

CV.—*The slow Oxidation of Methane at low Temperatures. Part II.*

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IN an earlier paper (Trans., 1902, 81, 535), we described a series of experiments on the interaction of methane (2 volumes) and oxygen (1 volume) in borosilicate glass bulbs at temperatures between 300° and 400°, which showed that part of the methane was oxidised to carbon monoxide, carbon dioxide, and steam without any liberation of free hydrogen or deposition of carbon. Moreover, the process was always marked by a diminution in the pressure of the cold gaseous products corresponding approximately with the oxygen which had disappeared, and at the end of the reaction a considerable proportion of the original methane always remained intact.

Since, under the experimental conditions, the rate at which hydrogen and oxygen combine was shown to be inappreciable, and as we were unable to detect the formation of any product intermediate between the original gases and the carbon monoxide, carbon dioxide, and steam finally obtained, we concluded provisionally that the first distinguishable stage in the combustion of methane at low temperatures involves the simultaneous oxidation of the carbon and hydrogen to carbon monoxide and steam respectively, thus, $2\text{CH}_4 + 3\text{O}_2 = 2\text{CO} + 4\text{H}_2\text{O}$. But, as was then pointed out, this explanation did not account for the whole of the observed facts, and it could therefore only be regarded as a first approximation to the truth. In the first place, on *a priori* grounds, it was difficult to believe that the primary reaction between methane and oxygen could possibly be pentamolecular. A second, and more serious, difficulty was the fact that a not inconsiderable proportion of the carbon of the methane burnt always appeared as carbon dioxide in the final products (in several cases, the ratio $\text{CO}_2 : \text{CO}$ exceeded 1 : 2, and occasionally it approximated to 1 : 1). Now, since the rate at which

carbon monoxide reacts with moist oxygen or with steam under the experimental conditions was shown to be negligible (*loc. cit.*, p. 538), this formation of carbon dioxide could not be explained by supposing that the carbon monoxide actually liberated during the primary reaction was subsequently oxidised through the agency of steam and oxygen or steam alone (p. 540).

Such considerations as these indicated the necessity of a closer study of the phenomena involved if we were ever to gain a clear insight into the mechanism of the oxidation of hydrocarbons; the present paper on methane, and another which we hope to publish shortly on ethane, will show how far we have succeeded in this direction.

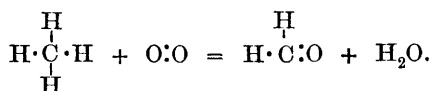
Our earlier experimental method involved the use of borosilicate glass bulbs of somewhat limited capacity (70 c.c.); but whilst this method afforded us the indispensable conditions for proving certain points of fundamental importance (for example, that no free hydrogen is liberated during the whole course of the oxidation), it was not so well adapted for the detection and isolation of transient intermediate products, and indeed, as we have already stated, the method failed to reveal the formation of any such substances. For the second stage of the inquiry, we devised an apparatus which has enabled us to experiment with much larger volumes (about 1200 c.c.) of the mixture of methane and oxygen, to follow from day to day the pressure changes in the reacting gases, and to remove from the sphere of action small quantities of intermediate products before they underwent further oxidation.

The results of these additional experiments, whilst they entirely confirm our previous conclusion that neither free hydrogen nor free carbon is produced at any stage of the oxidation, and that the final products consist simply of carbon monoxide, carbon dioxide, and steam, prove the transient formation of formaldehyde as an intermediate product. In one experiment, for instance, 13 per cent., and in another as much as 22 per cent., of the methane burnt was accounted for as formaldehyde removed from the sphere of action before it had been further oxidised.

This new observation not only affords a simple explanation of the production of so much carbon dioxide in our earlier experiments, but it also throws a new light on the whole question under discussion, and enables us to arrive at a clearer understanding of the mode in which the methane molecule is attacked by the oxygen.

