

THE SLOW OXIDATION OF METHANE. I. A KINETIC STUDY

Hsien-Cheng Yao

Scientific Laboratory, Ford Motor Company, Dearborn, Michigan

Introduction

A number of rate expressions have been proposed for the oxidation of methane based upon measurements of the changes which occur in the total pressure of the reacting gas mixture. Bone and Allum (1) found that the rates of reaction were affected by the initial composition of the mixture. The highest rate under a given set of conditions was obtained when the ratio of the initial pressure of methane to that of oxygen was 2 to 1. This result was confirmed recently by Egerton and his co-workers (2). Norrish and Foord (3) proposed the rate equation:

$$\text{rate}_{\max} = \frac{k(\text{CH}_4)_0^2(\text{O}_2)_0 P_0 d}{S} \quad (\text{I})$$

where $(\text{CH}_4)_0$, $(\text{O}_2)_0$, and P_0 are initial pressures of methane, oxygen, and total pressures of methane, oxygen, and total pressure respectively, d is the diameter of the reaction vessel, and S is the surface activity per unit area. Later, Hoare and Walsh (4) suggested the rate expression

$$\text{Max rate} \propto (\text{CH}_4)_0^m (\text{O}_2)_0^x (P_0)^t e^{-E/RT} \quad (\text{II})$$

where m , x , and t are reaction orders which vary with the reaction vessel used. The m values ranged from 1.6 to 2.4, the x value from 1.2 to 1.7, and the t values from 0.5 to 0.9.

Recently Egerton and his colleagues (2) and Karmilova *et al* (5) have followed not only the changes in the total pressures but also the changes in the concentrations of reactants, intermediates, and products in each experiment. This was done by repeatedly preparing identical systems and then quenching them at various time intervals; these quenched systems were then analyzed for each component. On the basis of such experiments, Karmilova proposed the expression

$$\frac{d(\text{CH}_4)_{\max}}{dt} = k(\text{CH}_4)_0^\alpha (\text{O}_2)_0^\beta P_0^\gamma \quad (\text{III})$$

where $\frac{d(\text{CH}_4)_{\max}}{dt}$ represents the rate values ("constant rates") obtained from the

slopes of the straight line portion of the rate curves (zero order plots). The values of α , β , and γ were given as 1.62, 0.96, and ≈ 0.1 respectively. The sum of these is approximately 2.7 which agrees well with the value ($n = 2.6$) obtained by Egerton *et al* (2) but which differs from that of Norrish and Foord (3) ($n = 4.0$).

The most recent equation has been proposed by Enikolopyan (6), Semenov (7), Karmilova (8) and their co-workers on the basis of a theoretical treatment of the mechanism of the oxidation:

$$\frac{d(\text{CH}_4)_{\text{max}}}{dt} = \frac{2k_2 k_3}{k_8} \left(\frac{k_2 k_3}{k_2' k_3'} \right)^{\frac{1}{2}} (\text{CH}_4)^2 (\text{O}_2) \quad (\text{IV})$$

In this equation, the k 's are rate constants of a series of free radical reactions and (CH_4) and (O_2) are instantaneous partial pressures of methane and oxygen.

Although these authors (8) believed that equation IV is in good agreement with equation III, these equations are not identical. The maximum rate in the former (III) expression is dependent upon the initial partial pressures of methane and oxygen and that in the latter (IV) upon the instantaneous partial pressures of the reactants. Moreover, equation IV does not agree with many of their experimental results. For example, equation IV demands that the rate be second order with respect to methane and first order with respect to oxygen. Yet, the experimental results show that in some cases the rate of methane and oxygen consumption and of carbon monoxide formation is constant up to 50% completion of the reaction (5).

The foregoing resume makes it clear that additional evidence is still needed before the extent of the validity of the previously proposed rate equations and reaction mechanisms for the oxidation of methane can be established. Such evidence is difficult to obtain from the experimental techniques customarily used. Measurements of the changes in total pressure are inadequate for the determination of the reaction order with respect to methane and to oxygen or of the activation energy. Also, while the quenching technique can provide such evidence, it is laborious, time-consuming, and requires a vast number of separate experiments to examine in detail all the parameters in the reaction.

In addition to the experimental limitations of the earlier work, the role of carbon monoxide - the most stable intermediate in the oxidation of methane - has not yet been clarified. Yet, evidence has shown (5) that the oxidation of methane and of carbon monoxide occur simultaneously in the later stages of the reaction. Thus, the rate equation cannot be complete without including an expression for the oxidation of carbon monoxide.

In the present work, the oxidation of methane has been re-examined in detail. The partial pressures of methane, oxygen, and carbon monoxide have been followed by periodic withdrawal and analysis of small samples of the reacting gas mixture by means of gas chromatography. This technique permits a rapid, convenient, and accurate analysis for the separate components throughout each oxidation experiment.

Using this new technique, data have been obtained from which the reaction order with respect to methane and to oxygen can be examined and from which the apparent energies of activation can be calculated. A study has also been made of the methane-initiated oxidation of carbon monoxide.

Experimental

I. Reactants

Research grade methane, 99.54% pure (Phillips Petroleum Co.) was used without further purification. Oxygen, 99.5% pure (Liquid Carbonic, Division of General Dynamics) and carbon monoxide, c.p. grade (Matheson Co.) were dried through a column of 5A molecular sieve material (Fisher Scientific Co.) before use.

