REACTION MECHANISMS AND RATE CONSTANTS OF ELEMENTARY STEPS IN METHANE–OXYGEN FLAMES

JOZEF PEETERS

Departement Scheikunde, Katholieke Universiteit, Leuven, Belgium

AND

GILBERT MAHNEN

Laboratoire de Physico-chimie de la Combustion, Université Catholique de Louvain, Belgium

The concentrations of all stable and unstable species have been measured in the reaction zone of lean and stoichiometric methane–oxygen flames burning at 40 torr.

The rate constant of Reaction [1], $CH_4 + OH \rightarrow CH_3 + H_2O$, was found to be $k_1 = 3 \times 10^{13} \times \exp(-6000/RT)$ mole^{-1} cm^3 sec^{-1}. In stoichiometric flames, half of the fuel is consumed via Reaction [1'], $CH_4 + H \rightarrow CH_3 + H_2$, and at $T = 1600°K$, k_1' is reported to be 3.2×10^{12}. It is shown conclusively that the great majority of the methyl radicals is removed by Reaction [2], $CH_3 + O \rightarrow CH_2O + H$, with $k_2 = 1.3 \times 10^{14} \exp(-2000/RT)$. The rate-determining step is a reaction resulting in an increase of the number of particles, Reaction [13]: $CH_2O + M \rightarrow CO + H_2 + M$; the value $k_{13} = 2.1 \times 10^{16} \exp(-35,000/RT)$ was derived. Another part of the formaldehyde disappears via Reaction [3]: $CH_2O + OH \rightarrow CHO + H_2O$; the rate constant is $k_3 \simeq 2.3 \times 10^{13}$ in the range $T = 1400°-1800°K$. Most of the CHO radicals react with O_2: $CHO + O_2 \rightarrow HO_2 + CO$; $k_4 \simeq 3 \times 10^{13}$ at $T = 1600°K$. In lean flames, HO_2 is removed mainly by reactions involving OH and O: $HO_2 + OH(O) \rightarrow O_2 + H_2O(OH)$; and $k_5 \simeq 5 \times 10^{13}$ at $T = 1600°K$. Carbon dioxide is formed by Reaction [6]: $CO + OH \rightarrow CO_2 + H$; the rate constant was found to be $k_6 = 2.8 \times 10^{11}$ at $T = 1750°K$, and the activation energy $E_6 = 5.5 \pm 2$ kcal/mole in the range $T = 1500°-1900°K$.

In the burned gas of lean flames, the radical "pool" decays by Reaction [11]: $H + O_2 + M \rightarrow HO_2 + M$, the rate constant (for $M = O_2$) being $k_{11} = 2.5 \times 10^{15}$ at $T = 1900°K$.

Introduction

The reaction mechanism of methane–oxygen flames is not yet fully understood.

Most important of all, no satisfactory rate-determining step has been proposed as yet, as is evident from the work of Bradley et al.,[1] who found none of the accepted reaction mechanisms in agreement with the experimental values and the pressure dependence of the burning velocity.
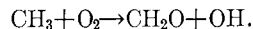
Another unresolved problem is the fate of the methyl radical. According to Fenimore,[2] CH_3 is destroyed by an O atom:

$$CH_3 + O \rightarrow \cdots \rightarrow CO.$$
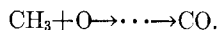
Fristrom,[3] as well as other authors, favors a

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* Experimental investigation carried out at the Laboratoire de Physico-chimie de la Combustion, Université Catholique de Louvain, Belgium.

reaction with O_2:

$$CH_3 + O_2 \rightarrow CH_2O + OH.$$

Other obscure points are: (i) the source of H_2, the production of which cannot be explained solely by removal of H by H atoms; (ii) the fate of the CHO radical; (iii) the role of HO_2 in the reaction mechanism; and (iv) the growth and decay of the concentrations of the main reactive species, OH, O, and H.

Finally, no sufficiently precise data are available for the rate constants of many of the elementary reactions.

In order to settle these questions unambiguously, we measured the concentrations of all species, unstable as well as stable, throughout the reaction zone of a few low-pressure methane–oxygen flames.

Experimental

The need for supersonic molecular-beam sampling, and subsequent mass-spectrometric analysis, is evident if a single technique is to be used for measuring all species. A few groups of workers have applied this technique in the past.[4–6]

The apparatus consists of three differentially pumped stages, the first one being equipped with a conical, thin-walled, deactivated quartz sampling probe, 25 mm high, with an apex angle of 40° and a 0.1-mm-diam orifice. The core of the supersonic gas jet emerging from this sampling orifice is allowed to enter the second stage through a 1.5×3 mm skimmer orifice in the tip of a brass cone, located 20 mm downstream of the sampling orifice. The molecular beam is modulated mechanically at 32 Hz, and passes through a 0.8×8-mm collimating slit into the third stage, where it traverses the modified ion source of an Edwards E 60 mass spectrometer. The output of the ion multiplier is fed to a PAR 121 lock-in amplifier.

The dimensions of the beam-forming elements (sampling probe and skimmer) were chosen as stated above, after a detailed study of their influence on the intensity and quality of the molecular beam. The following brief outline of the problem clearly shows the necessity for a compromise solution.

The angle of the sampling cone should be small to minimize the disturbance of the flame. However, this leads to appreciable reflection of jet molecules from the inner probe walls, and to a low conductance in the probe-skimmer region, both detrimental to the beam intensity. Moreover, a "secondary" beam might be formed, due to effusion of background gas or randomized jet molecules through the skimmer orifice. To minimize these effects, the sampling orifice should be made small—even though the ratio of wall collisions to gas-phase collisions is adversely affected and the theoretical final Mach Number is lowered[7]—and the "nozzle"-to-skimmer distance should be made much larger than usual to ensure a sufficiently high conductance.

The final beam intensity obtained with the stated beam-formation-element geometry is rather low, but the beam composition is really representative of the sample composition, except for a well-known mass discrimination effect,[8] and the flame disturbance is minimal, as was confirmed by several tests.

The over-all sensitivity of the apparatus depends, for all species in a nearly identical way, on the pressure, the temperature, and the mean molecular weight of the sampled gas. Therefore, relative values of the mole fractions of stable

species could be determined accurately by direct calibration.

The flame radicals and atoms were, for obvious reasons, measured at ionizing-electron energies a few electron volts above the respective ionization potentials. The accurate calibration of O, H, and OH was made possible by the fact that the four H_2/O_2-system reactions were found to be equilibrated to within a few percent in the burned gas of a lean-CH_4/O_2 flame.

