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Kinetics of Methane Oxidation. II. The Dependence on Methane Concentration[1]

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RECEIVED NOVEMBER 24, 1959

Further studies of the slow combustion of methane have been carried out in a quartz reactor at 815° in order to determine the effect of methane concentration on the course of the reaction. The results show that the maximum in the formaldehyde *vs.* time curve is proportional to the methane only at very low concentrations, while at higher concentrations the formaldehyde maximum is independent of methane. The maximum formaldehyde concentration can be expressed by $[CH_2O]\text{max.} = k_1[CH_4][O_2]/(1 + k_2[CH_4])$ with values of k_1 and k_2 of 28.2 and 1574 l./mole, respectively. The rate of reaction at the formaldehyde maximum is a complicated function of the methane concentration; the rate at first decreases with increasing methane and then increases. The time of appearance of the formaldehyde maximum increases with methane concentration up to a point and then remains constant. At high concentrations of methane the reaction proceeds smoothly, but at low concentrations the reaction exhibits a discontinuity, *after the formaldehyde maximum has been reached,* after which the methane is completely consumed. These results are related, as far as possible, to other work.

Introduction

It has been shown in a previous report from this Laboratory[3] that proposals of mechanisms for the slow reaction of methane with oxygen do not predict the correct dependence of the maximum formaldehyde on the oxygen concentration at 815°. Furthermore, it was shown that the mechanisms do not correctly predict the dependence of the rate at the formaldehyde maximum on the oxygen concentration at higher temperatures. Although previous mechanisms could only be based on data available at the time the mechanisms were proposed (reference 4 offers excellent discussions of some early mechanisms), very few improvements have been made by later workers to modify or extend earlier proposals so as to cover the wider ranges of experimental data that are now available. That this is true indicates the need for further experimental investigations that will give the analytical relationships of the reaction variables. The present work is a continuation of an effort to find such relationships.

Several mechanisms that have been proposed for the slow oxidation of methane have made predictions concerning the maximum in the graph of formaldehyde *vs.* reaction times. The usual predictions are that the formaldehyde maximum is either proportional to or a linear function of the methane concentration. For example, Lewis and von Elbe have predicted that equation 1 represents the relationship between the maximum formaldehyde and methane at the maximum.

$$[CH_2O]_{\text{max.}} = k_1[CH_4] - k_2 \qquad (1)$$

The formaldehyde dependence on the methane has been suggested by Norrish[4b] to be represented by equation 2. Semenov,[4c] like Norrish, suggests that the maximum formaldehyde concentration is represented by

$$[CH_2O]_{\text{max.}} = k[CH_4] \qquad (2)$$

Furthermore, the rate of reaction at the maximum in the formaldehyde–time curve was predicted by Lewis and von Elbe to depend on the methane according to equation 3, when the oxygen and pressure are constant.

$$-d[CH_4]/dt = K_1[CH_4](K_2[CH_4] - 1)/(K_2[CH_4] + 1) \qquad (3)$$

Norrish and Semenov on the other hand predict the rate at the formaldehyde maximum to be given by

$$-d[CH_4]/dt = K_1[CH_4]^2 \qquad (4)$$

again at constant pressure and oxygen concentration. The constants in equations 1 to 4 represent combinations of various rate constants from the mechanisms proposed in reference 4, together with functions of oxygen, pressure, vessel dimensions, etc., that are assumed to be constant.

