Kinetics of Methane Oxidation in Shock Waves*

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The oxidation of methane at comparatively low temperatures has been extensively studied and its mechanism has been well established by Semenov(1) and others(2). Although there have also been several papers(3-6) about the methane oxidation at higher temperatures, satisfactory results were not obtained because of experimental difficulties. However, the recent development of the shock tube technique has made possible such high temperature studies; Skinner and Ruehrwein(7) measured induction periods of visible light emission in the range of conditions, $1150 \leq T \leq 1740$°K and $0.25 \leq [O_2]/[CH_4] \leq 0.67$; he suggested that the initiating reaction is $CH_4 + O_2 \rightarrow CH_3 + HO_2$. Kistiakowsky and Richards(8) observed the emission of vacuum ultraviolet radiation from the shock-heated gas mixtures in the range of conditions, $1800 \leq T \leq 2700$°K and $0.5 \leq [O_2]/[CH_4] \leq 4.5$ and suggested that the step $H + O_2 \rightarrow OH + O$ controls the reaction rate during the induction period. On the other hand, Asaba et al.(9) measured the ignition delay by a pressure transducer over the wide range of conditions and proposed that the reaction $CH_3 + O_2 \rightarrow CH_2O + OH$ is rate-determining for methane-lean mixtures and that the reaction $CH_4 + O_2 \rightarrow CH_3 + HO_2$ is rate-determining for the methane-rich mixtures.

In the present study, in order to clarify the mechanism of methane oxidation, the induction period of the OH absorption (3067 Å) and that of the pressure increase were measured simultaneously, and also the reaction products of certain cases were analyzed by gas chromatography.

Experimental

Materials. — Takachiho methane (99.9% min.), Nippon Sanso oxygen (99.5% min.), and Nippon Sanso argon (99.999% min.) were used without further purification. The gas mixtures were prepared manometrically in a reservoir and allowed to stand for at least 24 hr. before being used. Helium was used as the driver gas in the shock tube at pressures up to 11 atm.

Shock Tube and Instrumentation.—A schematic diagram of the apparatus is shown in Fig. 1. A

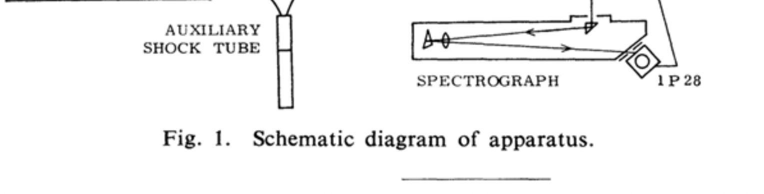

Fig. 1. Schematic diagram of apparatus.

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* A part of this paper was presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964, and at the Symposium on Chemical Reactions in Shock Tubes at Duke University, North Carolina, U. S. A., April, 1964.

1) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. II, Princeton University Press, New Jersey (1959), p. 217.

2) N. S. Enikolopyan, "7th Symposium (International) on Combustion," Butterworths, London (1959), p. 157; L. V. Karmilova, N. S. Enikolopyan and A. B. Nalbandyan, *Zhur. Fiz. Khim.*, **34**, 550 (1960).

3) B. P. Mullins, *Fuel*, 32, 343 (1953).

4) J. H. Burgoyne and H. Hirsch, *Proc. Roy. Soc.*, **A227**, 73 (1954).

5) G. I. Kozlov, "7th Symposium (International) on Combustion," Butterworths, London (1959), p. 98.

6) H. Vandenabeele, R. Corbeels and A. van Tiggelen, *Combust. Flame*, **4**, 253 (1960).

7) G. B. Skinner and R. A. Ruehrwein, *J. Phys. Chem.*, **63**, 1736 (1959).

8) G. B. Kistiakowsky and L. W. Richards, *J. Chem. Phys.*, **36**, 1707 (1962).