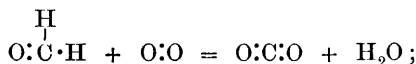
Reviewing now the whole of the evidence obtained during the course of our investigation, we are justified in concluding that the oxidation of methane involves at least two distinct and successive changes, each of a simple character, namely :

(1) The simultaneous production of formaldehyde and steam as the result of the bimolecular reaction :

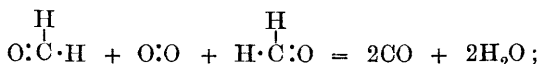


(2) The subsequent very rapid oxidation of the formaldehyde to carbon monoxide, carbon dioxide, and steam. This may be best considered as the result of two simultaneous reactions, namely :

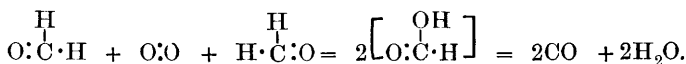
(a) the bimolecular reaction :



(b) the trimolecular reaction :



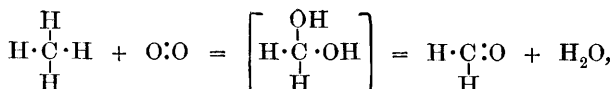
possibly the latter may involve the formation and very rapid decomposition of formic acid, thus :



For the present, it must remain a matter of conjecture as to whether the precise mechanism of the primary oxidation to formaldehyde and steam is better represented by the foregoing equations or by assuming

the formation and rapid decomposition of the hypothetical $\begin{array}{c} \text{OH} \\ | \\ \text{H} \cdot \text{C} \cdot \text{OH} \\ | \\ \text{H} \end{array}$,

thus :



both atoms of the oxygen molecule actually entering that of the hydrocarbon before the elimination of steam occurs.

It may be remarked that the foregoing views not only accord with and explain all the facts observed in the case of methane, but are also entirely confirmed by the results of experiments on ethane.

EXPERIMENTAL.

A. An Apparatus for the Investigation of Slow Combustion Processes.*

The apparatus we have devised for these and other similar experiments is shown in the accompanying diagram (Fig. 1, p. 1077). It is

* Two examples of the circulation apparatus have been installed in our laboratory for these experiments, and the present description will suffice for reference in any