Predictions similar to equations 1 to 4 are subject to experimental verification and thus offer a powerful key to the validity of a proposed mechanism. Numerous investigations of the methane–oxygen reaction have been made in which static reaction systems were used and the course of the reaction followed by measurement of the increase in pressure. These measurements give information concerning the maximum rate of reaction but do not show how the formaldehyde depends on various parameters. Norrish and Foord,[5] working with soda glass, found equation 4 to hold at 480°, when $-d[CH_4]/dt$ was the *maximum rate.* Hoare and Walsh[6,7] studied the methane–oxygen reaction in quartz vessels with surfaces prepared in different ways. Assuming that their results for the maximum rate were represented by

$$-d[CH_4]/dt \propto [CH_4]^m[O_2]^x[\text{total pressure}]^t e^{-E/RT} \qquad (5)$$

these authors found that m and x varied with temperature, reactant concentrations and with surface conditions. At 500°, m varied from 1.6 in a quartz vessel that had been treated with HF to 2.3 in an "aged" quartz reactor. At 650°, m had values ranging from -1.0 in the HF treated vessel to 1.0 in a reactor whose walls had been treated with PbO. The value of m in an aged

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[1] Presented in part at the 136th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1959.

[2] Esso Research and Engineering Company, Linden, N. J.

[3] E. M. Magee, THIS JOURNAL, **81**, 278 (1959).

[4] (a) B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951, p. 110. (b) R. G. W. Norrish, *Rev. inst. franc., petrole,* **4**, 288 (1949). (c) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. II (Translated by M. Boudart), Princeton University Press, Princeton, N. J., 1959, pp. 228 ff.

[5] R. G. W. Norrish and S. G. Foord, *Proc. Roy. Soc.* (*London*), **A157**, 503 (1936).

[6] D. E. Hoare and A. D. Walsh, "Fifth Symposium (International) on Combustion," Reinhold Publishing Corp., New York, N. Y., 1955, p. 467.

[7] *Ibid.*, p. 474.

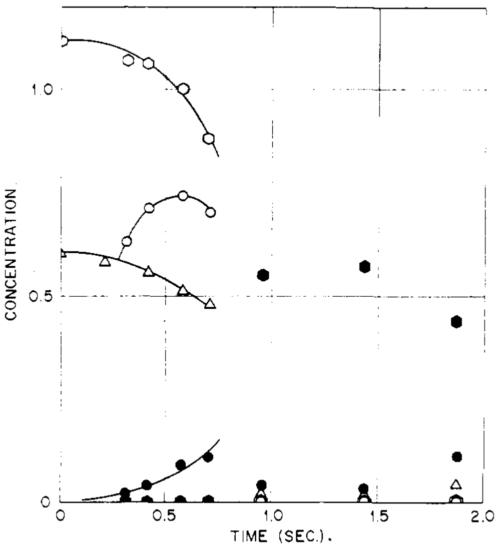

Fig. 1.—Concentration *vs.* time for 5.4% CH_4–10% O_2: O, $[CH_2O]$ mole/l. × 10^5; ⬢, $[CO_2]$; ⬡, $[O_2]$; Δ, $[CH_4]$; ●, [CO] all in moles/l. × 10^3.

reactor at 750° was shown to change from −0.4 to 0.4 as the methane was increased from 10 to 80 mm. Vanpée and Grard[8] have reported results similar to those of Hoare and Walsh in that *m* decreased from 1.45 at 570° to −0.14 at 666°.

Few data are available concerning the way in which the maximum formaldehyde concentration varies with methane. In an early report, Slotin and Style studied the production of formaldehyde as a function of methane and oxygen.[9] They attempted to show that the ratio of the maximum formaldehyde concentration to the methane concentration was constant but concluded that the ratio of formaldehyde to methane depended on the ratio of methane to oxygen in the mixture. More recent studies have been made of the maximum formaldehyde concentration,[10] in which the maximum was studied as a function of pressure, temperature and methane/oxygen. In this latter work as well as that reported by Slotin and Style the methane and oxygen were varied simultaneously so that it is difficult to separate the effects of methane, oxygen and pressure. The present work at a higher temperature was carried out to show the effect of varying the methane while the oxygen and pressure remained constant.

