[CONTRIBUTION FROM THE REFINING RESEARCH & DEVELOPMENT DIVISION, HUMBLE OIL & REFINING COMPANY]

# Kinetics of Methane Oxidation. I. The Dependence on Oxygen Concentration

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Experimental studies of the methane-oxygen reaction have been carried out in a quartz, flow-type reactor at 815° in order to determine the dependence of certain variables on the oxygen concentration. Results show that the maximum concentration of formaldehyde is proportional to the concentration of oxygen, a fact of great theoretical importance. The rate of disappearance of methane at the formaldehyde maximum is proportional to the concentration of oxygen raised to the 2.8 power and the concentration of oxygen at the formaldehyde maximum is 0.70 times the initial concentration. The time at which the maximum concentration of formaldehyde appears is a linear function of the reciprocal oxygen concentration. These results point out of the need for revision of previously proposed mechanisms for the slow oxidation of methane.

## Introduction

Although studies of methane oxidation have occupied numerous workers for many years, the details of the reaction are still obscure and a mechanism that explains the oxidation to the satisfaction of all investigators is still forthcoming. Most of the experimental work on the methane-oxygen reaction has consisted of measurements of the over-all pressure rise in static systems. While such work is of interest in showing general trends, it cannot give sufficient details to allow mechanism proposals to be proved. The absence of systematic investigations of quantitative relationships between the different variables in the system has seriously hampered communication of results between the various groups of workers and has resulted in a lack of specific criteria against which certain points of mechanism proposals could be compared. It was the object of the present work to obtain in a systematic fashion information that would be directly applicable to the elucidation of the mechanism of methane oxidation.

In the absence of a general method of solution of the system of differential equations associated with a reaction as complex as the methane-oxygen reaction, it is necessary to assume steady-state conditions for the free radicals in the reaction and to obtain as much information as possible from the resulting algebraic equations. In methane oxidation an equation relating the maximum concentration of the intermediate formaldehyde to the concentrations of methane and oxygen is usually obtained and this relationship is then used in the expression of the maximum rate of disappearance of methane in terms of the concentration of reactants. Thus, Lewis and von Elbe[1] predict that the maximum concentration of formaldehyde should be independent of the oxygen concentration and a linear function of the methane. Use of this function then shows the maximum rate to be proportional to the oxygen concentration if the methane is held constant. Similarly, Norrish[2] predicts that the maximum concentration of formaldehyde should be proportional to the methane concentration and independent of the oxygen and that the maximum rate of reaction is proportional to the oxygen at constant methane. Norrish, however, points out the fact that the prediction of no oxygen effect on the formaldehyde maximum is no proof of the accuracy of the mechanism since this has never been shown experimentally.[2]

Contrary to the above mentioned predictions, the work of Patry and Monceaux[3] indicates that actually the maximum concentration of formaldehyde increases as the oxygen is increased. These workers show also that the rate of disappearance of formaldehyde is independent of oxygen concentration. The more recent work of Egerton, *et al.*, indicates that the maximum concentration of formaldehyde cannot be proportional only to the methane concentration.[4]

The relationship between the formaldehyde maximum and the concentration of reactants is important, for this relationship will necessarily enter into any expression for the maximum rate of reaction and the maximum rate is the chief item of kinetic importance to emerge from pressure measurements in a static system. The present report shows the relationship of the formaldehyde maximum to the oxygen concentration together with other results of interest.

## Experimental

The experiments were carried out in a U-shaped, quartz, flow-type reactor consisting of three sections: a preheater, reaction zone and quenching zone. The reaction zone was a tube with an inside diameter of 1 cm. and a volume of 17 ml.; the preheater and quenching zones consisted of the annular space formed by two concentric tubes. The inside tube served as a thermocouple well in both the preheat zone and the quench zone so that the temperature of the gases entering and leaving the reaction zone could be measured. A third tube surrounded the tube leading from the reaction zone and air, blowing through the third tube, served to quench the reaction. Before the experiments were started, the reactor was washed with soapy water, rinsed and then washed with concentrated nitric acid and rinsed. Little difficulty was found in obtaining reproducible results, although it was necessary to discard the first few experiments at the beginning of the work, and if it were necessary to stop the experiments for extended periods of time, two or three experiments were necessary to return to reproducible conditions.