A calibration factor for CH_3 could be determined in a fuel-rich $C_2H_6/H_2/O_2$ flame at the point where the rate of formation of CH_4, mainly via $CH_3+H_2\rightarrow CH_4+H$, is equal to its rate of destruction, mainly by the reverse reaction.

For the other unstable species, use was made of reasonable estimates of ionization cross sections (error less than a factor of 2).

The temperature profile was determined, using a 0.1-mm-thick $BeO-Y_2O_3$ coated[9] $Pt-Pt/$ 10% Rh thermocouple. Radiation losses were compensated for by heating the thermocouple with an AC supply; exact compensation is attained when both the electrical-power input and the junction temperature are the same as in a vacuum.
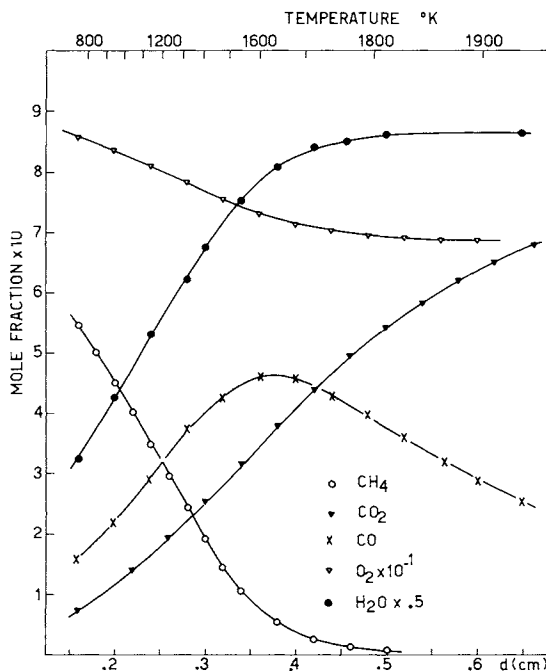
The area expansion ratios were measured only

FIG. 1. Temperature and mole fractions of CH_4, O_2, CO, CO_2, and H_2O versus distance from burner in lean methane-oxygen flame (9.5% CH_4–90.5% O_2); $v_0=67$ cm/sec; $p=40$ torr.

in the nonignited mixtures. The novel technique used here is based on the measurement of the heat transfer between the flowing gas and a wire normal to the flow direction. The heat exchange is proportional to the Nusselt Number,[10] which was experimentally found to be proportional to $Re^{0.25}$, whereas the Reynolds Number Re, itself, is inversely proportional to the area expansion ratio A.

The water-cooled flat-flame burner, with a diameter of 5 cm, was of the perforated disk type (2500 holes of 0.7 mm diam). All flames investigated burned at 40 torr.

Results

Detailed composition traverses were obtained for a lean-CH_4/O_2 flame (9.5% CH_4, 90.5% O_2), burning at 40 torr. The fresh-gas-stream velocity was 67 cm/sec. The distance scale was corrected each time for the slight shift of the flame away from the burner when the probe penetrates into the flame. The results are partially shown in Figs. 1, 2, and 3. For the sake of clarity, only every second or third experimental point is given. The mole fractions of OH, H, O, CO, H_2, and CO_2, from $z = 1.0$–4.5 cm, were also deter-
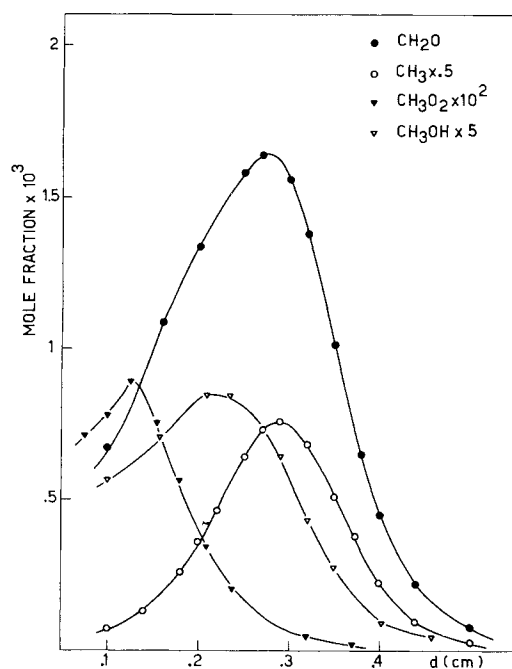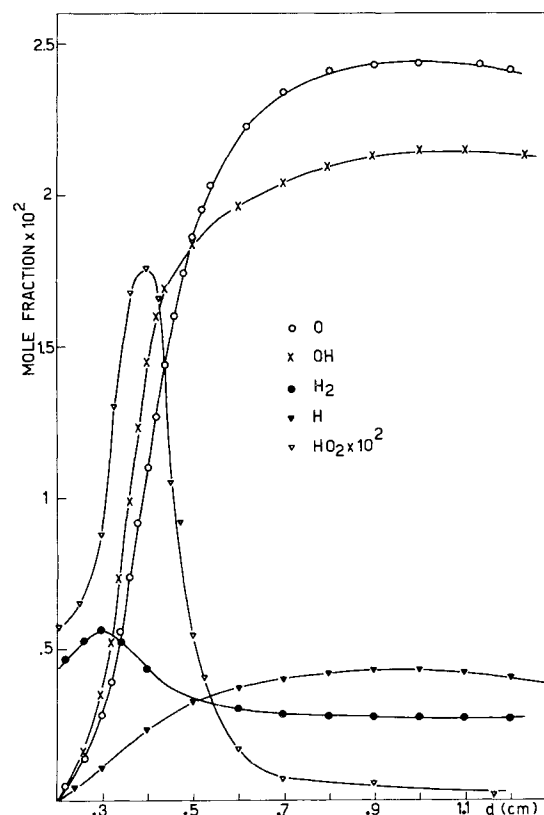
Fig. 3. Mole fractions of O, OH, H_2, H, and HO_2 versus distance from burner. Same flame as in Fig. 1. The HO_2 profile should be shifted 0.05 cm to the left.

Fig. 2. Mole fractions of CH_2O, CH_3, CH_3O_2, and CH_3OH versus distance from burner. Same flame as in Fig. 1.

mined. Small amounts of C_2H_6, C_2H_4, CHO ($X_{max} \simeq 10^{-5}$), and CH_2 ($X_{max} \simeq 5 \times 10^{-6}$) were also detected. The temperature is indicated in Fig. 1. The area expansion ratio is $A = 1 + 0.19z$, with z being the distance from the burner.