II. Apparatus

The apparatus consists of a gas introduction system, reaction vessel, gas sampling system, and a gas chromatograph connected as shown in Figure 1. The gas

chromatograph (Perkin-Elmer Corp. Model 154D) is equipped with a thermistor detector and a 2-meter column packed with molecular sieve material ("Column I").

III. Measurements of Partial Pressures

To measure the partial pressures of each of the gases during the oxidations, it was necessary to establish the relation between the chromatographic peak height and the quantity of each individual gas. For this purpose, gases were introduced through inlets 3 to the sampling capillary 9 located between stopcocks C and D. This capillary, 1 mm I.D. and 70 mm long, contained about 0.08 ml of gas. The pressure of the gas was measured on manometer 2. C and D are 3-way stopcocks with 1 mm. bore and Teflon plugs, while E is a 2-way glass stopcock with 2 mm. bore. By manipulating stopcocks C and D and also E, the gas trapped in the sampling capillary was pushed by the carrier gas, helium, into the gas chromatograph and a corresponding peak appeared on the recorder chart. The peak heights were plotted as a function of the pressures of the gases as shown in Figure 2. Thus for a given condition, $P = aH$ where P is the gas pressure, H is the peak height, and a is the proportionality constant. The value of a varies with the pre-set conditions, such as column temperature, flow rate of carrier gas, and volume of sampling capillary. In addition, repeated use of the chromatographic column may also change a . In the work reported here, the value of a for each individual gas was re-ascertained before each oxidation experiment.

IV. Oxidation Experiments

For the oxidation experiments, the separate gases were admitted through inlets 3 to the individual gas burets 5. The desired amounts (approx.) of the components of the reaction mixture were then pumped from the gas burets into the reaction vessel 7 using pump 6. The cylindrical reaction vessel was constructed of borosilicate glass (30 mm. I.D. with a volume of 100 ml.) and contained a thermocouple well along its longitudinal axis. In some experiments as indicated below, the vessel was used without further treatment and in others, it was first treated with hydrofluoric acid; for this treatment, the vessel was shaken with 20-25% hydrofluoric acid in water, then washed exhaustively with distilled water, and dried at 400°C at less than 1 mm. of Hg.

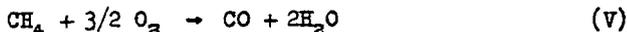
During the course of the oxidation experiments, the reaction vessel was maintained at the desired operating temperatures $\pm 1^\circ\text{C}$ by the thermocouple, temperature controller (Wheelco), variable transformer and furnace 8.

To determine the composition of the gases in the vessel at the start and during the experiments, a large fraction (ca. 55%) of the gas mixture was withdrawn from the reaction vessel and passed through the sampling capillary by lowering the mercury level in the modified 125 ml Toepler pump 11. Raising the level returned the gas through the capillary to the vessel. Two cycles were needed before each sampling in order to obtain reproducible analyses; each cycle required only about 15 seconds. The small sample of gas (0.08 ml.) was then pushed into the gas chromatograph with helium as described above. In such manipulations, some helium was inevitably introduced into the reaction vessel during sampling but it appeared to have no effect upon any of the reactions studied.

Results and Discussion

In many of the experiments reported earlier, carbon monoxide accumulated in much larger amounts than any other reaction intermediates, such as formaldehyde or hydroperoxide. In addition, Karmilova et al (9) were able to show by tracer techniques that the carbon dioxide formed in the oxidation of methane was produced almost

exclusively from the oxidation of carbon monoxide. Thus, although the less stable intermediates may contribute to the mechanism, the kinetics of the overall oxidation can be examined in terms of the stepwise reactions represented by equation V and VI.



I. The Oxidation of Methane to Carbon Monoxide (eq. V)

A. The reaction order with respect to methane and oxygen. To minimize the effect of carbon monoxide on the reaction kinetics, the ratio of the initial pressures of methane, $P_{\text{CH}_4}^0$, to that of oxygen, $P_{\text{O}_2}^0$, was increased in some experiments. When the ratio is about 3 or higher, the reaction is zero order with respect to oxygen and to methane; the results of typical experiments with both untreated and HF-treated vessels are shown in Figure 3. With such high ratios, the rates of consumption of methane and oxygen and the rates of accumulation of carbon monoxide are constant up to 90% completion of the reaction. These rates can be expressed as:

$$-\frac{dP_{\text{O}_2}}{dt} = k_1 \quad (\text{VII})$$

$$-\frac{dP_{\text{CH}_4}}{dt} = \frac{dP_{\text{CO}}}{dt} = 2/3 k_1 \quad (\text{VIII})$$

where k_1 is the zero order rate constant.

When the ratio of $P_{\text{CH}_4}^0$ to $P_{\text{O}_2}^0$ is reduced to unity or less, the rates are constant only up to about 30 to 70% completion. In these experiments, sufficient carbon monoxide accumulates so that it is oxidized competitively with methane. The rate equations (VII and VIII) can no longer be applied for the whole reaction but only for the initial stage where the rates are constant (Figure 4).