A fluidized sand bath served as a thermostat and the temperature was controlled by a Wheelco controller and was measured with chromel-alumel thermocouples. The reactor was lowered into the sand bath until the temperature of the entering gas was just 815°. The sand bath was very efficient at removing heat—no drastic temperature rise was observed with the thermocouple on the exit side of the reaction section except at high oxygen concentrations and high conversions, and even then the temperature rise was no more than 10-20°. Under most conditions, the temperature was constant at ±3°.

The methane used in this work was Phillips' Research Grade with a purity of 99.9%; the greatest impurity was

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[1] B. Lewis and G. von Elbe, "Combustion Flames and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951, p. 110.

[2] R. G. W. Norrish, *Rev. inst. franç. pétrole*, **4**, 288 (1949).

[3] M. Patry and P. Monceaux, *Trans. Faraday Soc.*, **42**, 341 (1946).

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

nitrogen. The oxygen and nitrogen were supplied by Air Reduction Sales Company and both were of C.P. quality; the nitrogen was the dry type. The gases were used without further purification and were metered with rotameters and pre-mixed before entering the reactor. In order to obtain best results, it was necessary to mix the required oxygen with nitrogen and to feed the two together. The gases emerging from the reactor were transported through a glass tube heated to 130° to two water bubblers maintained at 0° by means of an ice-bath. Formaldehyde produced in the reaction was almost entirely removed in the first scrubber—the second was used only as a check. After the formaldehyde had been removed the gas could be sampled (samples were caught over saturated $MgSO_4$) and was then passed through a wet test meter. A line that by-passed the reactor was used before an experiment to obtain a sample of the unreacted gas.

The water solutions of formaldehyde were analyzed by a mercurimetric method.[5] Some values were checked by polarography, but the titration was found to be more reproducible than the polarographic method. Oxygen, carbon monoxide and carbon dioxide were determined by analysis with a Burrell absorption apparatus. The methane was determined in some samples by gas chromatography.

From the measured values of the total rate in, the total rate out (less water and formaldehyde), oxygen concentration in the feed and exit gas, methane concentration in the feed and the concentration of carbon monoxide, carbon dioxide and formaldehyde in the exit gas, it was possible to calculate the concentration of water, hydrogen and methane and the total volume change on reaction. The concentration of methane was checked several times by chromatographic analysis to ensure that the calculations were accurate. The volume change was small (less than 5%) except at the highest conversions of the mixtures with highest oxygen concentration, and in no case was the volume change greater than 10%. The hydrogen concentration was in general very small and since its calculation involved subtraction of large numbers, no significant figures were obtained for this product.

The residence time in the reactor was calculated from the volume of the reactor and the average of the rate in and the rate out. The length of each experiment was 1 or 2 hr.—the shorter experiments were sufficient when the formaldehyde concentration was high, while the longer runs were necessary for low concentrations of formaldehyde.

In all experiments reported here, the initial concentration of methane was 24% ($2.69 \times 10^{-3}$ mole/l. at 815°). The initial oxygen concentrations were 6.5, 7.6, 10.0, 14.4 and 20.0 on a percentage basis or 0.73, 0.85, 1.12, 1.61 and 2.24 $\times$ $10^{-3}$ mole/l. at the reaction temperature. Sufficient nitrogen was used to keep the pressure at one atmosphere. Below 6.5% oxygen, the time of appearance of the maximum concentration of formaldehyde could not be determined with the present reactor. This was due to the fact that the maximum in the formaldehyde *vs.* time curve moved to longer times as the oxygen concentration was lowered, and inaccurate results were obtained for times greater than 3.5 sec. Higher concentrations of oxygen could not be used due to the consequent temperature rise.

## Results

Figure 1 shows a graph of the results for the experiments with an initial oxygen concentration of 20%. The methane and oxygen curves have the familiar reversed "S" shape while the CO curve is an "S." The formaldehyde curve goes through the usual maximum which is expected of an intermediate and the carbon dioxide, which is small, increases with no evident maximum rate; in the experiments below 20% oxygen, essentially no carbon dioxide was formed. Similar curves were found for the various components in the experiments at other concentrations of oxygen. In each case, the time of appearance of the maximum formaldehyde concentration was determined from the curve, and the concentrations of the other components were then found, for that time, from a smooth curve through the points. The slope of the methane curve was also measured at the time when the formaldehyde concentration was at its maximum value. The concentration of products and rate of methane disappearance at the formaldehyde maximum, together with the time of appearance of the maximum, are shown in the table.