Experimental

The apparatus and experimental method used in this work were the same as that reported in a previous publication[3]; the experiments were carried out by the flow method in a quartz reactor. Studies were made with an initial oxygen concentration of 7.6% while the initial methane concentration was 2.1, 5.4, 8.0, 16.0, 43.7 and 92.4 on a percentage basis. The pressures were all raised to one atmosphere by nitrogen. Another group of experiments was carried out using initial oxygen and methane concentrations of 10.5 and 5.4%, respectively.

The data were used to calculate the concentrations of reactants and products as reported previously.[3] Each experiment gave a point for each reactant and product on a graph of concentration *vs.* a residence time. The concentrations were those at 815°, the reaction temperature.

Results and Discussions

Except for the 10% O_2–5.4% CH_4 and 7.6% O_2–2.1% CH_4 mixtures, the series of experiments for each set of initial concentrations gave curves similar to those reported previously[3]; that is, an induction period was observed in the CO, CH_4 and O_2 *vs.* time curves while the formaldehyde *vs.* time curve passed through a maximum. The two exceptions behaved quite differently, however, as shown by Fig. 1. The concentration–time curves began, at short residence times, in the same manner as other combinations of initial concentrations. The main carbon product was CO (no CO_2 was found at the shorter times) which increased at a faster rate as the time was lengthened. Similarly, the oxygen and methane concentrations showed an induction period and the rate of their disappearance increased with time. The formaldehyde concentration increased at first, passed through a maximum and then began to decrease. After 0.7 second, however, (0.41 sec. for 2.1% CH_4–7.6% O_2), a discontinuity occurred in the concentration–time curves. After the break in the graphs, the major carbon product was CO_2. The methane concentration dropped almost to zero while the oxygen and formaldehyde concentrations were zero. After the discontinuity, the reaction was accompanied by a large temperature rise in the reactor. It is concluded that a flame occurred in the mixture at the break in the curve. The most significant facts apparent from the two cases in which flame occurred are that no CO_2 appeared *before* the flame and the flame appeared *after* the formaldehyde had reached its maximum.

The concentrations of the reactants and products at the time of the formaldehyde maximum were determined together with the rate of reaction $(-d[CH_4]/dt)$. These values are tabulated in Table I.

TABLE I

RESULTS AT CH_2O MAXIMUM

% CH_4, init.	% O_2, init.	Concn. exit gas at CH_2O max., mole/l. at 815° CH_2O × 10^5	O_2 × 10^4	CH_4 × 10^3	CO × 10^4	$-(d[CH_4]/dt)$ at CH_2O max., mole/l. sec. × 10^4	Time CH_2O max., sec.
2.1	7.6	0.43	7.8	0.20	0.6	3.99	0.35
5.4	7.6	.66	6.9	.52	0.9	2.96	0.92
8.0	7.6	.69	6.4	.75	1.0	2.56	1.41
16.0	7.6	.79	6.1	1.61	1.8	2.22	1.41
43.7	7.6	.82	5.7	4.68	2.2	2.40	1.39
92.4	7.6	.95	5.5	10.20	2.7	3.52	1.42
5.4	10.0	.74	9.8	0.51	0.9	2.95	0.57

Figure 2 shows how the maximum formaldehyde concentration depends on the concentration of methane at the maximum. The formaldehyde maximum at first increases with methane and then becomes independent of methane at higher concentrations. Thus, equation 2 could be satisfied only at very low concentrations of methane. Figure 2 is a graph similar to that for the equation

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[8] M. Vanpée and F. Grard, *ibid.*, p. 484.

[9] L. Slotin and D. W. G. Style, *Trans. Faraday Soc.*, **35**, 420 (1939).

[10] A. Egerton, G. J. Minkoff and K. C. Salooja, *Proc. Roy. Soc. London)*, **235A**, 158 (1956).