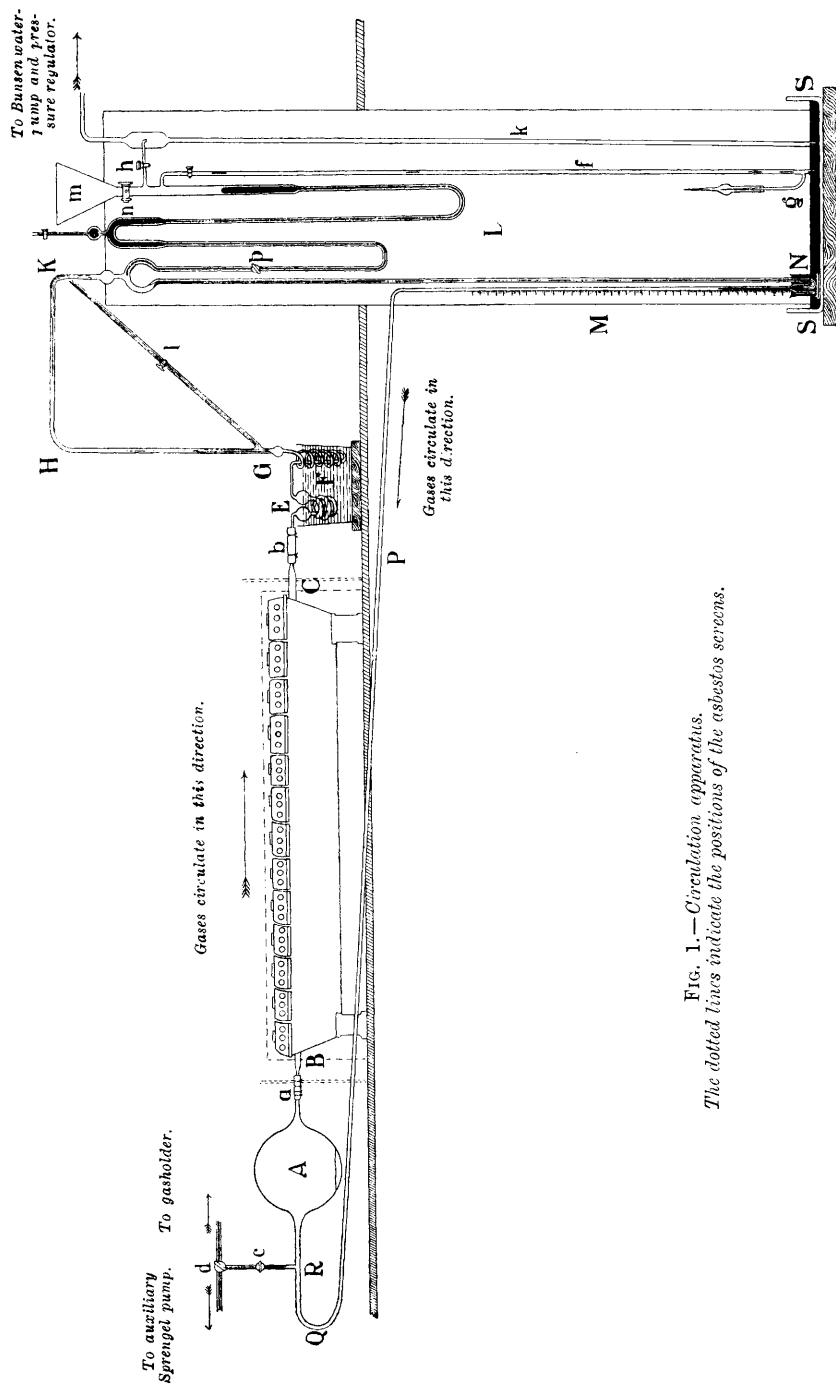


FIG. 1.—*Circulation apparatus.*
The dotted lines indicate the positions of the asbestos screens.

essentially a closed system in which the reacting gaseous mixture can be circulated continuously day and night, at a practically uniform rate, over a heated surface (maintained at a constant temperature), and afterwards through suitable washing and cooling arrangements for the removal of soluble or condensable intermediate products. By means of a manometric arrangement, the pressure of the gas in the apparatus can be recorded at regular intervals, so that, given regular working conditions, the velocity of a given reaction, or group of simultaneous reactions, can be measured.

The more detailed description of the various parts of the apparatus will perhaps be made clearer if we follow the course of the gas round the complete circuit. The starting point is the glass globe *A* (capacity 1200 c.c.), which serves as a reservoir for the circulating gases; in the actual experiments, the globe always contained a few cubic centimetres of distilled water, so that the gaseous mixture was kept saturated with water vapour at a temperature t° , indicated by a thermometer placed against the globe with its bulb actually touching the outer wall. The globe was carefully screened by asbestos cardboard both from radiation from other parts of the apparatus, and from draughts caused by open doors or windows. On leaving the globe, the gases traversed the Jena glass combustion tube, *BC* (length 75 cm.), filled with fragments of ignited porous porcelain; each end of the tube was drawn out to the diameter of ordinary quill tubing in such a manner that the narrower portions project several inches beyond the bed of the Lothar Meyer constant temperature furnace on which the tube rests. The two joints, *a* and *b*, connecting *BC* with the rest of the apparatus were made with very stout indiarubber pressure tubing, the two glass ends underneath being gradually pushed together until they actually came into contact; with these two exceptions, all the other joints in the apparatus were fused together by means of the blowpipe.

On leaving the combustion tube, the gases passed first through the glass worm, *E*, containing distilled water, and then through the long glass spiral, *F*. Both *E* and *F* were surrounded by a water-jacket, through which a stream of cold water was maintained throughout the experiment in order to ensure the rapid cooling of the hot gases. Since the mixture entered the combustion tube saturated with moisture at the ordinary temperature, any steam produced by the interaction of the gases, as well as any soluble or condensable intermediate product which survived the passage over the heated surface, would be condensed or absorbed in this part of the apparatus.

future communication we may make on the subject of "slow combustion." It may be added that the apparatus is well adapted for the determination of the velocity of gaseous reactions, and is now being employed for this purpose.