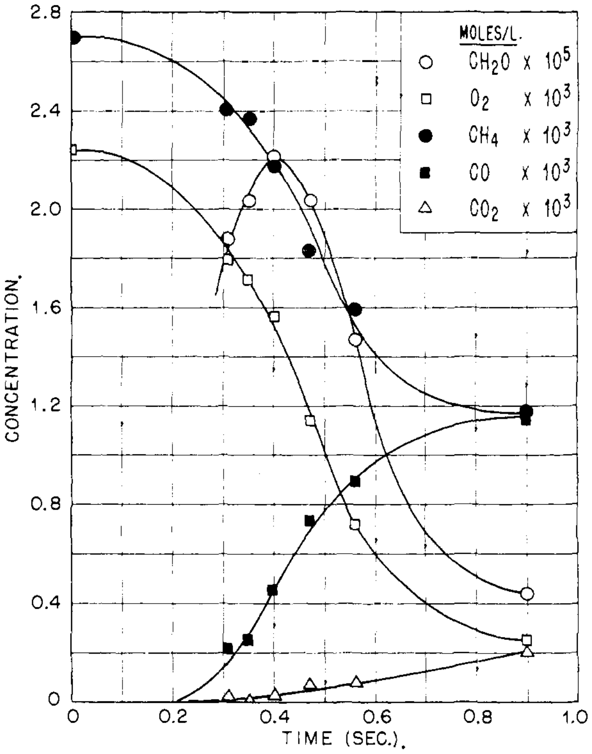

Fig. 1.—Concentration of reactants and products *vs.* time for mixture of 20% $O_2$, 24% $CH_4$.

The greatest source of error arose from control of the flow rates, and this error manifests itself in the determination of the time of appearance of the formaldehyde maximum. At this point, the rate of appearance of formaldehyde is zero and an error in the time of appearance makes a minimum of error in the concentration of formaldehyde. However, the other components are changing rapidly at the formaldehyde maximum and an error in time causes a maximum error in the concentrations. The formaldehyde concentrations are believed to be accurate to better than ± $0.1 \times 10^{-5}$ mole/l., while the other concentrations are accurate to better than ± $0.1 \times 10^{-3}$ mole/l.

The relationship of greatest interest in this work is that between the maximum formaldehyde concentration and the concentration of oxygen at the maximum. From the table it can be seen that the concentration of methane is almost constant at the maximum, thus the change in the maximum formaldehyde concentration is due to the change in oxygen concentration and the relationship between the two is shown in Fig. 2. The graph shows the maximum formaldehyde to be directly proportional to the oxygen concentration and the constant of proportionality is $1.43 \times 10^{-2}$.

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(5) J. F. Walker, "Formaldehyde," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1953, p. 387.

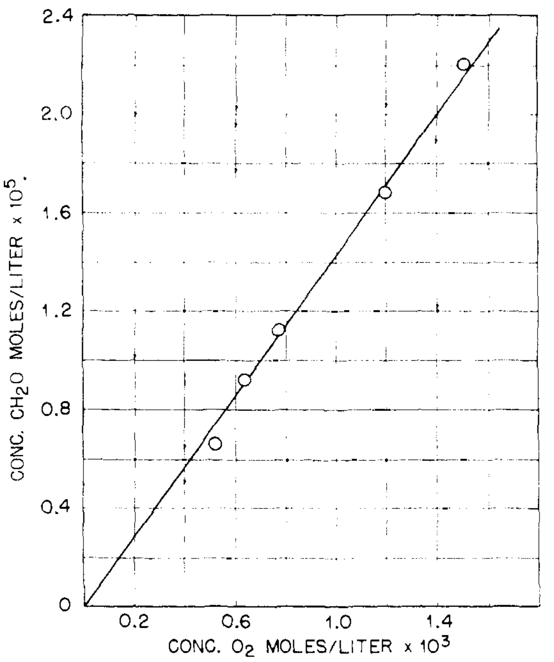

Fig. 2.—Maximum concentration of $CH_2O$ *vs.* concentration of $O_2$ at the maximum.

The second relationship of importance is that between the rate of disappearance of methane at the formaldehyde maximum and the concentration of oxygen. A plot of the logarithm of the rate of disappearance of methane *versus* the logarithm of the oxygen concentration at the maximum and *versus* the initial concentration of oxygen has least-squares slopes of the two lines of 2.82 and 2.72, respectively These curves show that the rate at the formaldehyde maximum is proportional to the oxygen concentration at the maximum raised to the 2.8 power and that the concentration of oxygen at the maximum is proportional to the initial concentration and the proportionality constant is 0.70.