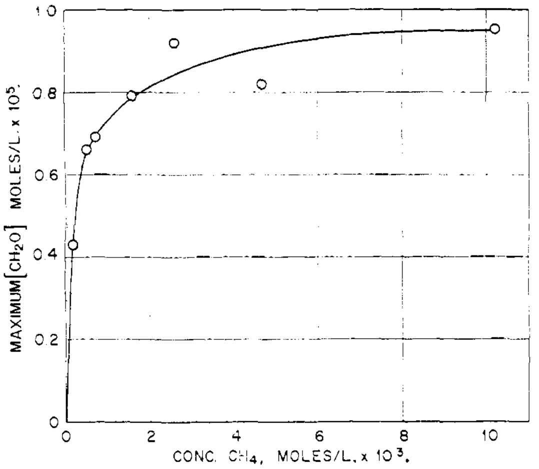

Fig. 2.—Maximum concentration of CH_2O *vs.* concentration of CH_4 at the maximum.

$y = ax/(1 + bx)$ and this equation fits the data shown by Fig. 2 quite well. It was shown previously[3] that the formaldehyde maximum was directly proportional to the oxygen concentration. Combining these facts, one arrives at an equation relating the maximum to both methane and oxygen

$$[CH_2O]_{max.} = k_1[CH_4][O_2]/(1 + k_2[CH_4]) \quad (6)$$

By rearranging (6) it is shown that if the equation holds, then a graph of $[CH_4][O_2]/[CH_2O]_{max.}$ *vs.* $[CH_4]$ should be a straight line with a slope of k_2/k_1 and an intercept of $1/k_1$. Such a graph gives a good straight line and least-square values of k_1 and k_2 are 28.2 and 1574 l./mole, respectively. The value of k_2/k_1 is determined very accurately from the slope of the graph, but $1/k_1$ from the intercept is much less accurate, hence the ratio of k_2 to k_1 is more accurate than the values of the individual constants. Substitution of these values for the constants into equation 6 then gives the quantitative relationship of the maximum formaldehyde concentration to the methane and oxygen concentrations at 815°, at one atmosphere total pressure and in the type of reactor used in these experiments. The graph of the left side of (6) *vs.* the right is shown in Fig. 3 together with the error that would result assuming a constant error of 0.1×10^{-3} mole/l. in methane and oxygen and again assuming the errors in the two concentrations to be 5% of their values. Results from these experiments together with results previously reported[3] are shown in Fig. 3. The points fit the line as well as could be expected considering possible errors in methane, oxygen and formaldehyde determinations.

As mentioned above, the work reported in references 9 and 10 involved measuring the maximum concentration of formaldehyde when both oxygen and methane concentrations were changed simultaneously and thus it is difficult to separate the effects of the two. However, it is possible, once a relationship is chosen, to determine whether the experimental data fit the relationship. Consequently, equation 6 was tested with the data in references 9 and 10 by constructing graphs of $p_{CH_4}p_{O_2}/p_{CH_2O}$ *vs.* p_{CH_4}. It was necessary to use

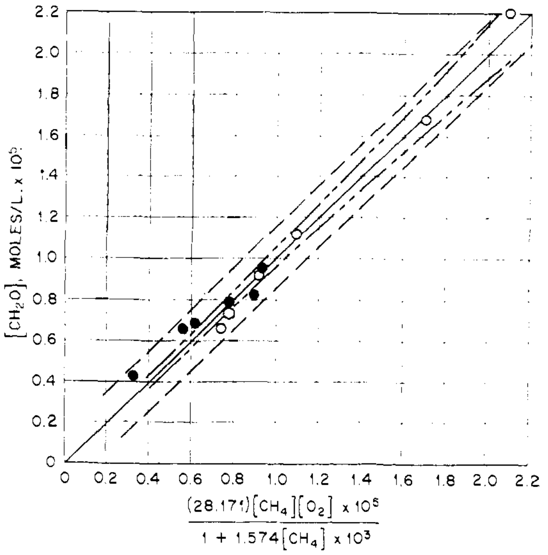

Fig. 3.—Relationship of CH_2O to CH_4 and O_2 at 815° ○, constant CH_4; ●, constant O_2; ⬡, 5.4% CH_4–10% O_2; - - - -, error assuming $\Delta O_2 = 0.05\, O_2$ and $\Delta CH_4 = 0.05\, CH_4$; ———, error assuming $\Delta O_2 = \Delta CH_4 = 0.1 \times 10^{-3}$ mole/l.

initial values of methane and oxygen in both cases since values at the maximum were not reported.