These constant rates have been observed by all previous investigators but have been generally identified by them only as "maximum rates" (equations I, II, and III). They were interpreted differently by previous investigators. Semenov (7, 10) has suggested that the oxidation of methane is a free radical chain degenerating process in which the formation of formaldehyde is the slow step of the reaction and the steady state of formaldehyde results in a constant rate. This interpretation has been accepted by many previous investigators. Recently, however, Karmilova *et al* (11) found that the rate remains constant even when the concentration of formaldehyde undergoes a marked decrease and, therefore, the postulation of the steady state concentration of formaldehyde as a controlling feature of the reaction is untenable. To explain these constant rates, they proposed that the oxidation of methane undergoes additional catalysis by one of the reaction products formed after formaldehyde. The observed constant rate may then result from a superposition of the rates of two autocatalytic processes, the increase in the rate of one due to oxidation of methane being compensated by the decrease in the rate of the other. They suggested several possible additional catalysts, such as hydrogen peroxide, hydroxy radical, etc. No evidence was given to support this view.

B. The effect of initial pressures of methane and oxygen. The results for the effect of $P_{\text{CH}_4}^0$ and $P_{\text{O}_2}^0$ on the value of k_1 are shown in Tables 1 and 2. In general,

k_1 increases with increasing either $P_{\text{CH}_4}^0$ or $P_{\text{O}_2}^0$, or both. $P_{\text{CH}_4}^0$ has more effect upon k_1 than does $P_{\text{O}_2}^0$. An empirical equation is proposed to account for the dependency of k_1 on the initial pressures:

$$k_1 = k_1' \frac{P_{\text{CH}_4}^{0a} P_{\text{O}_2}^0}{P_{\text{CH}_4}^0 + P_{\text{O}_2}^0} \quad (\text{IX})$$

where k_1' is a pressure independent rate constant. The values of k_1' are listed in Column 5 of Table 1 and Column 6 of Table 2. The validity of equation IX is indicated

by the linear relationship in the plot of k_1 vs $\frac{P_{\text{CH}_4}^{0a} P_{\text{O}_2}^0}{P_{\text{CH}_4}^0 + P_{\text{O}_2}^0}$ for the reactions at

different temperatures in an HF-treated vessel as shown in Fig. 5. For the reaction

in an untreated vessel, k_1 at 399°C increases linearly with $\frac{P_{\text{CH}_4}^{0a} P_{\text{O}_2}^0}{P_{\text{CH}_4}^0 + P_{\text{O}_2}^0}$ until it

appears to reach a limiting value of about 0.17 mm, min⁻¹ (Figure 6).

The increase in the maximum rates ("constant rates") as the initial partial pressures increase - observed in this as well as in earlier work (equations I, II and III) - is not accounted for by equation IV which is based on a free radical chain reaction mechanism.

The apparent energy of activation for the oxidation of methane calculated from k_1' values at four different temperatures (Figure 7) is 36.2 kcal/mole. This value differs from the values [43 (5, 6), 60.8 (12), and 61.5 (13)] obtained by earlier workers from the maximum rates.

C. The induction period. For the reactions below 455°C, an induction period has been observed which ranges from 1 min. to 350 min. as shown in Tables 1 and 2. The initial pressures of methane and oxygen affected this induction period but the exact relationship remains to be established. In general, the reactions in the untreated vessel had longer induction periods than those in the HF-treated vessel. It was noted that the induction period was extremely long when an untreated vessel was used for the first time. Also, the induction period is longer for reactions at lower temperatures than those at high temperatures. At 482°C and above with an HF-treated vessel, the induction period is negligible.

II. Methane-Initiated Oxidation of Carbon Monoxide (Equation VI)

In the course of the oxidation of methane when the ratio of the partial pressure of carbon monoxide to methane becomes appreciable, then the rate of disappearance of methane no longer follows the zero order equation (eq. V). Additional attention must therefore be devoted to the oxidation of carbon monoxide and to the role it plays in the oxidation of methane.

The oxidation of carbon monoxide itself requires temperatures of about 1000°C (14); however, in the presence of water vapor, this temperature may be lowered to about 400°C (15). There is no doubt that methane can also initiate the oxidation of carbon monoxide (15). A detailed study of this reaction is presented below.

A. Reaction in the presence of water. Since water can also initiate the oxidation of carbon monoxide, a comparison was made between the effect of methane and that of water. As shown in Fig. 8, when the mixture of carbon monoxide, oxygen and water vapor was heated at 427°C in an HF-treated vessel, the oxidation was slow. It became fast after methane was introduced.

B. Reaction order with respect to carbon monoxide and oxygen. In these experiments, dried carbon monoxide and oxygen were introduced into the HF-treated vessel at various temperatures ranging from 427° to 516°C. The reactions were extremely slow. However, the rate of reaction increased rapidly when a small amount of methane was introduced. The results of one such experiment are shown in Fig. 9. In all the present results, the methane-initiated oxidation of carbon monoxide is a second order reaction, first order with respect to carbon monoxide and to oxygen. The rate can be expressed as:

$$-\frac{dCO}{dt} = k_2 P_{O_2} P_{CO} \quad (X)$$

where k_2 is the second order rate constant. The temperature dependence of k_2 (Fig. 7 and Table 3) leads to an apparent activation energy of 60.7 kcal/mole.