The mole fluxes per unit inlet area, F_i, were computed using

$$F_i = AN_i(v + V_i), \qquad (1)$$

where N_i is the concentration (mole cm^{-3}) of species i, V_i its local diffusion velocity[11] (taking thermal diffusion into account), and v the local mass-average velocity. The mole fluxes per unit inlet area of CH_4, OH, O, and H are shown in Fig. 4. The maximum deviation of the derived total carbon-atom flux from the initial value is 8%. For the other elements, the maximum deviation is only a few percent.

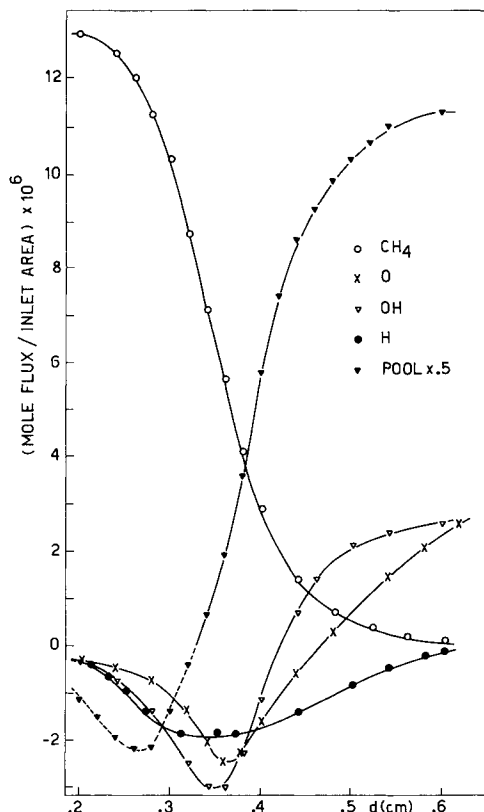The net chemical reaction rate K_i of all

Fig. 4. Mole fluxes per unit inlet area (mole cm^{-2} sec^{-1}) of CH_4, O, OH, and H versus distance from burner. The "pool-flux" profile, $F_p = 3F_H + 2F_{CO} + 2F_{H_2} + 2F_O + F_{OH} + F_{CH_3}$, is also shown. Same flame as in Fig. 1.

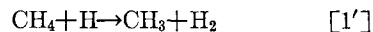species was calculated, using

$$K_i = (1/A)(dF_i/dz).$$ (2)

In the lean flame, the CH_4-disappearance rate peaks at $z = 0.34$ cm: $(-K_{CH_4})_{max} = 8.4 \times 10^{-5}$ mole cm^{-3} sec^{-1}.

Some measurements were also made on a stoichiometric $CH_4/O_2/Ar$ flame (9.5% CH_4) burning at 42 torr, with an initial stream velocity $v_0 = 67$ cm/sec. In this flame, the ratio K_{CH_4}/X_{CH_4} in the exponential decay zone is identical to that same ratio in the lean flame. The final temperature is about 2000°K. At the point where $-K_{CH_4}$ peaks, the ratios of the mole fractions in the stoichiometric flame to those in the lean flame are 2.3 for CH_3, 0.13 for O_2, 0.36 for O, 0.58 for OH, 3.9 for H, 6.3 for H_2, 0.7 for CH_2O, and about 4 for CHO.

Discussion and Conclusions

CH_4
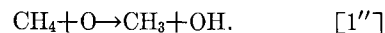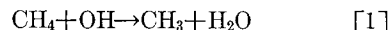
In the lean flame, H removal from CH_4 by H:

$$CH_4 + H \rightarrow CH_3 + H_2 \qquad [1']$$

can be neglected. Allowance was made, however, for

$$CH_4 + O \rightarrow CH_3 + OH. \qquad [1'']$$

Its rate was calculated using the known rate constant[12] and substracted from the observed $(-K_{CH_4})$ value, whence the rate constant of the most important process

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad [1]$$

could be derived at each point. The resulting plot of $\log k_1$ versus $1/T$ is shown in Fig. 5: $k_1 = 3 \times 10^{13} \exp(-6000/RT)$ mole^{-1} cm^3 sec^{-1}, in the range 1100°K < T < 1900°K. Combination
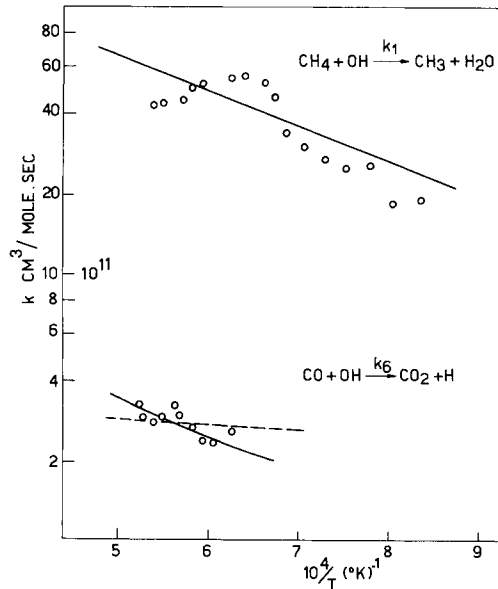

Fig. 5. Experimental values of the rate constants of Reactions [1] and [6] (lean-flame data).
(a) $CH_4 + OH \rightarrow CH_3 + H_2O$:
    $k_1 = 3 \times 10^{13} \exp(-6000/RT)$ mole^{-1} cm^3 sec^{-1}.
(b) $CO + OH \rightarrow CO_2 + H$:
    $- - - k_6 = 3.5 \times 10^{11} \exp(-800/RT)$
(in combination with result at 300°K of Ref. 19);
—— Dryer's analytical expression (Ref. 20).

of our data with Westenberg's result[13] at 300°K yields: $k_1 = 2.2 \times 10^{13} \exp(-5000/RT)$.

In the stoichiometric flame, the rate of destruction of CH_4 by H is about equal to that by OH. At $T = 1600°K$, the rate constant of Reaction [1'] was found to be $k_1' = 3.2(\pm 0.6) \times 10^{12}$, in excellent agreement with Walker's expression[14]: $k_1' = 1.26 \times 10^{14} \exp(-11,900/RT)$.

CH_3

Our results allow us to conclude definitively that CH_3 is mainly removed by O atoms, in lean flames as well as in stoichiometric flames

$$CH_3 + O \rightarrow CH_2O + H. \qquad [2]$$
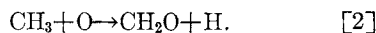
The conclusive proof follows from the X_{CH_3}, X_O and X_{O_2} values in the lean and stoichiometric flames. At the point where K_{CH_3} vanishes, $-K_{CH_4} = k_2[CH_3][Z]$, with Z being either O or O_2; X_{CH_3} is 2.3 times larger in the stoichiometric flame than in the lean one, X_O is 2.8 times smaller, and X_{O_2} is 7.8 times smaller, whereas the K_{CH_4} values and the temperatures are about equal. Clearly, only the product $[CH_3][O]$ correlates with $-K_{CH_4}$ and, hence, with the CH_3-removal rate.