It was found that the graphs thus obtained fit straight lines *when the methane–oxygen ratios were constant* as well as when the pressure was constant. In both references, more data were available at constant ratio than at constant pressure and thus the lines at constant ratio could be drawn more accurately. (Reference 9 had no data at constant pressure.) Since the methane concentration is a function of $P(P_{CH_4} = PR/(1 + R)$, where P = total pressure and $R = p_{CH_4}/p_{O_2})$, the methane pressure corresponding to a particular total pressure can be calculated. The lines of constant ratio are then connected at points of constant pressure. Figure 4 shows such a graph of data for 460° from reference 10 and within experimental error the graph of $p_{CH_4}p_{O_2}/p_{CH_4}$ *vs.* p_{CH_4} is a straight line at constant pressure. Similar straight lines were obtained for 480 and 500° from reference 10 and at 430° from reference 9. The data in the latter reference showed more scatter than those from the former and the lines were not as good.

As indicated above, if an equation is chosen relating the concentration of methane, oxygen and formaldehyde at constant pressure, then a different equation can be written that also relates the concentrations, if the variables, methane, oxygen and total pressure have all been varied simultaneously. In the present case, it can be shown that if the results from reference 10 are fit by the expression

$$[CH_2O]_{max.} = k_1[CH_4][O_2]/(1 + k_2[CH_4])$$

then they must also be expressed at constant pressure by

$$[CH_2O]_{max.} = k_3[CH_4][O_2]/(1 + k_4[O_2]) \quad (7)$$

It is thus difficult to choose between equations 6 and 7 for the results at low temperature.

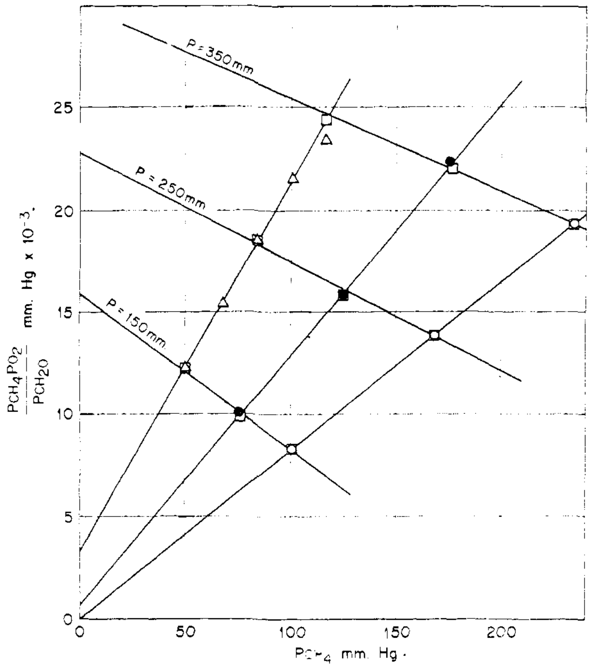

Fig. 4.—Relationship of maximum P_{CH_2O} to P_{CH_4} and P_{O_2} at 460° from ref. 9: ○, P_{CH_4}/P_{O_2} = 2; ●, P_{CH_4}/P_{O_2} = 1; △, P_{CH_4}/P_{O_2} = 0.5; □, calculated values.