TABLE I

RESULTS AT $CH_2O$ MAXIMUM

| Initial Concn. $O_2$, moles/l. $\times 10^3$ | Concn. in exit gas at $CH_2O$ max., moles/l. at 815° | | | | | $-(d[CH_4]/dt)$ at $CH_2O$ max., moles/l. sec. $\times 10^3$ | Time of $CH_2O$ max., sec. |
|---|---|---|---|---|---|---|---|
| | $CH_2O$ $\times 10^5$ | $O_2$ $\times 10^3$ | $CH_4$ $\times 10^3$ | CO $\times 10^4$ | $CO_2$ $\times 10^4$ | | |
| 0.73 | 0.66 | 0.52 | 2.53 | 1.31 | 0 | 0.122 | 1.96 |
| 0.85 | 0.92 | .64 | 2.60 | 1.85 | 0 | .194 | 1.48 |
| 1.12 | 1.12 | .77 | 2.45 | 2.52 | 0 | .385 | 1.12 |
| 1.61 | 1.68 | 1.20 | 2.44 | 2.77 | 0 | .965 | 0.64 |
| 2.24 | 2.20 | 1.51 | 2.19 | 4.50 | 0.25 | 2.94 | 0.40 |

Finally, a point of interest is the functional relationship between the time of the maximum formaldehyde $\tau$ and the oxygen at the maximum. The graph of $\tau$ *vs.* the reciprocal oxygen concentration is a straight line with a slope of 1.214 and an intercept of $-0.402$.

## Discussion

The results of the experiments shown here indicate a need for revision of mechanisms that have been proposed from time to time for methane oxidation. Because no temperature dependence of the maximum formaldehyde has been studied, the revisions are necessary, for the present, only in the region of 815°, and it is only in this temperature range that these discussions necessarily apply.

In the oxidation of methane, the formaldehyde is produced at a rate $R_A$ and disappears at a rate $R_D$. If it is assumed that the rate of disappearance of the formaldehyde can be factored into two terms, $R_D'F$, where $F$ is the concentration of formaldehyde, then the total rate of production of formaldehyde is given by

$$dF/dt = R_A - R_D'F \qquad (1)$$

At the maximum, the total rate is zero and hence

$$F_{Max} = R_A/R_D' \qquad (2)$$

From the results reported above, $R_A/R_D'$ is obviously proportional to the oxygen concentration when the methane is constant. In order to obtain such a relationship, it is necessary that $R_A$ be proportional to a once higher power of the oxygen concentration than $R_D'$. One such possibility is that the disappearance of formaldehyde is independent of the oxygen concentration and that the appearance is just proportional to the oxygen.

In the mechanisms proposed by Lewis and von Elbe[1] and by Norrish,[2] the disappearance of formaldehyde is brought about by reaction of the formaldehyde with oxygen (or free radical intermediates produced by reaction with oxygen), and this leads to a dependence of $R_D'$ on the oxygen concentration that cancels the dependence of $R_A$ on the oxygen. As mentioned above, the temperature dependence of the reactions may be such that the maximum formaldehyde is independent of the oxygen at lower temperatures, but at 815° this is not true.

The dependence of the rate of disappearance of methane at the formaldehyde maximum on the oxygen concentration makes necessary revisions in the above mentioned mechanisms. The value of 2.72 found above for the slope of log rate *vs.* log initial oxygen, may be compared to values found recently for the log of the *maximum* rate *vs.* the log of the initial oxygen concentration.[6-8] These slopes are not strictly comparable since the work reported in references 6–8 was carried out in static systems and the maximum rate of pressure rise was reported. For the relation max. rate = $(CH_4)^m(O_2)^x(\text{total pressure})^t e^{-E/RT}$, Hoare and Walsh[7] found that $m$ varied from 0 to 0.7, $x$ from 2.7 to 2.3 and $t$ from 0.4 to 0.6 in a heat-treated silica vessel at 650°. The value of $x$ reported by Hoare and Walsh for the dependence of the maximum rate on oxygen concentration is very close to the value found in the present work for the dependence of the rate at the formaldehyde maximum. At lower temperatures Hoare and Walsh found the values of $m$, $x$ and $t$ to change but, as they pointed out, the supposition of $m = 2$ and $x = t = 1$ is not a good assumption for quartz reactors. Vanpée and Grard, again measuring the maximum rate of pressure rise in a closed vessel, found the oxygen

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

(7) Ref. 6, p. 474.