Furthermore, one has in lean flames, at each point:

$$k_2/k_1 = \frac{\{[OH] + (k_1''/k_1)[O]\}[CH_4]}{[CH_3][Z]}$$

$$- \frac{K_{CH_3}}{k_1[CH_3][Z]}. \qquad (3)$$

Supposing $Z = O_2$,

$$CH_3 + O_2 \rightarrow (CH_3O_2) \rightarrow CH_2O + OH, \qquad [2']$$
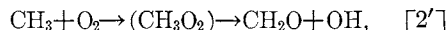
the k_2'/k_1 values could not be fitted to an $\exp(-\Delta E/RT)$ type function, as is shown in Fig. 6, and a much-too-large frequency factor would be required for k_2' (exceeding 10^{15} mole^{-1} cm^3 sec^{-1}). Only when [O] is still very small could an appreciable fraction of CH_3 perhaps react with O_2, explaining in this way the presence of some CH_3O_2 in the earlier stages of the flame (see Fig. 2). With $Z =$ atomic oxygen, however, the k_2/k_1 values were found to fit perfectly to an $\exp(-\Delta E/RT)$ type function (see Fig. 6), with $k_2 = 1.3 \times 10^{14} \exp(-2000/RT)$. This expression also agrees well with the low-temperature result of Niki et al.,[15] and with Clark's value[16] at 1500°K. The kinetic coefficient of [2] appears to be about 20 times larger than that of $CH_3 + OH \rightarrow \cdots$.[17]

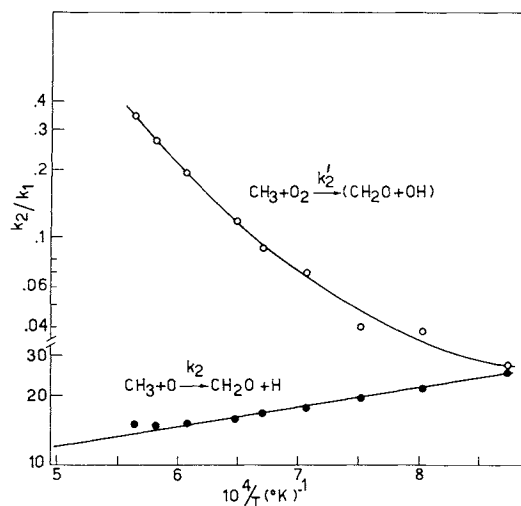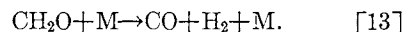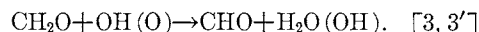FIG. 6. Log k_2/k_1 and log k_2'/k_1 versus $1/T$ (see text); $k_2/k_1 = 4.4 \exp(4000/RT)$.

CH_2O, CHO, and HO_2

As shown below, an appreciable fraction (40% in the lean flame) of the formaldehyde disappears by thermal decomposition:

$$CH_2O + M \rightarrow CO + H_2 + M. \qquad [13]$$

Our results indicate also that, in lean flames, the remainder reacts predominantly with OH, and a smaller part reacting with O

$$CH_2O + OH(O) \rightarrow CHO + H_2O(OH). \qquad [3, 3']$$

The rate constant of [3] was found to be about 2.5×10^{13} at $T = 1600°K$, with an activation energy near 1 kcal/mole. The kinetic coefficient of [3'] is therefore about 10^{13}.

The CHO mole fraction ($\simeq 10^{-5}$ in the lean flame and 5×10^{-5} in the stoichiometric flame) remains so low that only O_2 can be considered as the reaction partner,

$$CHO + O_2 \rightarrow CO + HO_2 \qquad [4]$$
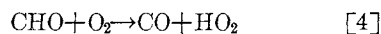
with $k_4 \simeq 3 \times 10^{13}$ at $1400°K < T < 1800°K$.

The hydroperoxyl radical reacts in the lean flame, mainly with O and OH,

$$HO_2 + OH(O) \rightarrow O_2 + H_2O(OH), \qquad [5, 5']$$
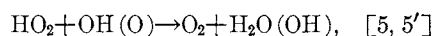
with measured rate constants $k_5 \simeq 5 \times 10^{13}$ (assumed identical for OH and O) at $T = 1400°$–
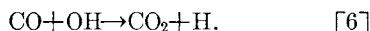
1800°K. The rate constant of

$$HO_2 + H \rightarrow 2\ OH \qquad [5'']$$

has been estimated[18] to be 7×10^{13}.

CO and CO₂

Our results demonstrate that, except perhaps for a few percent, all CO_2 is formed via

$$CO + OH \rightarrow CO_2 + H. \qquad [6]$$

The rate constant was evaluated taking the reverse reaction into account. In the range $T = 1600°-1900°K$, as shown in Fig. 5, $k_6 = 2.8(\pm 0.5) \times 10^{11}$. Combination with Greiner's result[19] at 300°K yields $k_6 = 3.5 \times 10^{11} \exp(-800/RT)$. However, our results fit better to Dryer's "variable activation energy" expression,[20] predicting an E value of about 5.5 kcal/mole in the range $T = 1600°-1900°K$ (see Fig. 5).

The fact that the experimental k_6 values in the postcombustion zone remain constant up to a point where the reaction is only some 30% from complete equilibrium, demonstrates the precision of the mole fraction data for OH and H.

H₂/O₂-System Reactions

Using, directly, the mass-spectrometer output currents, it was found that, in the constant T region ($T = 1900°K$, $z = 1.2-3.2$ cm) of the lean-CH_4/O_2 flame, the ratios
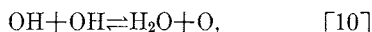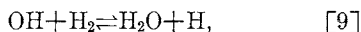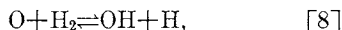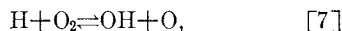
$$(i_O \cdot i_{OH})/(i_H \cdot i_{O_2}),$$

$$(i_{OH} \cdot i_H)/(i_O \cdot i_{H_2}),$$

and

$$(i_H \cdot i_{H_2O})/(i_{OH} \cdot i_{H_2}),$$

remained constant to within 5%. The individual O, H, and OH currents, however, decreased appreciably. It was concluded, therefore, that the four reactions

$$H + O_2 \rightleftharpoons OH + O, \qquad [7]$$

$$O + H_2 \rightleftharpoons OH + H, \qquad [8]$$

$$OH + H_2 \rightleftharpoons H_2O + H, \qquad [9]$$

$$OH + OH \rightleftharpoons H_2O + O, \qquad [10]$$

were fully balanced in the specified region. This fact enabled us to compute precise calibration factors for H, O, and OH.