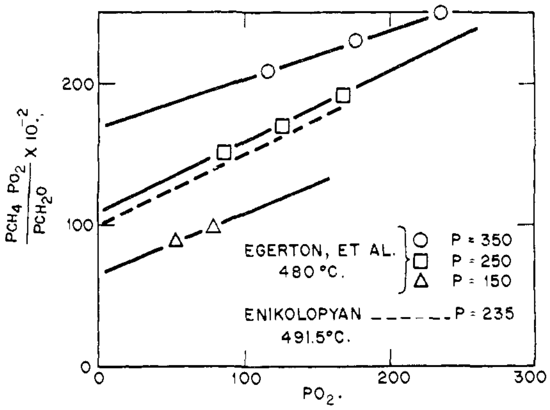

Fig. 5.—Relation of CH_2O, O_2, CH_4 at low temperature.

Fortunately, Enikolopyan[11] has studied the relationship of the maximum formaldehyde concentration and the concentrations of methane and oxygen at low temperatures, when the pressure as well as concentration of methane were constant. He used nitrogen to keep a constant pressure and found that the maximum concentration of formaldehyde increased at first with increasing oxygen concentration and then remained constant. Furthermore, Enikolopyan found that the maximum formaldehyde concentration at low temperatures was proportional to the methane concentration when the oxygen was held constant. It is immediately apparent that at low temperatures, the maximum concentration of formaldehyde may be represented by equation 7. Figure 5 shows the graph of data from references 10 and 11 plotted in a straight line form. The linearity of the lines shows that 7 accurately represents the data. The intercepts of the lines in Fig. 5 give the values of $1/k_3$ in equation 7 while the slopes give k_4/k_3. The excellent quantitative agreement between the results from references 10 and 11 shows that the use of nitrogen to maintain constant pressure has very little effect on the kinetics of the system. In any case, the use of nitrogen to maintain a constant pressure should have no more effect on the diffusional characteristics of the system than a change in the CH_4–O_2 ratio.

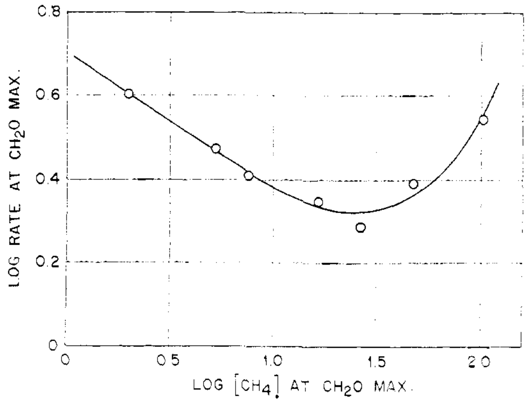

Fig. 6.—Rate of reaction *vs.* methane concentration.

The fact that the data of Enikolopyan[11] is represented by (7) but not by (6) indicates that (7) gives the general representation of the maximum formaldehyde concentration at low temperature. The profuse data from reference 10 then give the temperature dependence of k_3 and k_4 at 350 mm. as

$$\begin{aligned} k_3 &= 10^{-8.06}\, e^{13,160/RT} \qquad (8)\\ k_4 &= 10^{-12.61} e^{44,060/RT} \end{aligned}$$

The units of k_3 and k_4 are mm.$^{-1}$.

A general relationship then can be written expressing the dependence of the maximum concentration of formaldehyde to the concentration of reactants. This relationship is obtained by combining equations 6 and 7 to give

$$[CH_2O]_{max.} = \frac{(k_1 + k_3)[CH_4][O_2]}{1 + k_2[CH_4] + k_4[O_2]} \qquad (9)$$

It may be concluded that (9) gives a good representation of the data at high temperatures (815°) and at low temperatures (500°). The temperature coefficients have been roughly determined at low temperatures. It will be interesting to see if the nature of equation 9 holds at temperatures between 500 and 800° and to determine the activation energies of the constants more accurately. The nature of the equation and the activation energies of the constants offer a powerful key to the over-all mechanism of the reaction.