9) T. Asaba, K. Yoneda, N. Kakihara and T. Hikita, "9th Symposium (International) on Combustion," Pergamon, New York (1963), p. 193.

single-pulse shock tube consisted of a 2.4 m.-long driver section and a 3.5 m. experimental section which were made of 7.6 cm. inside diameter precision-bore stainless steel tubing, and a dumping tank 90 cm. inside diameter and 3.6 m. long. One of six piezo gauges (Murata $BaTiO_3$ Ceramic Vibrator) was used to trigger the oscilloscopes, while the others were used to measure the shock velocities along the tube. The gauge signals were displayed on a raster-sweep oscilloscope (Iwasaki SS-5102), which permitted the measurement of the shock velocity in each gauge interval to a 0.5% accuracy. A quartz pressure transducer (Kistler Model 603) was installed 5.5 mm. from the end of the tube in order to measure the pressure change of the reacting system. Also, at the end of the tube, 5.5 mm. from the end plate, two quartz windows, each with a slit 2 mm. wide, were inserted to provide an optical path through the tube. The light source used was an Ushio 500 W. xenon arc lamp, the power for which was supplied by batteries. The other optics consisted of a Shimadzu QL-170 spectrograph with a 0.3×8 mm. entrance slit and a 0.5×8 mm. exit slit set a 3067 Å and an RCA 1P28 photomultiplier. The outputs of the pressure transducer and the photomultiplier were fed to a dual-beam oscilloscope (Iwasaki DS-5305) and recorded with a Polaroid camera. Before each run, the experimental section was evacuated to 10^{-3} mmHg and the lamp had been lit for at least 20 min. The measured leak rate of the shock tube was 3 μHg per min.

Gas Analysis.—All the gas mixtures used and the produced gas mixtures, which were withdrawn through a valve near the end plate immediately after each run, were analyzed by gas chromatography. These analyses were performed with a Yanagimoto GCG-2 gas chromatograph at 50°C employing 1.5 m. columns of a molecular sieve 5A and silica gel, with helium as the carrier; the former column was used for the analysis of methane and carbon monoxide, and the latter, for ethane, ethylene, acetylene and carbon dioxide. The chromatograph was calibrated carefully for the peak area with pure gas specimens, using neon as an internal standard. The reproducibility of the analyses was maintained within an error of ±1%.

Calculations

The temperatures, pressures and other parameters of the gas behind the reflected shock waves were calculated by means of the one-dimensional theory, assuming rotational and vibrational relaxations but no chemical relaxation. Numerical calculations were made by a USS 90 computor using Strehlow's method.(10)

Gas chromatographic analysis was applied to the reaction products of the methane-rich mixtures. For these mixtures, the second-order reaction was assumed by other researchers.(8,9) In order to evaluate the second-order rate constant from the analytical results of the reaction products, the following procedure was adopted, extending the method of Asaba et al.(11) The rate of the consumption of methane was considered to be given by Eq. 1:

$$dx/dt = k(a-x)(b-nx) \tag{1}$$

where a and b denote the initial concentrations of methane and oxygen respectively; x and nx, the quantities of methane and oxygen respectively consumed during t, and k, the rate constant. In this equation, it is implicity assumed that, during the whole reaction time, methane reacts with n-fold oxygen; the value of n can be determined by the material balance from the results of the analysis of the products. The integration of Eq. 1 gives:

$$x = \frac{ab\{1-\exp[(na-b)kt]\}}{b-na\exp[(na-b)kt]} \tag{2}$$

As is shown in Fig. 2, the dwell time of gas molecules exposed to a high temperature varies along the distance from the end plate; accordingly, the extents of reaction are not equal along all the distance. The quantity of methane decomposed at a distance of l from the intersection of a reflected shock wave with a rarefaction wave may be expressed as follows by using Eq. 2:

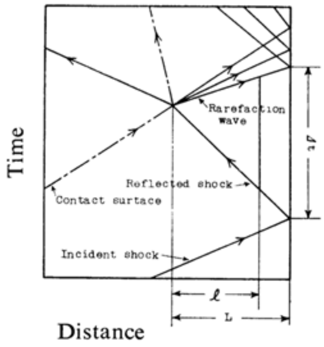

Fig. 2. Distance-time diagram.