The same reactions were also very nearly balanced in the burned gas of the stoichiometric flame.

In the lean-flame reaction zone, Reaction [7] is never less than 50% balanced. Using the known rate constant[21] and the equilibrium constant, the net O_2-removal rate computed by [7] is about 70% of the measured O_2-disappearance rate in the region where [7] is less than 90% balanced (up to $z = 0.4$ cm). It should be noted that, at 90% equilibrium, a 10°K error in T leads to a 30% error in the computed rate.

The other H_2/O_2-system reactions are also quite fast, in particular [9] and [10].

In order to check the mechanism of the degradation of CH_4 to CO, the flame reactions were divided into two groups, the first one comprising the $CH_4 \rightarrow CO$ conversion reactions, and the second group the Reactions [6]-[10].

The basic idea is that the amount of H_2O, H_2, OH, O, and H produced (or destroyed) by the first group of reactions can be evaluated indirectly by substracting the rates of formation or removal of these species by the second group from the net observed reaction rates.

The net rates of [8], [9], and [10] were computed, using the known rate constants[21-24] and the equilibrium constants, whereas the net rates of [6] and [7] were derived from the observed CO_2 and O_2 mole flux gradients. Thus, it was found that the $CH_4 \rightarrow CO$ degradation reactions result in the formation of 1.4 H_2O, 0.75 H, and 0.5 H_2 particles and the destruction of 0.65 OH and 1.7 O particles per CH_4 molecule consumed in the lean flame.

These "over-all stoichiometric coefficients" correspond to the mechanism comprising the Reactions [1]-[5], such that, in the lean flame, (i) CH_4 reacts 75% with OH, 15% with O, and 10% with H (based on known or derived rate constants); (ii) CH_3 is destroyed by O atoms; (iii) CH_2O disappears 40% by thermal decomposition (see below), 40% by reaction with OH, and 20% by O attack (based on total OH and O reaction rates); (iv) CHO reacts with O_2; (v) HO_2 is destroyed 45% by OH, 40% by O (rate constants assumed equal), and 15% by H (rate constant known[18]).

It should be noted that the net O, OH, and H reaction rates are initially negative, and that they vanish at the point where the CH_4 removal rate peaks (see F_{OH}, F_H and F_O in Fig. 4).

Radical and Atom Decay

The "pool" concept[25,26] was used to investigate radical and atom decay in the burned gas region. However, since that concept was found to be useful also in connection with the highly im-

portant question of the formation of atoms and radicals (see below), a concise new derivation of the "pool laws" and of their implications will first be given here.

The "pool laws" are simply linear combinations of the element conservation laws and of the expression for the conservation of the total number of chemical bonds in a system, the latter being valid only if solely binary reactions of the type A+B→C+D occur. If $F(C_xH_yO_z)_i$ is the mole flux of the ith species, containing b_i chemical bonds (whether single or multiple), any linear combination of the four conservation equations,

$$F_p = p_i \sum_i x_i F(C_xH_yO_z)_i + q_i \sum_i y_i F_i$$
$$+ r_i \sum_i z_i F_i + s_i \sum_i b_i F_i, \quad (4)$$

can be written as a weighted sum of mole fluxes, or as a species pool flux,

$$F_p = \sum_i [(px_i + qy_i + rz_i + sb_i) F(C_xH_yO_z)_i], \quad (5)$$

each species having a weight factor

$$m_i = px_i + qy_i + rz_i + sb_i. \quad (6)$$

A pool flux that is of particular interest is one with $m_i = 0$ for all major products. For a lean flame, where the m_i values of O_2, CO_2, and H_2O should be zero, it is easily found, using Eq. (6), that the relevant pool is a linear combination, Eq. (4), with coefficients $p=4$, $q=3$, $r=2$, and $s=-4$, one of these being chosen arbitrarily:

$$m_i = 4x_i + 3y_i + 2z_i - 4b_i. \quad (7)$$

Therefore, in the burned gas of a lean-CH_4/O_2 flame, using Eq. (7), one has

$$F_p = 3F_H + 2F_{CO} + 2F_{H_2} + 2F_O + F_{OH}. \quad (8)$$

Obviously, F_p should remain rigorously constant unless reactions occur with a change in the number of chemical bonds or, what amounts to the same in the absence of cyclic compounds, with a change in the number of particles. In that case, the chemical rate of change of the pool, $K_p = (1/A)(dF_p/dz)$, is equal to -4 (the value of the coefficient s) times the net rate of formation of chemical bonds, or four times the net production rate of particles.

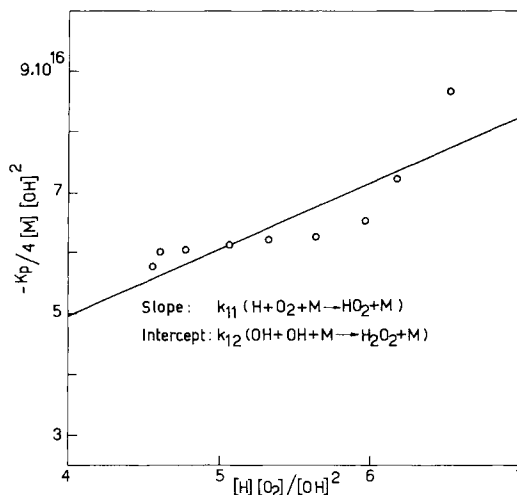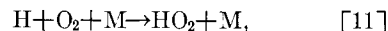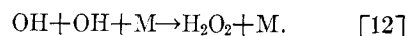In the lean-flame burned gas, the pool decay

FIG. 7. Rate constants of $H + O_2 + M \to HO_2 + M$: $k_{11} = 1.12 \times 10^{16}$ mole^{-2} cm^6 sec^{-1}; and of $OH + OH + M \to H_2O_2 + M$: $k_{12} \simeq 0.5 \times 10^{16}$; $K_p = (1/A) \times (dF_p/dz)$ (lean-flame data in the region $d = 1.2$–4.5 cm); $T = 1900°K$; burned gas composition: $X_{O_2} = 0.69$, $X_{H_2O} = 0.18$, $X_{CO_2} = 0.093$.

is consistent with the recombination process

$$H + O_2 + M \to HO_2 + M, \quad [11]$$

and, to a lesser extent, with

$$OH + OH + M \to H_2O_2 + M. \quad [12]$$

In Fig. 7, $-K_p/(4[M][OH]^2)$ is plotted versus $[H][O_2]/[OH]^2$, the slope of the resulting straight line being equal to the rate constant of [11]: $k_{11} = 1.12 \times 10^{16}$ mole^{-2} cm^6 sec^{-1}, and the ordinate intercept to $k_{12} \simeq 0.5 \times 10^{16}$. Using the known relative efficiencies[21] of O_2, H_2O, and CO_2 as the third body, it follows that $k_{11}(M = O_2) = 2.5 \times 10^{15}$ at $T = 1900°K$.