As shown in Fig. 9, the linear relationship of the second order plot was maintained despite the decrease in pressure of methane from 13 mm to almost zero during the course of the reaction. This was observed in every experiment on the methane-initiated oxidation of carbon monoxide. k_2 does not depend, therefore, upon the instantaneous pressure of methane. Instead, there appears to be some relationship (Table 4) between k_2 and the initial pressure of methane - analogous to that exhibited by k_1 - although no satisfactory correlation has yet been obtained.

In another type of experiment (Fig. 10), additional carbon monoxide was added to a reacting mixture of methane and oxygen (and carbon monoxide produced) when the methane had decreased to 3.2 mm. A linear relationship was again obtained for the

second order plot of $\log \frac{2P'_{O_2} - P_x}{P_{CO}}$ versus time t . In this expression, P'_{O_2} is the

pressure of oxygen at the time when carbon monoxide was introduced, P_x is the pressure of carbon dioxide produced after that time, and P_{CO} is the instantaneous pressure of carbon monoxide. In this experiment k_1 , 8.9 mm, min⁻¹, was determined from the initial rate of consumption of oxygen and k_2 , 8.2 x 10⁻⁵ mm⁻¹, mm⁻¹, was obtained from the slope of the second order plot. This value of k_2 agrees well with those of Table 3 and once again appears to be related to the initial pressure of methane. If it depended upon the instantaneous pressure of methane when the carbon monoxide was added, viz. 3.2 mm, k_2 should be below 2.6 x 10⁻⁵ mm⁻¹, mm⁻¹ (Table 4).

III. Nature of the Oxidative Process

In the present work, during each sampling procedure, about 55% of the gas mixture was withdrawn from the reaction vessel to the Toepler pump at room temperature for about 15 seconds and then returned to the vessel. In the second cycle, this was repeated so that more than 80% of the reaction mixture may have been quenched during

each sampling. Even in the experiments which had relatively long induction periods, the sampling procedure had no discernible effects upon the rate curves. Therefore, it appears that the oxidation of methane must be a heterogeneous reaction inasmuch as quenching would affect the kinetics of a homogeneous reaction. Also, the apparent energy of activation for the oxidation of methane is 36.2 kcal/mole whereas that of carbon monoxide is much higher, i.e., 60.7 kcal/mole. It is difficult on the assumption of a homogeneous reaction to reconcile this wide disparity in energies of activation with the observations that both gases oxidize competitively during the reaction. Likewise, the rate of oxidation of methane depends upon the initial pressures of methane and oxygen rather than upon the instantaneous pressures as would be expected for a homogeneous reaction.

Some consideration of the possible nature of the heterogeneous process is warranted. On the basis of the present results, it appears that methane and oxygen react initially to form certain active sites or intermediate complexes on the surface of the reaction vessel. These active sites in turn can catalyze the oxidation of both methane and carbon monoxide which are zero order and second order reactions, respectively. The activity of these sites per unit area depends upon the initial concentrations and remains constant throughout the reaction. As the oxidation proceeds, carbon monoxide is produced in the reaction. This product in turn competes with the methane for the same active sites. A similar suggestion has been made by Von Meersche (16). As the concentration of the carbon monoxide becomes significant with respect to that of methane, then the consumption of methane deviates from the zero order rate. If the methane and carbon monoxide did not compete for the active sites but instead competed for the remaining oxygen, then the zero order rate for the consumption of methane should remain constant throughout the reaction. However, this has not been observed.

The detailed mechanism of this reaction and the nature of the active sites remain to be studied.

Summary

1. A stepwise oxidation of methane to carbon monoxide and then to carbon dioxide is demonstrated. The oxidation of methane to carbon monoxide is a zero order reaction with respect to both methane and oxygen. The zero order rate constant is dependent upon the initial pressures of both methane and oxygen. The correlation of this constant with initial pressures is indicated by an empirical equation. The apparent energy of activation for this reaction was calculated to be 36.2 kcal/mole.

2. The reaction in an untreated vessel has a longer induction period and slower rate than that in an HF-treated vessel.

3. The oxidation of carbon monoxide is initiated by methane or its oxidation product and is a second order reaction, first order with respect to oxygen and to carbon monoxide. The second order rate constant appears to vary with the initial pressure of methane. The apparent energy of activation for this reaction is 60.7 kcal/mole.

4. The oxidation of methane appears to be a heterogeneous process. It is suggested that during the induction period, methane and oxygen react to form active sites or intermediate complexes on the surface of the reaction vessel. Methane and its oxidation product, carbon monoxide, then compete for these sites rather than for oxygen.

Acknowledgment

The author is indebted to Dr. C. H. Ruof for his encouragement and guidance in the course of this work.