(8) M. Vanpée and F. Grard, ref. 6, p. 484.

exponent to vary between 2.40 at 570° to 3.8 at 666°, a result similar to those discussed above.

It is significant that the work reported by Hoare and Walsh and by Vanpée and Grard, together with the present work, has been performed in quartz. That the nature of the surface is an important variable in determining the maximum rate has been pointed out by a number of observations (see for example reference 6). Norrish and Foord,[9] working in soda glass, found that the maximum rate corresponded to values of $m = 2$, $x = t = 1$ in the neighborhood of 500°. However, on going to a quartz vessel and a higher temperature (620°), they found an over-all order closer to 3 rather than 4.

The proportionality between the oxygen at the formaldehyde maximum and the initial oxygen illustrates how it may be possible to relate the dependence of a variable such as the rate of reaction at the formaldehyde maximum to the initial oxygen concentration when, strictly speaking, the variable should be related to the oxygen concentration at the maximum. The significance of this observation is still obscure at the present time.

The relationship between the time at which the maximum formaldehyde concentration appears and the oxygen concentration at the maximum is similar to observations that have been reported for other oxidation systems. Chamberlain and Walsh[10] reported the induction period for the oxidation of isopropyl ether to be a linear function of the reciprocal oxygen concentration. The relationship between this observation and the mechanism of reaction is, however, not clear.

The work reported here, along with other recent experiments on methane oxidation, show that no mechanism so far proposed is sufficiently general to cover entirely the slow oxidation of methane. Before better proposals can be made, however, it will be necessary to obtain more experimental data of the type reported here that show detailed relationships between variables of kinetic importance. The variation of the maximum formaldehyde concentration with methane concentration is being investigated along with other factors of significance in order that such relationships can be found. It is believed that when sufficient data are available, explanations can be found for the phenomena observed in methane oxidation.

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[9] R. G. W. Norrish and S. G. Foord, *Proc. Roy. Soc.* (*London*), **157A**, 503 (1936).

[10] G. H. N. Chamberlain and A. D. Walsh, *Rev. inst. franç. petrole*, **4**, 301 (1949).

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# Free Radicals by Mass Spectrometry. XIV. Ionization Potentials of Propyl and Butyl Free Radicals

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The ionization potentials of *n*-propyl, *n*-, *sec*-, iso-, and *t*-butyl radicals have been measured by electron impact on radicals which were generated thermally by the pyrolysis of appropriate alkyl nitrites, and allowed to flow into the ionization chamber of a mass spectrometer. The ionization potentials were found to be: *n*-propyl 8.69 v., *n*-butyl 8.64 v., isobutyl 8.35 v., *sec*-butyl 7.93 v., and *t*-butyl 7.42 v. Values calculated by a group orbital method are in good agreement with these. The thermal decomposition of the alkyl radicals was found to proceed by a split into a radical (or H atom) and an olefin without intramolecular migration of a hydrogen atom.

## Introduction

Some years ago Hipple and Stevenson[2] measured the ionization potentials of the methyl and ethyl radicals by direct electron impact on radicals generated thermally close to the ionization chamber of a mass spectrometer. A number of recent redeterminations of these ionization potentials have been made, and the agreement is, in general, quite good. A spectroscopic measurement of the ionization potential of the methyl radical[3] agrees closely with the electron impact data. Ionization potentials for a number of other radicals have been measured by electron impact and a summary of the values has appeared recently.[4]

With the exception of the *sec*-propyl radical,[5] no direct measurements of the ionization potentials of the higher alkyl radicals have been made. Values have been derived indirectly for the *n*-propyl, *sec*-propyl, *n*-butyl and *t*-butyl radicals[6-8] by combining appearance potentials of propyl and butyl ions with thermochemical data. Some uncertainties arise in the indirect method owing to the difficulty of identifying the structure of the propyl and butyl ions produced in the dissociative ionization processes. The appearance potentials of these ions from normal paraffins, for example, were found to be consistent, not with a primary structure for the ions as might be expected but with the formation of

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[1] National Research Laboratories Post-doctorate Fellow 1955–1957.

[2] J. A. Hipple and D. P. Stevenson, *Phys. Rev.*, **63**, 121 (1943).

[3] G. Herzberg and J. Shoesmith, *Can. J. Phys.*, **34**, 523 (1956).

[4] F. P. Lossing, *Ann. N. Y. Acad. Sci.*, **67**, 499 (1957).

[5] J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

[6] D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951).

[7] D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

[8] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.