The Rate-Determining Step

In the reaction zone of a lean-CH_4/O_2 flame, the pool flux given by Eq. (5), using the m_i values of Eq. (7), is equal to

$$F_p = 3F_H + 2F_O + F_{OH} + 2F_{H_2} + 2F_{CO} + F_{CH_2}. \quad (9)$$

The m_i values of CH_4, O_2, CH_2O, H_2O, and CO_2 are indeed zero, and the species with $X < 10^{-4}$ were neglected. Equation (9) shows that if the active species necessary for flame propagation,
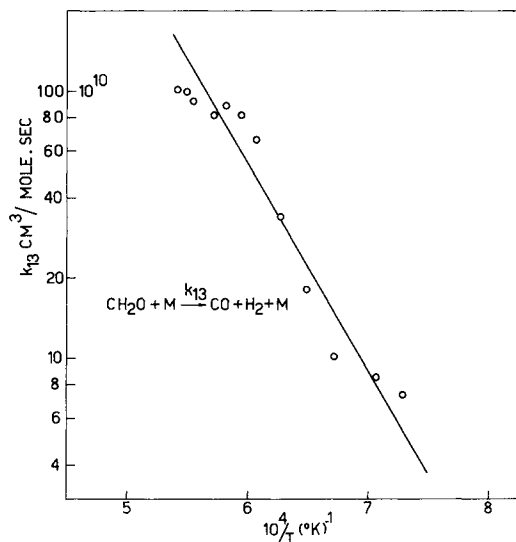
FIG. 8. Log k_{13} versus $1/T$;
$k_{13} = (dF_p/dz)/(4A[CH_2O][M]$ (lean-flame data);
$k_{13} \simeq 2.1 \times 10^{16} \exp(-35,000/RT)$ mole^{-1} cm^3 sec^{-1}.

OH, O, and H, are to be present in the flame at all, the value of F_p must be positive. Since its value is zero in the fresh gases of a CH_4/O_2 flame, OH, O, and H cannot have formed, and a flame cannot exist, unless a reaction occurs that decreases the number of chemical bonds (see above). Such a reaction can be either a thermal decomposition process or an $A+B \to C+D+E$ type reaction.

A body of evidence has been gathered that, in CH_4/O_2 flames, this process—the real rate-determining step, as can be shown[29]—is the reaction

$$CH_2O + M \to CO + H_2 + M. \qquad [13]$$
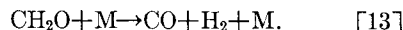
Its rate being equal to $K_p/4 = (1/4A)(dF_p/dz)$, it could be found from the pool flux (see Fig. 4) that 40% of the fuel is oxidized in the lean flame, according to a scheme comprising the decomposition process. The rate constant of [13] was also determined from the F_p gradient: $k_{13} \simeq 2.1 \times 10^{16} \exp(-35,000/RT)$ (see Fig. 8), with a possible error of 5 kcal/mole in the activation energy.

One of the arguments for Reaction [13] is that it explains quantitatively the formation via the $CH_4 \to CO$ conversion reactions of about 0.5 H_2 molecules per CH_4 molecule consumed (see above). Another argument is that the derived activation energy is in good agreement with the

over-all "activation energy" of lean-CH_4/O_2 flames (about 40 kcal/mole). On that basis also, a low-activation-energy reaction such as

$$CH_2O + O \to CO + H + HO$$
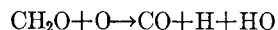
must be rejected as the rate-determining step. The same applies to

$$CHO + M \to CO + H + M,$$
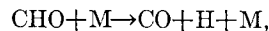
with an activation energy[27] of only 15 kcal/mole. Moreover, using the known rate constant[27,28] of that reaction, it is found that the CHO mole fraction required to account for the observed rate of increase of the pool flux is about twenty times the measured value in the lean flame, and about five times the actual value in the stoichiometric flame. Reaction [13], on the other hand, is consistent with the experimental pool flux increase in both these flames.

Accepting a Lindemann–Hinshelwood mechanism for Reaction [13],

$$CH_2O + M \underset{k_b}{\overset{k_a}{\rightleftharpoons}} CH_2O^* + M,$$

$$CH_2O^* \overset{k_c}{\to} CO + H_2,$$
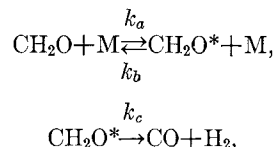
it might be argued that the pressure at which the transition to first-order kinetics occurs is quite low $(P_{1/2} < 1$ atm), since k_c is probably small. First-order kinetics for Reaction [13] would explain the observed[1] pressure dependence of the burning velocity of CH_4/O_2 flames $(\sim p^{-1/2})$.

It appears then that the rate-determining decomposition process in CH_4/O_2 flames is probably Reaction [13] (pseudomonomolecular or bimolecular); however, no direct proof could be found as yet.

The rate constant k_{13} reported here is some 3 orders-of-magnitude larger than the values given by Gay et al.,[30] and by Schecker and Jost,[31] for the kinetic coefficient of the decomposition of formaldehyde. Moreover, these authors consider

$$CH_2O + M \to CHO + M + H \qquad [14]$$
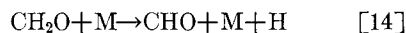
to be the major decomposition path. In shock-tube studies, $CH_2O + M \to CO + H_2 + M$ cannot contribute significantly to the removal of CH_2O— even if it were somewhat faster than Reaction [14]—since the major part of the CH_2O is con-

sumed by H atoms in a chain mechanism initiated by Reaction [14].

The much larger rate of decomposition in flames may be due to the fact that CH_2O is formed here (together with an H atom) by a highly exothermic process (Reaction [2] with $\Delta H = -67$ kcal/mole), while at the same time its average lifetime in the flame is only 5×10^{-6} sec, during which it undergoes only some 700 collisions. It might be argued, therefore, that the CH_2O in the flame front is vibrationally quite "hot," resulting in an appreciable decrease of the activation energy and, hence, a much larger rate of decomposition. Moreover, the results of Refs. 30 and 31 were obtained with Ne or Ar as diluents, whereas in the flames investigated here the "third body" is mainly O_2, H_2O, and CO_2. Many instances are known where such species are an order-of-magnitude more effective than Ne or Ar.