The cooled gases passed onwards to the automatic Sprengel pump, *L*, through the triangular arrangement *GHK*, the object of which will be explained later. The pump delivered the gases into the vertical manometric tube *M*, standing over mercury in the vessel *N*; thence they passed forward through the horizontal tube *P*, round the curve *Q*, past the T-piece *R*, back into the globe *A*, thus completing the circuit. A millimetre scale placed behind the manometer *M* enabled the pressure of the moist gases to be read at regular intervals, the automatic Sprengel pump being thrown out of action for a moment by shutting the tap *p*.

The apparatus was closed by the glass tap *c*, working in a mercury cup and sealed into the vertical branch of the T-piece *R*. On the other side of *c* was sealed the glass T-tap *d*, through which communication could be made either with (1) the glass gas-holder containing the mixture to be investigated, or (2) an auxiliary Sprengel pump (not shown in the diagram). This latter was used either during the preliminary exhaustion of the apparatus or (if necessary) for the removal of samples of gases during the course of an experiment. All the joints between this auxiliary pump or the gas-holder and the tap *c* were fused by means of the blowpipe.

As it was necessary, for the complete success of an experiment, to ensure a continuous circulation of the gases in the apparatus at a uniform rate by day and night, for, if need be, many days together, special arrangements had to be made for working the automatic Sprengel pump under constant conditions throughout. For a long time, this constituted a serious experimental difficulty, but happily it was finally entirely overcome. We may briefly indicate the general character of these arrangements.

The automatic working of the Sprengel pump was secured by means of a Bunsen water-pump, the suction of which was kept constant by inserting an automatic pressure regulator (the action of which depended on the making and breaking of a mercury seal within narrow limits of pressure) between the two pumps; to this regulator was attached a large glass bottle of some 20 litres capacity, the effect of which was to keep the suction perfectly steady. The suction of the water-pump raised the mercury from the glass trough *SS* up the vertical tube *f* to a height a little above the junction with the side piece *g*, which had a capillary termination. Minute quantities of air drawn in through this capillary broke the column of mercury in *f* into short threads and drove them to the head of the pump. In the event of the mercury being drawn up *f* faster than it fell down the fall-tube of the pump, the excess overflowed through the horizontal branch *h* into the vertical tube *k*, which also indicated the suction of the water-pump. At the outset of an experiment, it was occasionally

necessary to start the Sprengel pump by a head of mercury in the funnel m ; in a few minutes, however, this was cut off by the tap n and the automatic working started. The glass tap p served to adjust the rate of fall of the mercury in the fall-tube and to throw the pump momentarily out of action whenever the pressure of the gas in the apparatus was read.

It will be readily understood that a continuous circulation could only be maintained with an automatic Sprengel of this type so long as the pressure of the gas at the top of the fall-tube kept below a certain limit, in this particular case about 600 mm. In order that we might have higher pressures than this in the main apparatus, and still ensure continuous and satisfactory working, we adopted a device represented by the triangle GHK . Into each of the sides GH , HK , was sealed a length of very fine capillary tubing, whilst a perfectly free passage was allowed through the base GK . By closing the tap e , the circulating gases were compelled to pass through the capillaries, so that, although the pressure in the main apparatus might be nearly atmospheric, a low pressure could be maintained between K and the top of the fall-tube of the automatic Sprengel pump. By opening e , the capillaries could be thrown out of circuit and the gases allowed a free passage through GK .

The total capacity of the apparatus was about 1450 to 1500 c.c., and when filled under 600 mm. pressure it contained 1150 to 1200 c.c. of the mixture under examination (measured under atmospheric pressure). It may be understood that the speed at which the mixtures were circulated, although constant throughout a given experiment, varied in different experiments and was such that the whole gaseous mixture would complete a circuit once in 1 or 2 hours, each portion of the gases probably remaining about 3 to 6 minutes in the combustion tube during each cycle; these times represent, approximately, the maximum and minimum speeds respectively.

