.

Blank Experiments.—Experiments were made to ascertain the extent to which impurities in any part of the apparatus, such as vapours from tap grease or wax, might have contributed to the hydrocarbon formation in any of the present work. For this purpose, use was made of a platinum strip, instead of carbon, and a complete experiment carried through, as in part III above, and another as in part I. It was found in both cases that the amount of methane was less than 5 per cent. of that obtained when using carbon under the same conditions.

Part IV.—Rate of Reaction of Acetylene and Ethylene with Hydrogen, and rate of Decomposition of Methane at various temperatures.

In the present work, which extends some preliminary measurements already made by one of us (Trans., 1910, **97**, 508), a simple means was devised to follow continuously the course of the reaction between acetylene and hydrogen, and the measurements were extended to the reaction between ethylene and hydrogen. The rate of decomposition of the methane formed into carbon and hydrogen could also be observed.

Apparatus.—A porcelain tube of 2 cm. internal diameter and 60 cm. long was arranged inside an electrical wire resistance furnace, so that the tube could be heated to any temperature up to 1200°, which could be read by means of a thermocouple placed alongside. The tube was provided with a manometer, and gases could be introduced at one end and removed at the other by means of a Töpler pump, whereby the tube could be exhausted.

A mixture of the hydrocarbon and hydrogen could be admitted, and in virtue of the volume change, the reaction could be followed by the change of pressure indicated by the manometer. Accurate measurements could thus be made of the relative rates of the formation of methane from hydrogen and acetylene, or ethylene, and of its decomposition; thus, in the case of acetylene and hydrogen reacting according to the equation $C_2H_2 + 3H_2 = 2CH_4$, or

$$C_2H_2 + H_2 = C + CH_4,$$

the methane formed is, in either case, equal to the contraction. When all this methane is decomposed, the volume will again assume its original value. It was found that this second change, the decomposition of methane, was very slow compared with the first, so that the first could be measured independently of the second without appreciable error.

The acetylene used was prepared from calcium carbide, and, after washing through concentrated potassium hydroxide solution, was liquefied by liquid air, redistilled, and then collected over a heavy oil in a gas-holder. A sample of the gas was analysed, and found to contain 95·5 per cent. of acetylene. This and another holder filled with hydrogen were placed in connexion with the porcelain tube, and, after exhausting, either gas could be admitted to the heated tube and the volume ascertained by reading the manometer.

The temperature of the tube was kept constant to within about 10° throughout the experiment.

The pressure at first was always atmospheric, and the course of the reaction could be followed by the rise of mercury in the manometer. After a definite period, the remaining gas was removed and submitted to analysis.

Expt. 1.—Temperature 720°. $C_2H_2=21$; $H_2=79$.*

Time (mins.)	0	5	8	13	16	18	21
Pressure (mm.)	760	717	702	686	677	672	668

Final composition of gas, $C_2H_2=9\cdot5$; $C_2H_4=2\cdot0$; $CH_4=10\cdot0$. Contraction = 12 per cent.

Expt. 2.—Temperature 980°. $C_2H_2=26\cdot7$; $H_2=73\cdot3$.

Time (mins.)	0	1	2	3	6	17	28	36	40
Pressure (mm.) ...	760	733	725	718	703	682	682	683	683·5

Final composition of gas, $C_2H_2=3\cdot08$; $C_2H_4=0\cdot56$; $CH_4=11\cdot9$; $CO=2\cdot9$. Contraction = 10·1 per cent.

Expt. 3.—Temperature 745°. $C_2H_2=24\cdot8$; $H_2=75\cdot2$.

Time (mins.)	0	1	3	6	10	16	25	40	143	183	188	283
Pressure (mm.) ...	760	747	730	714	697	680	662	648	612	610	610	607

Final composition, $C_2H_2=1\cdot91$; $C_2H_4=1\cdot0$; $CH_4=16\cdot9$; $CO=0\cdot8$. Contraction = 20 per cent.

No other hydrocarbons but the above were found in any of these experiments.

Reaction between Ethylene and Hydrogen.—This was investigated in the same manner as above.

The ethylene used for this purpose was of 98 per cent. purity.

Expt. 1.—Temperature 860°. $C_2H_4=32$; $H_2=68$.

Time (min.)	0	2	3	4	8	12	18	28	32	40
Pressure (mm.) ...	760	742	739	735	722	711	707	703	702	702

Final composition, C_2H_2, *nil*; $C_2H_4=8\cdot5$; $CH_4=8\cdot3$; $CO=4\cdot5$. Contraction = 7·6 per cent.

Expt. 2.—Temperature 1000°. $C_2H_4=32$; $H_2=68$.

Time (mins.)	0	3	10	20	30	40	50	60	70	80	90	100	110
Pressure (mm.)	760	733	714	710	711	714	715	716	718	718	719	720	721

Final composition, C_2H_2, *nil*; $C_2H_4=3\cdot5$; $CH_4=12\cdot3$; $CO=3\cdot6$. Contraction = 5·5 per cent.