References

- (1) W. A. Bone and R. E. Allum, Proc. Roy. Soc. A134, 578 (1932).
- (2) A. C. Egerton, G. J. Minkoff and K. C. Solooja, Proc. Roy. Soc., A235, 158 (1956).
- (3) G. W. Norrish and S. G. Foord, Proc. Roy. Soc., A157, 503 (1936).
- (4) D. E. Hoare and A. D. Walsh, Fifth Symposium on Combustion, Reinhold Publishing Corporation, New York, 1955, PP 467-484.
- (5) L. V. Karmilova, N. S. Enikolopyan and A. B. Nalbandyan, Zhur. fiz. Khim, 31, 851 (1957); *ibid* 34, 550 (1960).
- (6) N. S. Enikolopyan, Seventh Symposium on Combustion, Butterworths Scientific Publications, London 1959, P. 157.
- (7) N. N. Semenov, Some Problems of Chemical Kinetics and Reactivity, Pergamon Press, New York, 1959, Vol. 2, PP 103-117.
- (8) L. V. Karmilova, N. S. Enikolopyan, A. B. Nalbandyan and N. N. Semenov, Zhur. fiz. Khim 34, 1176 (1960).
- (9) L. V. Karmilova, N. S. Enikolopyan and A. B. Nalbandyan, Zhur. fiz. Khim, 35, 1458 (1961)
- (10) N. N. Semenov, Chemical Kinetics and Chain Reactions, Oxford 1935
- (11) L. V. Karmilova, N. S. Enikolopyan, A. B. Nalbandyan Zhur. fiz. Khim, 35, 1435 (1961)
- (12) A. C. Egerton, G. J. Minkoff and K. C. Salooja, Combustion and Flame, 1, 25 (1957).
- (13) R. Fort and C. N. Hinshelwood, Proc. Roy. Soc. A129, 284 (1930).
- (14) J. H. Burgoyne and H. Hirsch, Proc. Roy. Soc. A227, 73 (1954).
- (15) D. E. Hoare and A. D. Walsh, Trans Faraday Soc. 50, 37 (1954).
- (16) M. Von Meersche, Ann. Min. Belg., 48, 643 (1949).

Table 1 - Oxidation of Methane in an HF-Treated Vessel at Various Temperatures

Expt. No.	T°C	P _{O₂} , mm	P _{CH₄} , mm	k ₁ , mm, min. ⁻¹	k ₁ ' x 10 ⁵ , mm ⁻¹ , min. ⁻¹	Induction Period, min.
32	399	127	317	1.5	5.22	40
33	"	83.4	364	1.44	5.83	35
34	"	380	330	3.02	5.18	16
35	"	378	148	0.89	5.65	20
36	427	399	151	2.82	17.1	14
37	"	151	344	6.5	18.0	5
38	"	154	126	1.7	19.5	10
39	"	154	346	5.64	15.3	4
40	"	372	364	11.7	17.5	5
41	454	347	161	8.0	45.2	3
42	"	185	355	18.2	42.2	1
43	"	115	106	2.55	43.4	3
44	"	204	187	8.9	48.9	3
45	"	265	234	16.6	57.1	3
46	"	312	306	23.2	49.1	4
47	"	308	371	33.0	52.9	4
24	482	383	306	47.5	86.4	< 1
25	"	209	298	32.0	87.4	"
26	"	122	308	23.1	86.2	"
27	"	278	267	37.5	101	"
28	"	196	272	32.5	105	"
29	"	186	107	6.5	89.4	"
30	"	112	342	28.3	98.1	"
31	"	111	346	24.3	83.6	"

Table 2 - Oxidation of Methane in an Untreated Vessel at 399°C

Expt. No.	P _{O₂} , mm	P _{CH₄} , mm	k ₁ , mm, min. ⁻¹	k ₁ ' mm ⁻¹ , min. ⁻¹	Induction Period, min.
2*	79	408	0.13	4.8 x 10 ⁻⁶	350
3	96.4	306	0.17	7.0 x 10 ⁻⁶	55
4	226	288	0.17	4.7 x 10 ⁻⁶	50
5	151	265	0.16	6.3 x 10 ⁻⁶	48
6	83.6	273	0.15	8.6 x 10 ⁻⁶	56
7	39	372	0.15	11.4 x 10 ⁻⁶	40
8	74	311	0.16	8.6 x 10 ⁻⁶	50
9	243	111	0.042	5.0 x 10 ⁻⁶	150
10	220	71.4	0.043	11.2 x 10 ⁻⁶	60
11	236	156	0.17	12.0 x 10 ⁻⁶	40
12	280	94	0.06	9.0 x 10 ⁻⁶	40
13	287	95.5	0.033	8.6 x 10 ⁻⁶	50
14	179	75	0.05	12.7 x 10 ⁻⁶	120
15	246	120	0.06	6.2 x 10 ⁻⁶	150

*E2 was in a new vessel used for the first time.

Table 3 - Dependency of k_2 on Temperature

Expt. No.	$P_{CH_4}^0$, mm	T°C	k_2 , mm ⁻¹ , min ⁻¹
E104	13.0	516	1.70×10^{-4}
E98	12.5	516	1.20×10^{-4}
E103	13.5	504	7.36×10^{-5}
E99	14.0	482	2.27×10^{-5}
E102	13.4	482	3.125×10^{-5}
E101	11.0	454	5.5×10^{-6}

Table 4 - Dependency of k_2 on $P_{CH_4}^0$ (482°C)

Expt. No.	$P_{CH_4}^0$	k_2
118	3.7 mm	2.6×10^{-5} mm ⁻¹ , min ⁻¹
116	8.1	4.8×10^{-5}
117	14.9	5.0×10^{-5}
115	19.7	6.7×10^{-5}