$$x(l) = \frac{ab\left\{1-\exp\left[(na-b)k\frac{l\Delta t}{L}\right]\right\}}{b-na\exp\left[(na-b)k\frac{l\Delta t}{L}\right]} \tag{3}$$

Here, Δt is the dwell time at the end plate and L, the distance from the intersection to the end of the tube. Thus, the average of $x(l)$ over the range $l=0$—L is given by the equation:

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10) R. A. Strehlow, Ballistic Research Laboratories Report No. 978, April, 1956, Aberdeen Proving Ground, Maryland, U. S. A.

11) T. Asaba, K. Yoneda and T. Hikita, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 1925 (1961).

$$\bar{x}=\frac{1}{L}\int_0^L x(l)\mathrm{d}l=a-\frac{1}{kn\Delta t}$$
$$\times\ln\frac{b-na\exp[(na-b)k\Delta t]}{b-na} \tag{4}$$

Since a, b and Δt can be obtained from the experimental conditions combined with calculated shock parameters and $\bar{x}$ and n, from the analytical data of the reaction products, the rate constant, k, can be calculated from Eq. 4.

Results

The Methane-Lean Mixtures.—A typical oscillogram, obtained for the mixture consisting of 70% argon, 9% methane and 21% oxygen, is shown in Fig. 3. The OH absorption appears after the induction time τ_1. Its intensity increases exponentially to a limiting value, again increases as an explosive reaction starts, and decreases when the mixture is cooled by a rarefaction wave. On the other hand, the pressure increases suddenly after the induction time τ_2 which is longer than τ_1. The time of this pressure increase agrees with that of the second increase in OH absorption. From the data obtained in the range of conditions, $1050 \leq T \leq 2100$°K, $3 \leq p \leq 9$ atm. and $4.1\times10^{-3} \leq [O_2] \leq 1.5\times10^{-2}$ mol./l., it was found[12] that the logarithmic values of $\tau_1[O_2]$ and $\tau_2[O_2]$ are linearly proportional to $1/T$, but that other plots, such as $\log\tau_1[CH_4]$ or $\log\tau_1[CH_4][O_2]$, are not linearly proportional to $1/T$. Also, the apparent activation energies obtained from the slope of these straight lines are 21.5 and 33.8 kcal./mol. respectively.

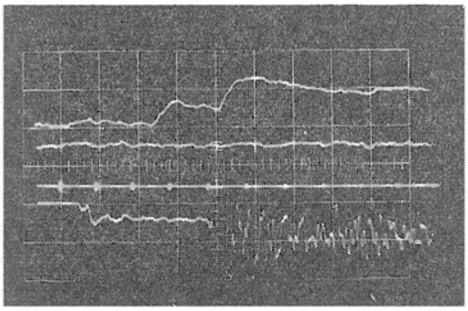

Fig. 3. Typical oscillogram obtained from the mixture of 70% Ar, 9% CH_4 and 21% O_2. The uppermost beam shows the change in the OH absorption, the second the noise level of Xe-lamp, the third timing markers and the lowest the pressure change. Sweep velocity is 100 μ sec./division.

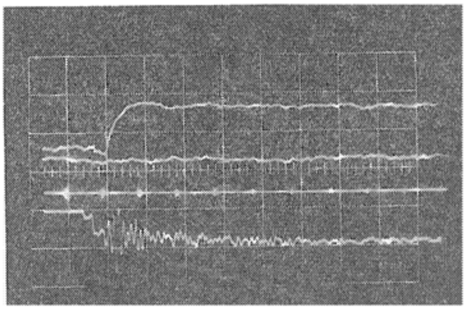

Fig. 4. Typical oscillogram obtained from the mixture of 30% CH_4 and 70% O_2. The four traces are the same as in Fig. 3.