Method of Conducting an Experiment.—At the outset of an experiment, the apparatus was thoroughly exhausted, the tube BC being heated to between 250° and 300° in order to expel all air enclosed in the pores of the porcelain it contained. All permanent gas having thus been withdrawn from the apparatus, the pumps were stopped, the furnace turned out, and the whole allowed to remain for at least 12 hours in order to test the tightness of taps and the two joints a and b .

The gaseous mixture under investigation was then slowly admitted into the apparatus from the holder until the desired pressure (usually a little over 600 mm.) was attained. The tap C was then closed and the mixture circulated in the cold for 12 hours in order that it might become thoroughly saturated with water vapour at the temperature (t°) of the room, and that all adjustments necessary for the regular and

continuous working of the automatic Sprengel pump might be made. A sample of the mixture was then withdrawn for analysis through the auxiliary Sprengel pump, after which the pressure of the cold moist gas, at the room temperature (t°), was finally taken. The furnace was lighted and covered by an asbestos screen (indicated by dotted lines in the diagram); the gas supply of the furnace passed through a Stott's governor, and a practically constant temperature (T°) in the combustion tube could be maintained throughout an experiment. As soon as the furnace had acquired the desired maximum temperature (T°), which was recorded by a Geissler mercurial thermometer filled with nitrogen under pressure and graduated up to 550° , all the screens were finally adjusted in position and the pressure of the moist gas in the apparatus again determined. The experiment was then allowed to run its course through many consecutive days, pressure and temperature records being taken at regular intervals until it was thought that the reaction had gone far enough. Finally, the furnace was turned out, the screens removed, and the whole apparatus allowed to cool down during several hours to the room temperature. The pressure of the cold moist gas was again determined, samples of the gaseous product being subsequently withdrawn for analysis through the auxiliary Sprengel pump. Lastly, the worm *E* and spiral *F* were removed and the contents examined.

B. *Details of Experiments.*

The methane was prepared by the action of an aluminium mercury couple on a solution of methyl iodide in methyl alcohol, and purified according to the method described in our previous paper (*loc. cit.*, p. 541); great care was taken to ensure the complete removal of last traces of free hydrogen by repeatedly passing the gas over oxidised palladium sponge at 100° .

The oxygen was obtained by heating potassium permanganate in small glass bulbs; it was washed through strong caustic potash solution. The mixtures were made in graduated glass holders over strong sulphuric acid.

1st Experiment.—This extended over 24 consecutive days, during which the furnace temperature only varied between 450° and 455° . Leaving out of the reckoning a small percentage of nitrogen, the original mixture had the percentage composition: * methane, 66.45; oxygen, 33.55.

* In order to make all measurements in the various experiments strictly comparable we propose, throughout this paper, as in our last communication, to express the compositions of the various gaseous mixtures, and also all pressure records, in terms of the 'nitrogen free' gases. Since in analysing the gases the nitrogen

The speed of circulation was slow, the capillaries in the triangle *GHK* being in circuit the whole time. The daily records showed a continuous fall of pressure in the reacting gases, but owing to small variations in the rate of circulation (this was the first experiment made with the apparatus) the daily fall of pressure was not quite so regular as in the subsequent experiment. However, during a period of several days, any small variations in the speed of circulation ceased to affect the general result, and the pressure falls over successive intervals of 2 or 3 days were quite regular. We need only record the corrected pressures for the dry 'nitrogen free' gas at the outset of the experiment, and at the end of 8, 16, and 24 days respectively.

Time in days from commencement.	Pressure of dry 'nitrogen free' gas at 0° in mm.	Corrected pressure fall in mm.	Percentage pressure fall.
0	591.4	54.8	9.25
8	536.6	46.6	7.90
16	490.0	38.0	6.45
24	452.0		
		Totals 139.4	23.60

The residual 'nitrogen free' gases, analysed according to the method described in our previous paper (*loc. cit.*, p. 545), had the following percentage composition :

Carbon monoxide	4.46	Methane	70.40
Carbon dioxide	9.84	Oxygen	15.30
			100.00

The ratio *C/A*, determined by exploding the residual gas, after removal of the oxygen and the oxides of carbon with excess of oxygen and air, was exactly 2.00, proving the entire absence of free hydrogen in the products.