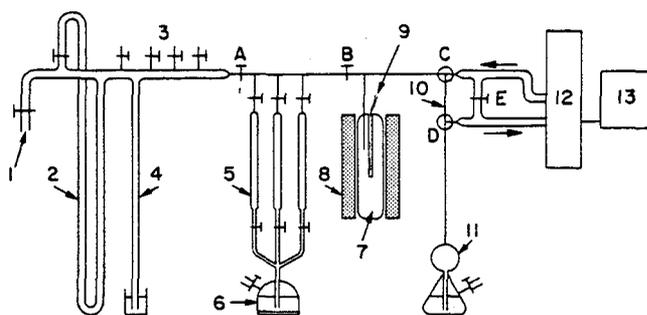


Fig. 1. - Reaction system. 1. Vacuum inlet; 2. Manometer; 3. Gas inlet; 4. Pressure relief device; Gas burets; 6. Mercury pump; 7. Reaction vessel (100 ml.); 8. Furnace; 9. Thermocouple; 10. Sampling capillary; 11. Toepler pump (125 ml.); 12. Gas chromatograph; 13. Recorder.

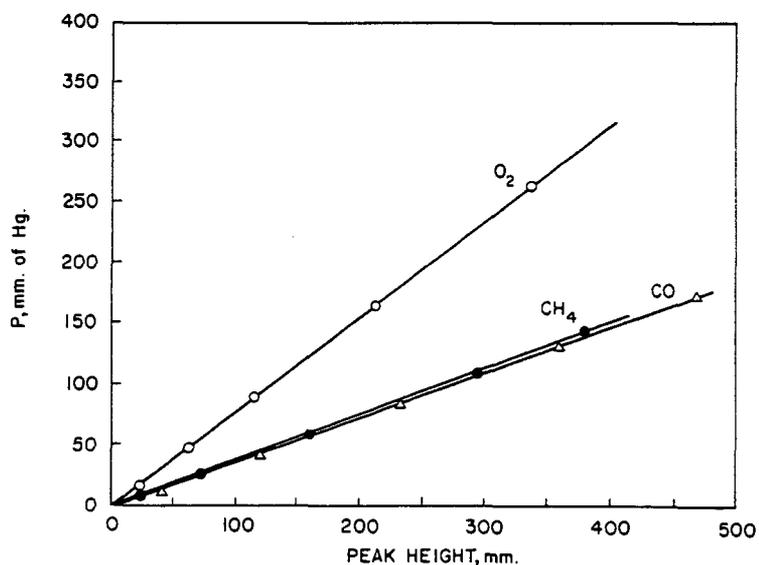


Fig. 2. - Calibration of peak heights against pressures.

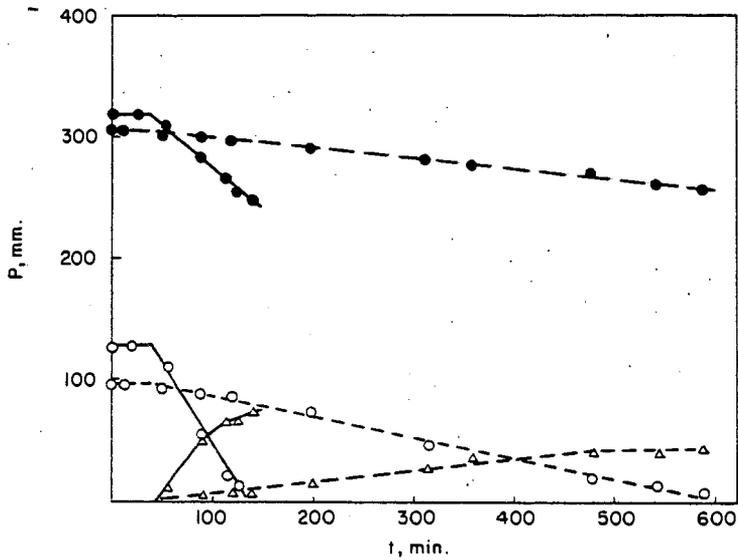


Fig. 3. - Rate curves for the oxidations of methane at 399°C. O, O₂; ●, CH₄; Δ, CO. Broken lines, untreated vessel (E3); solid lines, HF-treated vessel (E32).