To conclude, it can be shown[29] that a decomposition-type reaction is a *conditio sine qua non* for all hydrocarbon–oxygen flames, except for those burning hydrogen or acetylene, which are therefore both very fast flames.

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COMMENTS

A. R. Hall, Ministry of Defence, Rocket Propulsion Est., Westcott, Aylesbury, Bucks, England. The illustration of your apparatus indicated the use of a supersonic, rather than an effusive, molecular beam for sampling the flame gases. Gordon J. Williams (in work to be reported elsewhere) has noted that the well-known mass-discrimination effects with such a beam depend on the composition, pressure, and temperature of the source gas, and on the distance between sample orifice and skimmer. How have you corrected for the effect in obtaining your concentration profiles, especially for the lower-molecular-weight constituents?

Authors' Reply. We have observed that, in our system, at source Knudsen Numbers of about 0.02 to 0.08, mass discrimination is adequately described (to within 5%) by the expression $X_b/X_0 = M/\bar{M}$, where X_b and X_0 are the respective mole fractions in the beam and in the sample, M the molecular weight of the considered species, and $\bar{M}$ the mean molecular weight of the mixture. No attempt was made yet to check this expression at higher or lower Knudsen Numbers, and the investigated molecular-weight range was rather limited (16 to 44). However, as both the pressure and the nozzle-skimmer distance were kept constant in our experiments, and since the effect of the composition on the mass discrimination was known (i.e., the mean molecular weight), we had to be concerned only with possible changes in the mass discrimination with temperature, which does vary considerably in the flame. Fortunately, there were no such changes, since, upon adding traces of argon and helium to the lean methane flame, it was found that the ratio of the beam signals of these species was the same behind the flame front (1900°K) as in the fresh gases (300°K). A slight discrepancy of about 5% could be ascribed entirely to radial thermal diffusion of helium toward the central, hotter parts of the flame. In our opinion, it is primarily due to the low jet density in front of the skimmer and to the absence of jet-skimmer interactions, that only the simple and easily understood type of mass discrimination occurs in our system.

↓

K. D. Bayes, Dept. of Chemistry, University of California, Los Angeles, Cal. In the room-temperature reaction of oxygen atoms with methane, we have observed directly the HCO radical (I. T. N. Jones & K. D. Bayes: J. Am.

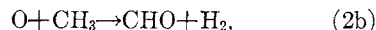Chem. Soc., in press). The kinetic behavior of the HCO requires that it be formed in the reaction

$$O + CH_3 \rightarrow HCO + H_2.$$
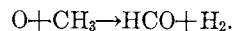
This is not necessarily the major reaction path, but it is significant. Would the inclusion of this source of HCO, and especially H_2, alter your interpretation?
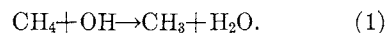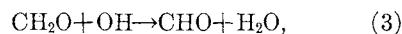
Authors' Reply. Our arguments for accepting

$$O + CH_3 \rightarrow CH_2O + H, \tag{2}$$

and not

$$O + CH_3 \rightarrow CHO + H_2, \tag{2b}$$
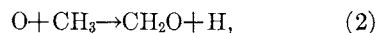
as the major reaction path, are based on the following: the assumption that the sole product is CH_2O leads to a reasonable value for the ratio k_3/k_1,

$$CH_2O + OH \rightarrow CHO + H_2O, \tag{3}$$
$$CH_4 + OH \rightarrow CH_3 + H_2O. \tag{1}$$

At $T = 1600°K$, we find $k_3/k_1 = 6 \pm 2$ (assuming also that 40% of the CH_2O disappears by thermal decomposition, and that k_3 is at least as large as k_3').[1] This result is entirely consistent with the value $k_3/k_1 = 33 \pm 3$ at $T = 800°K$, as reported by Blundell et al.,[2] and with a $(E_1 - E_3)$ value of about 5 kcal/mole as found by us (an upper limit of $E_3 \simeq 2$ kcal/mole can also be inferred from the work of Herron et al.[1]).

However, the derived value of k_3/k_1 would remain almost unchanged if it were assumed that Reaction (2b) accounts for 40% of the total CH_3 removal, and if, at the same time, thermal decomposition of CH_2O (40% of its removal rate) were dropped entirely from the reaction scheme. It would be very tempting indeed to adopt this alternative—especially since it still explains, quantitatively, the observed H_2 production—if it were not for the difficulty of finding another decomposition reaction (within the pool concept) that fits the experimental results.

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⬥

Dennis M. Zallen, Purdue University, W. Lafayette, Ind. There seems to be considerable disagreement with respect to the formaldehyde and formyl radical reactions being used in the methane–oxygen mechanisms. Skinner[1] completely deletes CH_2O and HCO species, since relevant reactions occur in rapid succession and formaldehyde does nothing but decompose very rapidly. Bowman[2] also neglects CH_2O, uses
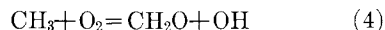
$$CH_3 + O_2 = HCO + H_2O \qquad (1),$$

and neglects

$$CH_3 + O = HCO + H_2 \qquad (2)$$
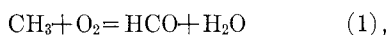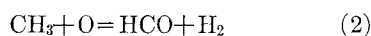
during the induction period. Seery and Bowman[3] used

$$CH_3 + O = CH_2O + H \qquad (3)$$
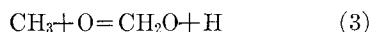
in addition to (1). Higgin and Williams[4] used

$$CH_3 + O_2 = CH_2O + OH \qquad (4)$$

in place of (1), and Lifshitz[5] considers (4) to be one of the two predominant reactions controlling induction times. Asaba[6] considers the mechanism of oxidation of formaldehyde to explain the branching-chain type ignition and the activation energy. Would you please comment as to the importance of these species and the reactions necessary in methane–oxygen flames.

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Authors' Reply. As explained in our reply to Dr. Bayes' comment, our results strongly

indicate that the larger part of the methyl radicals in the flame yield formaldehyde upon oxidation. Moreover, in the very lean to stoichiometric flames investigated by us, reaction between CH_3 and O_2 is negligible in the main reaction zone, as could be established beyond reasonable doubt. Indeed, in a series of four investigated flames, there was no correlation whatsoever between the $[CH_3][O_2]$ product and the CH_3-removal rate, whereas the latter was directly proportional (to within 15%) to the $[CH_3][O]$ product.