These results show that at temperatures between 700° and 900° acetylene reacts with hydrogen to give methane and ethylene. The amount of methane formed, as ascertained by analysis, was found

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* The composition of the gases is given in percentages.

to correspond approximately with the contraction, as would follow from either of the reactions below:

$$(a)\ C_2H_2 + H_2 = CH_4 + C,$$
$$(b)\ C_2H_2 + 3H_2 = 2CH_4.$$

The amount of methane formed, however, was always considerably less than the loss of acetylene. This loss could not have arisen from the decomposition of the methane at first formed, as this reaction was found to be extremely slow, even when large quantities of methane were present. Consequently, even assuming all the methane to have been formed according to equation (*a*), some of the acetylene must have undergone decomposition according to the equation $C_2H_2 = 2C + H_2$, and a similar decomposition with the ethylene (compare Bone and Coward, Trans., 1908, **93**, 1197).

It is also seen from these results that, in the form of apparatus used, in which about one-half of the total volume of gas was heated to the particular temperature, the decomposition of acetylene in presence of hydrogen into methane and into carbon and hydrogen takes place at 720° to the extent of one-half in about twenty minutes. At 980° seven-eighths is similarly decomposed in forty minutes. The reaction between ethylene and hydrogen also takes place at about the same rate. The decomposition of methane into carbon and hydrogen, on the other hand, was too slow to be measured.

It follows from these measurements that in the experiments made on the synthesis of hydrocarbons by the circulation method (p. 1802) at temperatures below 1200—1300°, the acetylene or ethylene would be separated largely as such. Sufficient time had not been allowed for the formation of the quantities of methane obtained from the observed amounts of ethylene and acetylene. Consequently, most of the methane which was formed in these cases, and which was always largely in excess of the other hydrocarbons, must have arisen directly from the elements, or else through the intermediate formation of some hydrocarbon at present unknown.

At the higher temperatures of 1500° and upwards, the ethylene present would certainly account for most of the methane observed.

These results further show that the presence of ethylene will play a very large part in those experiments in which hydrogen was left in contact with the heated carbon over a long interval, even at 1200° (parts I and II). The amount of methane, on account of its comparatively great stability, would be raised above the equilibrium quantity at the temperature of the rod, on account of the polymerisation of the traces of ethylene formed with hydrogen in the cooler parts of the vessel.

The formation of methane from acetylene and hydrogen as conducted with the heated porcelain tube is an interesting example of an intermediate product arising in quantities much larger than are permanently stable at the particular temperatures used.

The above work, which has demonstrated the synthesis of methane and also of ethylene at temperatures from 1200° upwards, still leaves undecided the question of the equilibrium between methane and hydrogen, and shows that this cannot be ascertained in the form of apparatus hitherto used.

Berthelot, using a method in which the whole of the reacting substances were at a uniform temperature, could detect no hydrocarbons at 1200—1300°, but the porosity of the vessel probably led to their oxidation.

Summary of Results and Conclusions.

The reaction between carbon and hydrogen has been investigated by quickly removing the products from the neighbourhood of the heated carbon, and circulating the gas in large quantities through charcoal cooled by liquid air. Any traces of hydrocarbons were thus retained in the charcoal by condensation, and afterwards analysed. At a temperature of 1200°, and at pressures from 10 to 60 cm., carbon was found to combine with hydrogen to give methane and ethylene, the rate of formation of the latter being about 1/100th that of the methane. The amount of acetylene formed at this temperature is very much less, and could not be detected.

Measurements which were made of the rate at which acetylene and ethylene react with hydrogen to give methane, show that the amount of the latter hydrocarbon formed in these circulation experiments could not all be attributed to the initial formation of ethylene. At higher temperatures the ratio of ethylene to methane increased, at 1400° the amounts found being in the proportion of 1 to 10. In this case the amount of methane formed from ethylene would, of course, be much greater than at 1200°.

At 1650° methane, ethylene, and acetylene are obtained, and, as at higher temperatures, the quantity of ethylene formed is about twice that of the acetylene.

Palladium in contact with the carbon was found to assist catalytically the formation of methane to the same degree as platinum, whilst silicon had no appreciable effect.

It was found that the presence of a highly charged electric field surrounding the carbon made no difference to the rate of formation of methane at temperatures between 1200° and 1600°, so that no complication is produced in the reaction by ionisation from heated carbon. It is conceivable, however, that a disturbance might have been caused by carbon vapour distilling from the rod and reacting in the cooler parts of the vessel, or minute particles of carbon are possibly dispersed from the rod and act similarly.

The formation of ethylene which has not before been observed, nor suspected at these low temperatures, has, in this work, been detected at 1200°, and at 1400° it is comparable with the methane formed. The equilibria between the different hydrocarbons and hydrogen are now being investigated by the use of high gaseous pressures.

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