The presence of so large a proportion of carbon dioxide in the products is partly due to the circumstance that carbon monoxide and moist oxygen react under the experimental conditions (see footnote, p. 1085).

We may now examine how far these gaseous products account for the methane and oxygen originally introduced into the apparatus ; this may best be done by comparing the partial pressures of the methane and oxygen in the original mixture with the partial pressures

was in each case determined "by difference," after all other constituents had been estimated, the numbers for the percentage compositions of our 'nitrogen free' gas will always add up to 100 exactly.

of the various gaseous products at the end of the experiment, as follows :

Partial pressures of methane and oxygen in original mixture.

$$\begin{array}{rcl} & \text{mm.} & \text{mm.} \\ \text{Methane} & = 591.4 \times 0.6645 & = 393.1. \\ \text{Oxygen} & = 591.4 \times 0.3355 & = 198.3. \end{array}$$

Partial pressures of the products.	mm.	Corresponding with mm. of the original	
		Methane	Oxygen
CO = 452×0.0446 =	20.15	20.15	30.20
CO ₂ = 452×0.0984 =	44.45	44.45	88.90
CH ₄ = 452×0.7040 =	318.20	318.20	—
O ₂ = 452×0.1530 =	69.20	—	69.20
		<hr/> 382.80	<hr/> 188.30

Hence, of the methane (393.1 mm.) and oxygen (198.3 mm.) originally introduced into the apparatus, only 382.8 mm. of methane and 188.3 mm. of oxygen respectively are accounted for in the gaseous products. The natural inference is, therefore, that practically equal volumes (CH₄=10.33 mm., O=10 mm.) had reacted to form some soluble or condensable intermediate product. This first led us to suspect the formation of formaldehyde by the interaction of equal volumes of the original gases, thus, CH₄ + O₂ = CH₂O + H₂O.

The liquid in the worm *E* at the end of the experiment was neutral to litmus, but on testing it with a solution of rosaniline hydrochloride previously decolorised by sulphurous acid a very pronounced aldehyde reaction was obtained. Hence, we may conclude that of the 75 mm. of original methane which the foregoing numbers show had been oxidised during the experiment, 10 mm., or over 13 per cent., were accounted for as formaldehyde.

2nd Experiment.—This was perhaps the best we have made with methane and oxygen; it extended over 10 days, during which time the rate of circulation was practically constant throughout.* At the end of the experiment, nearly the whole of the original oxygen had disappeared.

The original mixture contained some 0.8 per cent. of nitrogen, but leaving this out of the reckoning its percentage composition was methane, 66.5; oxygen, 33.5.

The pressure of the cold dry 'nitrogen free' mixture charged into the circulation apparatus was 513 mm. at 16°. After ascertaining

* The rate of circulation in this experiment was approximately twice as great as that maintained during the first experiment; the temperature of the combustion tube was also higher. These two circumstances account for the more rapid oxidation observed in the second experiment.

this pressure, the furnace was lighted and the temperature of the combustion tube raised during the first 3 or 4 hours to 460° , and afterwards to just above 500° ; during the remainder of the experiment, the furnace temperature only varied between 497° and 510° .

The following were the daily records taken :

Day.	Temperature of combustion tube, T° .	Temperature of gas in globe <i>A</i> , t° .	Corrected pressure of dry 'nitrogen free' gas at 22° , mm.
0	460°	22.0°	554.7
1	510	24.5	482.3
2	510	22.3	462.8
3	510	22.0	439.7
4	505	23.0	424.0
5	498	23.5	411.7
6	498	24.5	395.3
7	498	25.7	384.9
8	497	22.8	375.7
9	497	22.0	367.0
10	498	24.2	350.0

The pressure curve (ordinates = pressures, abscissæ = time in days) for this experiment (Fig. 2, p. 1085) shows how regularly and continuously the pressure diminished throughout; the proportionately larger falls observed during the first and tenth days, respectively, are to be attributed to a slight acceleration in the rate at which the gases were circulated over the heated surface.