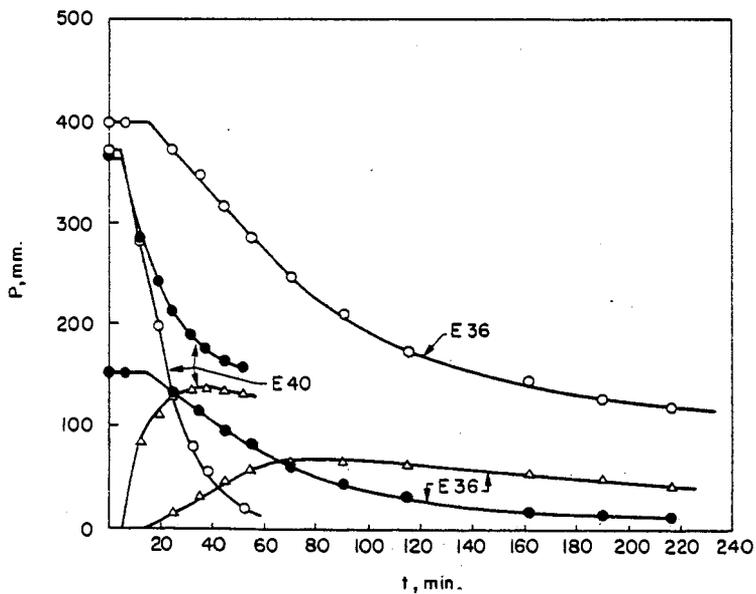


Fig. 4. - Rate curves for the oxidations of methane in HF-treated vessel at 427°C. Experiment 36, $P_{\text{CH}_4}^0/P_{\text{O}_2}^0 = 0.38$; Experiment 40, $P_{\text{CH}_4}^0/P_{\text{O}_2}^0 = 0.98$. O, O₂; ●, CH₄; Δ, CO.

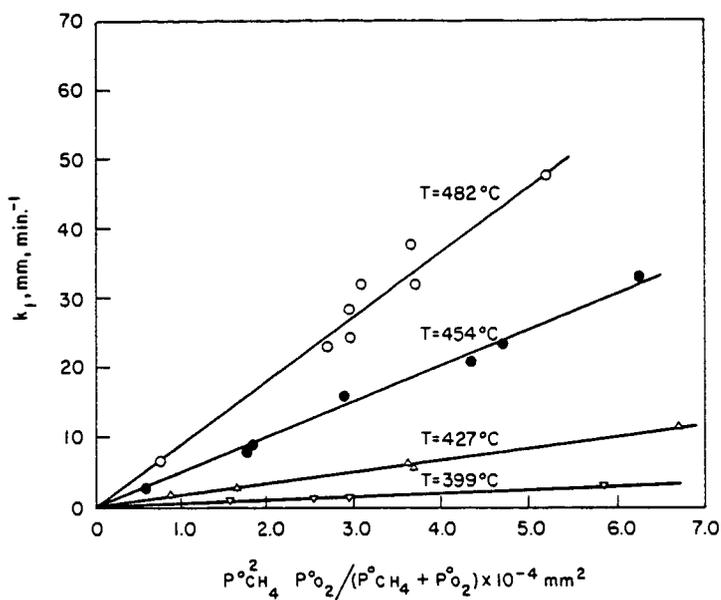


Fig. 5. - Dependence of k_1 on initial pressures of methane and oxygen (oxidations in HF-treated vessel).

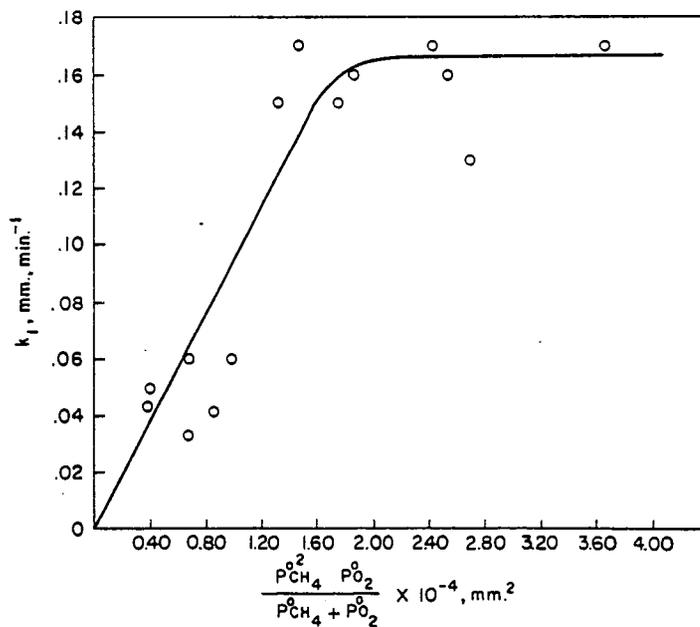


Fig. 6. - Dependence of k_1 on initial pressures (oxidations in untreated vessel at 399°C).

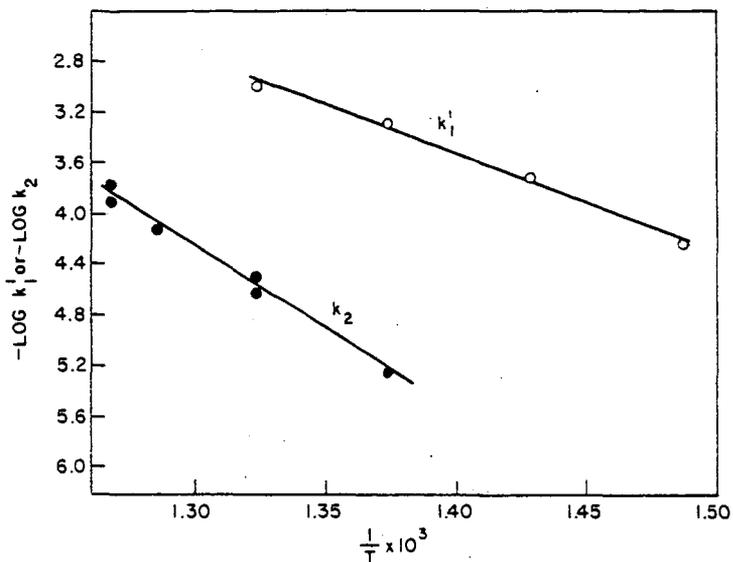


Fig. 7. - Arrhenius plot for the determination of the apparent activation energy.