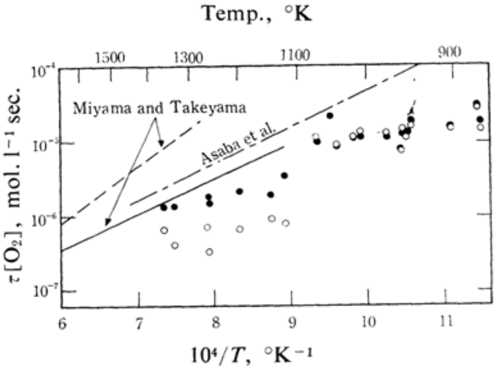

Fig. 5. Induction period vs. reciprocal temperature. Solid and open circles are from the pressure and OH-absorption measurements, respectively. Solid and dashed lines are obtained from the mixture with 70% Ar, measuring the OH-absorption and the pressure change, respectively.

A typical oscillogram obtained for the mixture of 30% methane and 70% oxygen without argon is shown in Fig. 4. The OH absorption appears almost simultaneously with the pressure increase. Data obtained over the range of conditions, $870 \leq T \leq 1360$°K, $3.7 \leq p \leq 6.6$ atm. and $2.4\times10^{-2} \leq [O_2] \leq 6.0\times10^{-2}$ mol./l. are plotted in Fig. 5. Obviously, the data obtained for the mixtures without argon deviate markedly from those for the mixtures with a large amount of argon. Also, the data of Asaba et al.[9] obtained for the mixtures without argon are shown for purposes of comparison.

The Intermediate Mixtures.—The same measurements as have been described above were conducted for mixtures of 70% argon, 18% methane and 12% oxygen and those of 60% methane and 40% oxygen over the range of conditions $1420 \leq T \leq 2010$°K, $4.2 \leq p \leq 7.1$ atm. and $2.9\times10^{-3} \leq [O_2] \leq 2.2\times10^{-2}$ mol./l. The OH absorption and pressure change appeared at the same time in both mixtures. The induction periods measured are shown in Fig. 6 as a plot of $\log(\tau[CH_4][O_2])$ vs. $1/T$, which presents a fairly straight line in spite of the rather wide range of oxygen and methane concentrations, although the other

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[12] H. Miyama and T. Takeyama, *J. Chem. Phys.*, **40**, 2049 (1964).

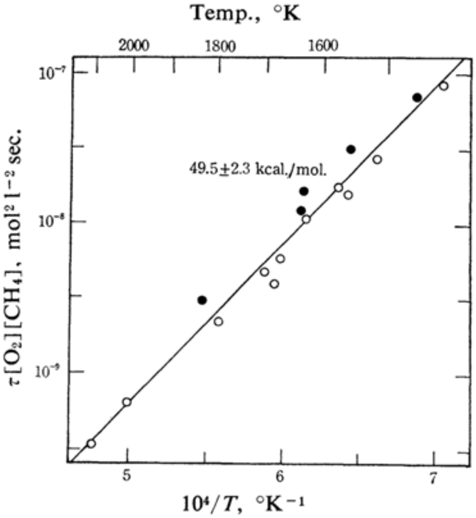

Fig. 6. Induction period vs. reciprocal temperature. Open and solid circles are obtained from mixture with and without argon, respectively. Solid line is a least-squares fit to these points.

plots, such as $\log(\tau[O_2])$ vs. $1/T$ and $\log(\tau[CH_4])$ vs. $1/T$, showed marked deviations of the measured points. The least-squares equation obtained for this line is:

$$\log\tau[CH_4][O_2] = -14.62\pm0.12+(10810\pm500)/T \qquad (5)$$

From the slope of this line, the apparent activation energy is found to be 49.5±2.3 kcal./mol.

The Methane-Rich Mixtures. — Experiments were performed for mixtures of 86% argon, 12% methane and 2% oxygen and those of 86% methane and 14% oxygen. However, for the latter mixtures, it was very difficult to define the reaction temperature because the reflected shock wave interacted with the contact surface to produce a new shock wave and reheat the gas. Therefore, only the results obtained for the former mixtures will be reported. For the methane-rich mixtures, it was impossible to apply the above technique because the carbon precipitation obscured the OH absorption and the pressure increase was not appreciable. Therefore, the reaction products obtained by using a single pulse shock wave[13] were analyzed by gas chromatography.