Probably no other feature of the methane–oxygen reaction has been so thoroughly studied as the maximum rate of reaction. The over-all rate is the simplest variable to measure in a static system and as a result the maximum rate of reaction has been used as the basis for most mechanism proposals. Despite the numerous studies, no clear idea is available as to how the maximum rate depends on the concentration of methane and oxygen.

Figure 6 shows a log–log plot of the rate of reaction at the formaldehyde maximum *vs.* the methane

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(11) N. S. Enikolopyan, "Seventh Symposium (International) on Combustion," Butterworths Scientific Publications, London, 1958, p. 157.

concentration at 815°. The behavior of the relationship of rate to methane concentration is somewhat unusual in that it decreases at first as the methane increases and then begins to rise again. The slope of the graph varies from -0.3 to 1.0 over the concentration range studied. This type of curve is similar to that reported previously[6,7] for a quartz vessel treated with HF at 650° and for an "aged" quartz vessel at 750°. The rates shown in Fig. 6 are rates at the formaldehyde maximum whereas those reported in references 6 and 7 are maximum rates.

It is believed that at least some of the discrepancies in the relationship of the maximum rate to methane and oxygen concentrations that have been reported by different investigators can be explained. If curves such as Fig. 6 exist at all temperatures and if the position of the curve moved to higher methane concentrations with increasing temperature, then the exponent in the equation, Rate = $k(\mathrm{CH_4})^m$, would seem to decrease with increased temperature. This decrease in the exponent has actually been the case. (Table III of reference 8 shows values of the methane exponent as high as 2.3 at 376–400°. References 5, 6, 7 and 8, together with the present work, show the exponent decreasing with increasing temperature.) It is hoped that eventually this dependence of the maximum rate (or the rate at the formaldehyde maximum) may be expressed analytically.

It was shown previously[3] that as the concentration of oxygen is increased, the time of appearance of the formaldehyde maximum, τ, decreases. A graph of τ *vs.* $1/(\mathrm{O_2})$ was shown to be a straight line. Results from the present work show a different dependence of τ on the methane concentration. It can be seen from the above table that τ *increases* at first with an increase in methane concentration and then becomes constant. In all the data reported here and in reference 3, the formaldehyde maximum appears *before* the point where the rate reaches its maximum value. This observation leads one to the conclusion that at least at high temperatures the branched chains cannot come directly from reactions of formaldehyde. If the branching occurred as a direct result of formaldehyde reactions, then the maximum rate would necessarily occur *at* or *before* the time when the formaldehyde reached its maximum value. This statement is due to the fact that the rate would depend on the concentration of reactants and/or formaldehyde. If the rate depended on reactants alone, it would be greatest at the beginning of the reaction where the concentration of reactants would be largest. If the rate depended only on formaldehyde, it would be greatest at the formaldehyde maximum. Finally, if the rate depended on both the formaldehyde and the reactants, it would reach its maximum value between the two extremes. The obvious conclusion is that a second intermediate is present in the reaction and causes chain branching. It seems probable that this second intermediate comes from formaldehyde by means of some reaction scheme since several reports have stated that addition of formaldehyde to a mixture of methane and oxygen removes the induction period (see, for example, reference 5). The maximum concentration of this second intermediate must reach its maximum value *after* the formaldehyde maximum has been reached since again the maximum rate must appear *before* the maximum concentration of the second intermediate.

In conclusion, it should be pointed out that despite the several recent reports of experimental work on the methane–oxygen reaction, no mechanism has been proposed which satisfactorily accounts for all the facts observed. This work shows the relationship between the maximum formaldehyde concentration and the concentration of reactants at low and high temperatures. Furthermore, the way in which the maximum rate changes with temperature and reactant concentrations has been indicated. Evidently, despite the number of experimental facts that may be used to test proposed mechanisms, the key that will unlock the secret to the mechanism has yet to be found. It is hoped that this situation will not long remain static.

Acknowledgment.—The author acknowledges the helpful assistance of Mr. G. C. McCollum in carrying out much of the experimental work reported here.