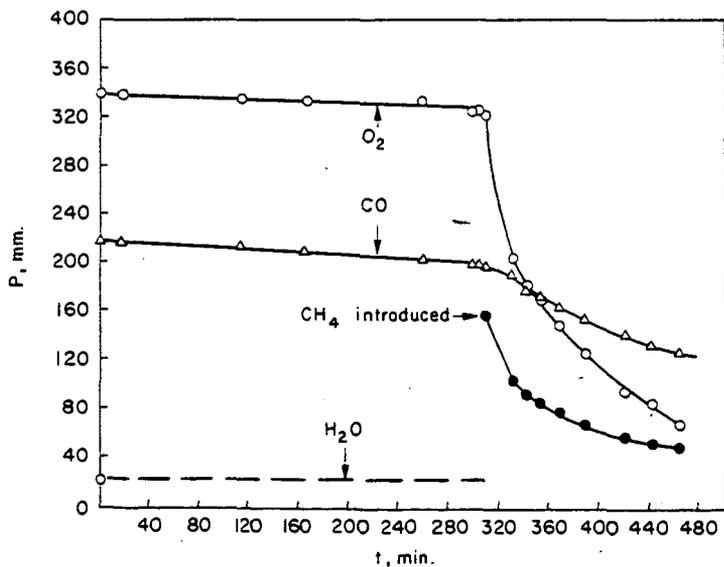


Fig. 8. - Oxidation of carbon monoxide in the presence of water (22 mm. of Hg) and methane at 427° C (E60).

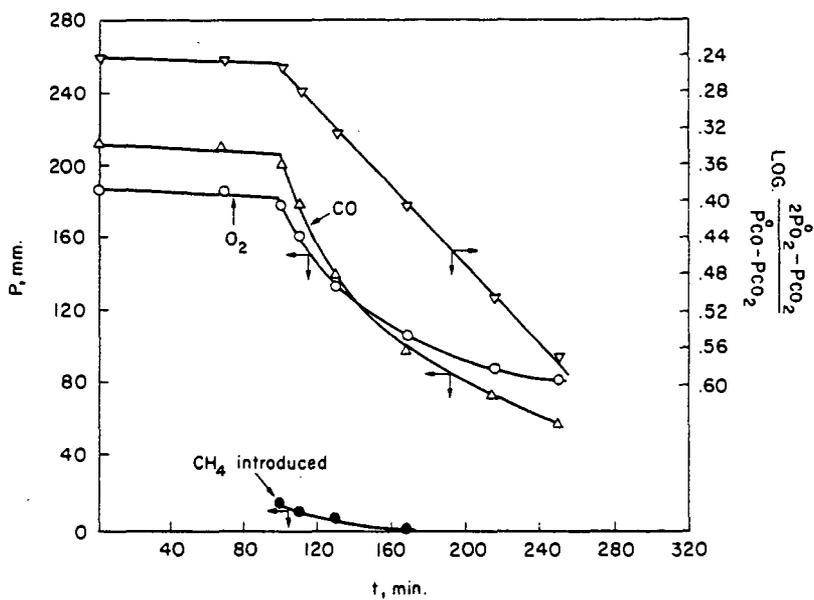


Fig. 9. - Rate curves for the methane-initiated oxidation of carbon monoxide at 504°C.

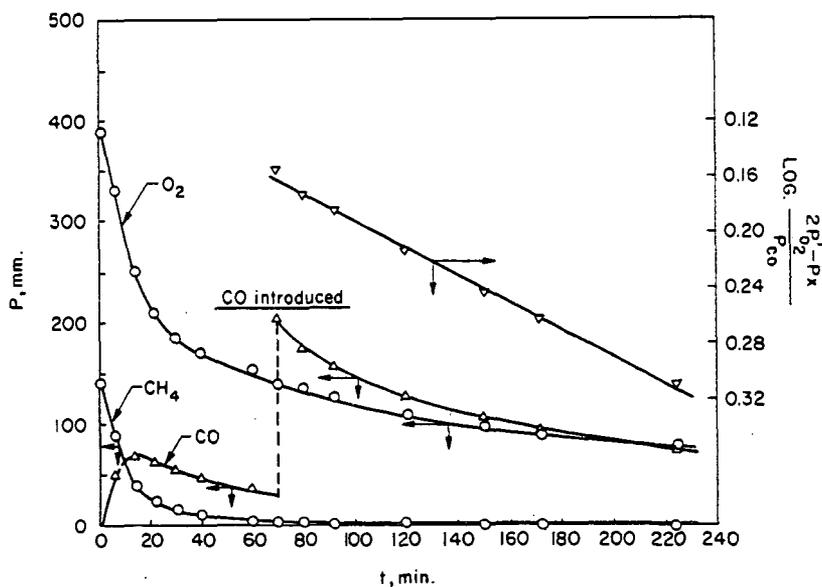


Fig. 10. - Determination of k_1 and k_2 in the oxidation of methane.