The dwell time during which the reaction mixture was exposed to a high temperature was measured by a pressure transducer at the endplate and was adjusted to be about 1 msec. In Fig. 7, percentages of the products, based on the initial methane concentration, are plotted against the reaction temperatures. Using the analytical data shown in Fig. 7, the rate constants of methane oxidation were calculated on the assumptions[7,9] that the rate of consumption of methane is proportional to the product of methane and oxygen concentrations, and that the change in the concentration of various species during the cooling process in the rarefaction waves can be neglected.*

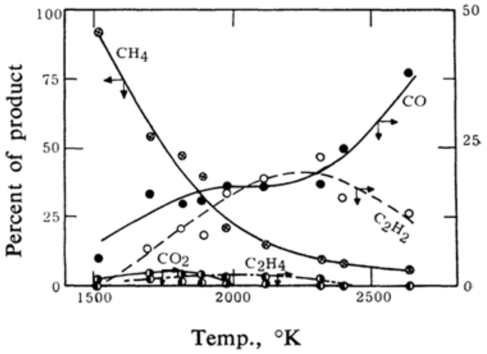

Fig. 7. Percentage composition of CH_4 and its products for various reaction temperatures.

⊗ CH_4, ○ C_2H_2, ● CO, ◐ CO_2, ◑ C_2H_4

TABLE I. DETAILS OF EXPERIMENTS AND CALCULATED SECOND-ORDER RATE CONSTANTS

Run No.	T °K	P atm.	$a\times10^3$ mol./l.	$b\times10^3$ mol./l.	$\Delta t\times10^3$ sec.	n	$\bar{x}\times10^3$ mol./l.	k l./mol. sec.
1	1617	6.250	5.652	0.9420	0.9	0.3474	0.4262	2.101×10^5
8	1703	5.318	4.568	0.7614	1.3	0.2075	2.062	2.355×10^6
9	1822	5.122	4.111	0.6852	1.3	0.1449	2.166	2.924×10^6
37	1975	4.866	3.605	0.6008	1.1	0.1222	2.858	1.229×10^7
38	2121	4.593	3.168	0.5280	1.1	0.1143	2.709	1.973×10^7
39	2320	3.728	2.350	0.3916	1.0	0.1071	2.141	4.593×10^7
43	1886	5.438	4.218	0.7030	0.8	0.1375	2.554	6.331×10^6
44	2400	3.287	2.003	0.3338	0.9	0.1348	1.838	8.231×10^7

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[13] H. S. Glick, W. Squire and A. Herzberg, "5th Symposium (International) on Combustion," Reinhold, Pittsburgh (1955), p. 393.

* The latter assumption is not justified for the reaction of a small activation energy. In the case of hydrazine decomposition,[14] the activation energy is 35 kcal./mol. and about 25% of the total reaction occurs in the cooling process. However, this assumption may be approximately applicable in the present case since the activation energy is 51 kcal./mol.

[14] H. B. Palmer and B. E. Knox, *AIAA*. 1, 1195 (1963).

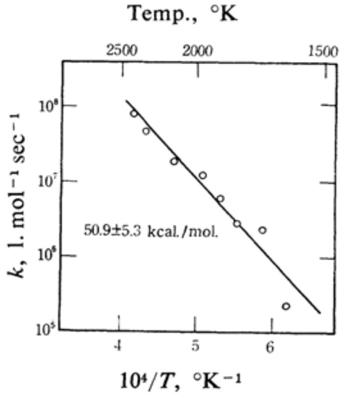

Fig. 8. Arrhenius plot of second-order rate constants. Solid line is a least-squares fit.