The pressure of the cold dry 'nitrogen free' products after the furnace had been put out and the apparatus allowed to cool down to the room temperature was 335.9 mm. at 16° . Hence, the total diminution of pressure of the cold dry gas, at 16° , during the experiment was $(513 - 335.9) = 177.1$ mm. or 34.5 per cent. This alone is sufficient to prove the formation of some condensable or soluble intermediate product, for had the whole of the oxygen originally present reacted with methane to form CO_2 and steam (and the analysis of the product indicated that a portion of the original oxygen remained over), the diminution of pressure would only have been 33.5 per cent.

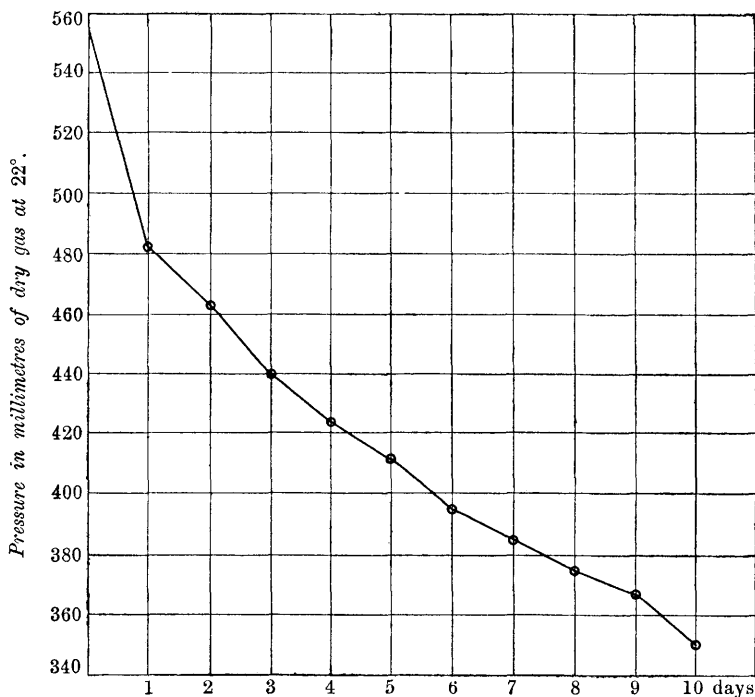
Three very concordant analyses of the gaseous products showed that the 'nitrogen free' gas contained :

Carbon monoxide	0.50	Oxygen	4.15
Carbon dioxide	19.85	Methane	75.50
			100.00

The ratio C/A , found by exploding the residual gas, after removal of CO_2 , CO , and oxygen with excess of oxygen and air, was 1.992,

again proving the entire absence of free hydrogen in the products. In this instance, also, it should be pointed out that the extremely large ratio, CO_2/CO , in the gaseous products is largely due to the fact that carbon monoxide and oxygen combine quite readily at 500° under the experimental conditions.*

FIG. 2.



Curve showing daily pressure fall in the mixture $2\text{CH}_4 + \text{O}_2$ when circulated over a surface maintained at 500° (second experiment).

Comparing now, as in the case of the first experiment, the partial pressures of the original mixture, as introduced into the apparatus,

* That this is so we have proved directly by examining moist mixtures of carbon monoxide (2 vols.) and oxygen (1 vol.) in the circulation apparatus, the temperature of the combustion tube being kept constant at 450° , and any carbon dioxide being absorbed as fast as it was produced by a suitable absorbent in the worm *E*. In one experiment, nearly 80 per cent. of the mixture combined in eight days. We are now investigating the velocity of the reaction with a view to determining its order and character. The curves obtained indicate that the velocity is nearly proportional to the pressure of the reacting mixture. We hope before long to communicate the details of these experiments.

with those of the final gaseous products, we obtain the following numbers:

Partial pressures for original mixture (nitrogen free).

$$\text{Methane} = 513 \times 0.665 = 341.1 \text{ mm.}$$

$$\text{Oxygen} = 513 \times 0.335 = 171.9 \text{ ,,}$$

Partial pressures of gaseous products. mm.	Corresponding with mm. of the original	
	Methane.	Oxygen.
CO = $335.9 \times 0.005 = 1.7$	1.7	2.5
CO ₂ = $335.9 \times 0.1985 = 66.6$	66.6	133.2
O ₂ = $335.9 \times 0.0415 = 14.0$	—	14.0
CH ₄ = $335.9 \times 0.7550 = 253.6$	253.6	—
	<hr/> 321.9	<hr/> 149.7

Thus, out of the 341.1 mm. of methane and 171.9 mm. of oxygen originally introduced into the apparatus, only 321.9 and 149.7 mm., respectively, are accounted for in the gaseous products. The remaining 19.2 mm. of methane and 22.2 mm. of oxygen (again nearly equal volumes) must have reacted forming soluble 'intermediate' products. This would represent no less than 22 per cent. of the methane burnt.

The liquid in the worm *E* was found to be distinctly acid to litmus; it had a pronounced aldehydic smell, and instantly restored the magenta colour to a solution of rosaniline hydrochloride previously decolorised by sulphurous acid. With a solution of *p*-bromophenylhydrazine acetate in dilute acetic acid, it gave an immediate canary-yellow precipitate of a bromohydrazone, which proved to be identical with that prepared directly from a dilute solution of formaldehyde. The acidity of the liquid may be attributed to the presence of a small quantity of formic acid, the formation of which would also explain why rather more of the oxygen than of the methane of the original mixture was unaccounted for in the gaseous products (see previous paragraph). We cannot say definitely whether the formic acid was due to the further oxidation of formaldehyde vapour in the heated tube or of liquid formaldehyde in the worm. It may, however, be pointed out that no formic acid was produced in the first experiment, where the rate of circulation was much slower,* and that in neither experiment could we detect any formation of methyl alcohol. The proportionately larger amount of formaldehyde found in the second experiment (22 per cent. of the methane oxidised, as compared with

* This fact favours the view that the formic acid detected in the second experiment originated in the hot combustion tube.

only 13 per cent. in the first experiment) is undoubtedly due to the more rapid rate at which the reacting gases were circulated over the heated surface, and afterwards through the water in the worm and spiral.

Other similar experiments with methane and oxygen have been made at various times, but since the results are identical with the foregoing, they need not be further described. In no case was there any sign of a deposition of carbon or liberation of free hydrogen, and they were all characterised by a continuous and regular diminution of pressure, and by the formation of formaldehyde.

It was just possible that this formaldehyde might have been produced by the rapid combination of carbon monoxide and free hydrogen liberated in a primary reaction of the following type: $\text{CH}_4 + \text{O}_2 = \text{CO} + \text{H}_2 + \text{H}_2\text{O}$, followed by $\text{CO} + \text{H}_2 = \text{CH}_2\text{O}$. This, of course, could only be the case did carbon monoxide and hydrogen combine with a velocity infinitely great as compared with the oxidation velocity of methane or of formaldehyde, since no free hydrogen was ever found in the final products. We therefore circulated a mixture of equal volumes of carbon monoxide and hydrogen in the apparatus for 2 days, the furnace being maintained at temperatures ranging between 460° and 480° . The results were entirely negative; no change in the pressure of the mixture was observed, and not a trace of formaldehyde was produced. Hence the view of the formation of formaldehyde just indicated is inadmissible.

These experiments are being extended to other hydrocarbons (ethane, propane, ethylene, acetylene, &c.) in the hope that by a thoroughly systematic examination of typical cases, sufficient data may in time be accumulated to justify a general theory of the mechanism of the oxidation of hydrocarbons.

In conclusion, we desire to express our indebtedness to the Government Grant Committee of the Royal Society for grants, which have materially helped us to meet the expenses of these researches.

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