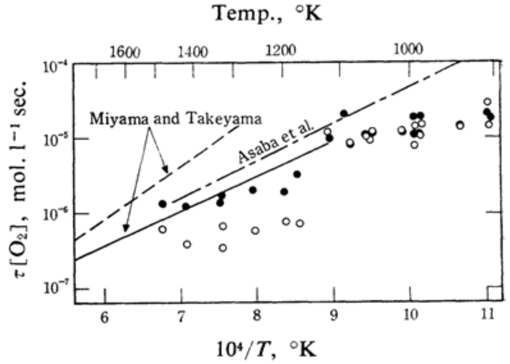

Fig. 9. Induction period vs. reciprocal temperature. The lines and symbols have the same significance as in Fig. 5. Temperatures were recalculated as described in the text.

Numerical calculations were conducted by using Eq. 4 combined with the values shown in Table I, where the calculated values of k are also tabulated in the last column. Figure 8 shows an Arrhenius plot of these rate constants. The equation of the least-squares line is:

$$\log k = 12.56 \pm 0.21 + (-11070 \pm 1150)/T \qquad (6)$$

The apparent activation energy obtained from the slope of this line is 50.9±5.3 kcal./mol. Further, the first-order rate constants were calculated in an analogous method, assuming that the rate of consumption of methane is proportional to the concentration of methane or oxygen. However, the Arrhenius plot did not show a straight line.

Discussion

As is shown in Fig. 5, the data obtained for the methane-lean mixtures without argon deviate markedly from those for the mixtures with argon. At about 800°K, the vibrational relaxation time of oxygen molecule[15] is of almost the same order of magnitude as the induction periods described above, although that of methane is negligibly small.[16] Therefore, the temperatures and pressures of reflected shock waves were recalculated by assuming that the vibrational energy of the oxygen molecule is *frozen* but that the other relaxation conditions are the same as have been described above. The corrected data are plotted in Fig. 9. The agreement between the data for the mixtures with and without argon is thereby improved a little. However, there is still a large discrepancy. Other factors which possibly cause this discrepancy are considered to be as follows: when the mixture is not diluted with argon, the large concentrations of reactants release an appreciable amount of heat of reaction, even during the induction period; when the shock wave passes through the large concentration of polyatomic gases, bifurcation occurs as a result of the interaction between the reflected shock wave and the boundary layer;[17] and because of the high concentration of reactants, the abundance of reactive species such as radicals changes the reaction mechanism.

Since not enough data are available to explain the above-described discrepancies, however, the results obtained for the methane-lean mixtures without argon will not be discussed further.

According to Semenov,[1] the mechanism of methane oxidation at relatively lower temperatures may be considered to be as follows:

$$CH_4 + O_2 \rightarrow CH_3 + HO_2 \qquad \text{(I)} \quad E = 55 \text{ kcal./mol.}$$

$$CH_3 + O_2 \rightarrow CH_2O + OH \qquad \text{(II)} \quad E = 20 \text{ kcal./mol.}$$

$$OH + CH_4 \rightarrow H_2O + CH_3 \qquad \text{(III)} \quad E = 8 \text{ kcal./mol.}$$

$$OH + CH_2O \rightarrow H_2O + HCO \qquad \text{(IV)} \quad \Delta H = -38 \text{ kcal./mol.}$$

$$CH_2O + O_2 \rightarrow HCO + HO_2 \qquad \text{(V)} \quad E = 32 \text{ kcal./mol.}$$

$$HCO + O_2 \rightarrow CO + HO_2 \qquad \text{(VI)} \quad \Delta H = -20 \text{ kcal./mol.}$$

$$HO_2 + CH_4 \rightarrow H_2O_2 + CH_3 \qquad \text{(VII)} \quad E = 11 \text{ kcal./mol.}$$

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[15] D. R. White and R. C. Millikan, *J. Chem. Phys.*, **39**, 1803 (1963).

[16] F. D. Rossini, "High Speed Aerodynamics and Jet Propulsion," Vol. I, "Thermodynamics and Physics of Matter," Princeton University Press (1955), p. 701.

[17] R. A. Strehlow and A. Cohen, *J. Chem. Phys.*, **30**, 257 (1959).

$$HO_2 + CH_2O \rightarrow H_2O_2 + HCO$$
$$\text{(VIII)} \quad \Delta H = -12 \text{ kcal./mol.}$$

$$OH \xrightarrow{\text{wall}} \text{destruction}$$
$$\text{(IX)}$$

$$CH_2O \xrightarrow{\text{wall}} \text{destruction}$$
$$\text{(X)}$$

At higher temperatures in shock waves, Asaba et al.[9] proposed to adopt reactions I, II, III, V, VI and VII, and they concluded from the measurements of the ignition delay that the rate-determining step for a methane-rich mixture with a methane-oxygen ratio above unity is reaction I, while the rate-determining step for a methane-lean mixture with a methane-oxygen ratio below unity is reaction II.

The results described in the preceding section for the methane-rich mixtures and for the intermediate mixtures support their conclusion regarding rich mixtures; the consumption of methane is a second-order reaction with an activation energy of 50.9±5.3 kcal./mol., which is first order with regard to both methane and oxygen. However, in the case of methane-lean mixtures, it was found that the induction periods, τ_1s and τ_2s, were inversely proportional to the concentration of oxygen. In addition, apparent activation energies of 21.5±1.2 and 33.8±1.0 kcal./mol. were obtained from the plots of $\log(\tau_1[O_2])$ vs. $1/T$ and $\log(\tau_2[O_2])$ vs. $1/T$ respectively. In order to establish the actual meaning of these findings, it is assumed that, during the induction period τ_1, OH, HO_2, HCO and CH_2O are steady-state intermediates and that the principal chain carrier is the CH_3 radical. Therefore, the rate of increase of the CH_3 radical is expressed in Eq. 7:

$$\begin{aligned} d[CH_3]/dt &= k_1[CH_4][O_2] - k_2[CH_3][O_2] \\ &\quad + k_3[OH][CH_4] + k_7[HO_2][CH_4] \\ &= 2k_1[CH_4][O_2] + k_2[CH_3][O_2] \end{aligned} \tag{7}$$

The integration of Eq. 7 gives Eq. 8, assuming $[CH_4] = [CH_4]_0$ and $[O_2] = [O_2]_0$:

$$\begin{aligned} &\frac{2k_1[CH_4][O_2] + k_2[CH_3][O_2]}{2k_1[CH_4][O_2] + k_2[CH_3]_0[O_2]} \\ &\quad = \exp\{k_2[O_2](t-t_0)\} \end{aligned} \tag{8}$$

Here, t_0 is any reference time following which Eqs. 7 and 8 are valid, and the subscript zero on a concentration denotes the value of that concentration at time t_0. Defining the origin of time as the time when the rate of reaction II becomes equal to that of initiation I, i. e., at $t=0$:

$$k_1[CH_4][O_2] = k_2[O_2][CH_3]_0 \tag{9}$$

Eq. 10 is obtained from Eq. 8.

$$[CH_3] = 3[CH_3]_0\{\exp(2k_2[O_2]t) - 2/3\} \tag{10}$$

The steady-state expression for [OH] in terms of $[CH_3]$ is:

$$[OH] = [CH_3](k_2[O_2]/k_3[CH_4]) \tag{11}$$

so [OH] also increases exponentially according to:

$$[OH] = 3[OH]_0\{\exp(2k_2[O_2]t) - 2/3\} \tag{12}$$

$[OH]_0$ is given by Eqs. 9 and 11.

Defining $[OH]_{\tau_1}$ and $[CH_3]_{\tau_1}$ as the concentrations of [OH] and $[CH_3]$ respectively at $t=\tau_1$, the following relations are obtained:

$$\begin{aligned} &[CH_3]_{\tau_1}/[CH_3]_0 = [OH]_{\tau_1}/[OH]_0 \\ &\quad = 3\{\exp(2k_2[O_2]\tau_1 - 2/3\} \end{aligned} \tag{13}$$

It can be assumed, in analogy with the hydrogen-oxygen reaction,[18] that the ratio $[OH]_{\tau_1}/[OH]_0$ remains approximately constant over the temperature range studied. Therefore;

$$k_2[O_2]\tau_1 = \text{const.}$$

Thus, a plot of $\log(\tau_1[O_2])$ vs. $1/T$ should give a straight line, the slope of which gives the activation energy of reaction II.

On the other hand, after the induction period τ_1 formaldehyde can no longer be assumed to be a steady-state intermediate and its concentration accumulates, since reaction II is faster than reaction V. Hence, the rate of increase of $[CH_3]$ is:

$$d[CH_3]/dt = 2k_1[CH_4][O_2] + k_5[CH_2O][O_2] \tag{15}$$

Since the first term may be disregarded for the methane-lean mixtures,[9] Eq. 16 should approximately hold when Eq. 15 is integrated:

$$[CH_3]_{\tau_2} = k_5[O_2]\int_0^{\tau_2}[CH_2O]dt \tag{16}$$

Here, $[CH_3]_{\tau_2}$ is the concentration at the end of the induction periods τ_2, and its value is considered to be approximately a constant which depends upon the detectability of the pressure transducer. Therefore, Eq. 17 may be obtained from Eq. 16:

$$[CH_3]_{\tau_2} = k_5[O_2]\tau_2[CH_2O]_{av} \tag{17}$$

where:

$$[CH_2O]_{av} = \frac{1}{\tau_2}\int_0^{\tau_2}[CH_2O]dt$$

If it is assumed that $[CH_2O]_{av}$ reaches a certain limiting value at the start of the explosive reaction, $\tau_2[O_2]$ is inversely proportional to k_5:

$$\tau_2[O_2] \propto 1/k_5 \tag{18}$$

Thus, a plot of $\log(\tau_2[O_2])$ vs. $1/T$ should also give a straight line, the slope of which gives the activation energy of reaction V.

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[18] G. L. Schott and J. L. Kinsey, *J. Chem. Phys.*, **29**, 1177 (1958).

Therefore, the results presented in the previous paper[12] suggest that the rate-determining step for OH formation is reaction (II) and that that for the over-all reaction is reaction V. The discrepancy about the rate-determining step of the over-all reaction for the methane-lean mixtures between the present study and that of Asaba et al. might be explained by the difference in experimental conditions which was discussed at the beginning of this section. For the intermediate mixtures under the present experimental conditions, it may be considered from the value of the apparent activation energy and the distinct dependence of τs on the product of methane and oxygen concentrations that the over-all reaction is controlled also by the reaction $CH_4 + O_2 \rightarrow CH_3 + HO_2$.

According to the recent papers of Kistiakowsky and his coworkers,[19,20] the kinetics at lower partial pressures of reactants differ from those observed or proposed for reactions taking place at much higher partial pressures or at much lower temperatures; that is, ion molecules must be taken into account under the former conditions. In the present studies, the partial pressures of reactants ranged from 250 to 5000 mmHg and so are much higher than those chosen by them (a few mmHg). Thus, it may be reasonable to suppose that reactions I, II, III, V, VI and VII occur during the induction periods under the present experimental conditions, as has been proposed by Semenov as occurring at lower temperatures.

Summary

The mechanism of methane oxidation in reflected shock waves has been studied by measuring the induction period of the OH absorption and that of the pressure increase simultaneously, and also by using the single-pulse technique combined with gas chromatography.

As a result, it has been found under the present experimental conditions that the rate-determining step for the over-all reaction of the methane-rich mixtures with the ratio $[CH_4]/[O_2]=6$ is $CH_4 + O_2 \rightarrow CH_3 + HO_2$, and that the rate-determining step for the over-all reaction of the methane-lean mixtures with the ratio $[CH_4]/[O_2]=3/7$ is $CH_2O + O_2 \rightarrow HCO + HO_2$. Also, the rate-determining step for the OH formation of the lean mixtures has been found to be $CH_3 + O_2 \rightarrow CH_2O + OH$ under the present conditions. In the case of the intermediate mixtures with the ratio $[CH_4]/[O_2]=1.5$, the over-all reaction is considered to be controlled mainly by the reaction $CH_4 + O_2 \rightarrow CH_3 + HO_2$.

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