Most probably, however, matters are entirely different during induction periods of CH_4/O_2 explosions, or during the exponential growth period behind shock waves: as long as $[O_2]$ is still very much larger (perhaps 1000 times) than $[O]$, the reaction between CH_3 and O_2 must, of course, outrun that between CH_3 and O.

Although degenerate branching is probably important in low-temperature oxidation (and maybe also during ignition), it certainly is not in flames: due to the high activation energy of

$$CH_2O + O_2 \rightarrow CHO + HO_2$$
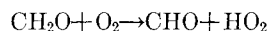
($E \simeq 40$ kcal/mole), its rate is negligible compared to that of

$$H + O_2 \rightarrow OH + O,$$
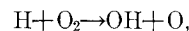
which is indeed the fastest of all the reactions occurring in the flames investigated by us. This difference between low-temperature systems and flames is again the consequence of the strongly different concentrations of highly reactive species, such as H atoms.

⬥

G. Dixon-Lewis, Univ. of Leeds, England. I am concerned about the high values quoted for the rate constants of the reactions:

$$OH + HO_2 = H_2O + O_2, \qquad (5)$$

$$O + HO_2 = OH + O_2. \qquad (5')$$
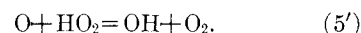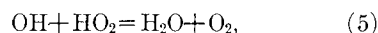
Both of these are quoted as $\simeq 5 \times 10^{13}$ at $T = 1400°–1800°K$. Work on hydrogen–oxygen flames (This Symposium) suggests a *maximum* value of $k_5 = 7 \times 10^{13}$ at around 900°K, *assuming that* $k_{5'} = 0$; where another possible combination was $k_5 = 4 \times 10^{12}$, with $k_{5'} = 3.3 \times 10^{13}$; activation energies were not high.

*Authors' Reply.* Assuming that $k_{5'} = 0$, the value of k_5 required to account for the observed

HO_2-destruction rate in the lean flame would be about 10^{14} at $T = 1600°K$. In my opinion, this upper limit agrees reasonably well with the analogous maximum value of 7×10^{13} at $T = 900°K$, reported by Dr. Dixon-Lewis.

It should be emphasized, however, that HO_2 is one of the few species (together with CHO, CH_2, and CH_3O_2) for which concentrations had to be obtained from estimated ionization cross sections at ionizing electron energies a few eV above the threshold. When similar cross-section estimation methods were applied to O, OH, H, and CH_3, concentrations were found that were, respectively, 1.5, 3, 1.1, and 2 times lower than the values obtained by calibration. The values of k_5 and $k_{5'}$ (and also of k_4) reported here are, therefore, also expected to be in error by a factor of about 2.

On the other hand, the results derived by Dr. Dixon-Lewis depend upon, among other things, the values of the rate constants of Reaction (5″) and upon those of reactions (7)– (9); not all of these are known as precisely as one might wish.

♦

G. *Dixon-Lewis*. I should like also to comment briefly, as well as to interject a word of caution, on two of the arguments advanced by the authors in connection with their proposed reaction:

$$CH_2O + M = CO + H_2 + M. \qquad (1)$$
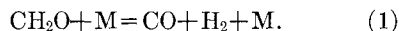
First, the fact that the "over-all activation energy" of lean-CH_4/O_2 flames is about 40 kcal mole^{-1} leads them to the rejection of low-activation-energy reactions, such as

$$CH_2O + O = CO + H + OH, \qquad (2)$$
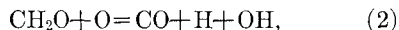
as steps determining the rate of growth of the radical pool. However, in the case of a rich-H_2/O_2 supported flame, we have recently used a reaction mechanism having no step with activation energy greater than 16.5 kcal mole^{-1}, in order to investigate the effect of a small change of initial temperature on the computed burning velocity.[1] The "over-all activation energy," obtained by plotting $\log(S_{u,\text{calc}})^2$ against $1/T_b$, turned out to be around 50 kcal mole^{-1}. Clearly, in the H_2/O_2 case, an argument involving an over-all activation energy would have led to an incorrect conclusion, and it may be that such arguments are generally invalid.

The second point concerns the pressure dependence of burning velocity, for which global reaction-rate approaches, such as those of Zeldowich, Semenov, and Frank-Kamenetskii, predict $S_u \propto p^{-1/2}$ for first order, and S_u independent of pressure for second-order kinetics. On the basis of these results, Peeters and Mahnen use the observed pressure dependence of CH_4/O_2 burning velocities ($\sim p^{-1/2}$) to argue that their radical pool-controlling step probably is first order, i.e., a pseudounimolecular decomposition. However, detailed computation on a single H_2/O_2 flame[2] again does not support the conclusions of the global reaction approaches. Instead, it was found that, for a flame mechanism containing only a mixture of second- and third-order reactions, $S_{u,\text{calc}} \propto p^{-1/4}$, approximately. Extreme caution is therefore necessary in drawing conclusions about elementary reaction steps from these over-all flame properties.

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1. Day, M. J., Dixon-Lewis, G., and Thompson, K.: Proc. Roy. Soc. (London), In press.
2. Dixon-Lewis, G., Isles, G. L., and Walmsley, R.: Proc. Roy. Soc. (London), In press.

Authors' Reply. The computed results for the "over-all activation energy" of the rich H_2/O_2 flame are indeed unexpected, and should weaken our confidence in arguments based on over-all flame properties. It is puzzling, however, that the measured "over-all activation energy" of hotter, near-stoichiometric $H_2/O_2/N_2$ flames is much lower (about 20 kcal/mole).[1]

Nevertheless, there remain other arguments against the importance of the reactions

$$CH_2O + O \rightarrow CO + H + OH,$$

$$CH_2O + OH \rightarrow CO + H + H_2O,$$

and also

$$CH_3 + O \rightarrow CO + H + H_2;$$
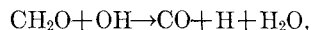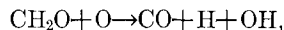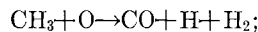
for their rates to match the observed pool-growth profile, activation energies of about 15 to 20 kcal/mole and preexponential factors of about 10^{15} cm^3 mole^{-1} sec^{-1}, or larger, would be required.

The computed negative-pressure dependence of the H_2/O_2 burning velocities ($\sim p^{-1/4}$) is due to third-order chain-termination processes. In the 40-torr CH_4/O_2 flames, however, the rate of the fastest termolecular recombination reactions is only 1% of that of the bimolecular branching and termination processes. It is justified, then, in my opinion, to neglect the third-order processes, also, in the reaction zone of CH_4 flames burning at 0.25 atm, where their rates can be estimated to be about 5% of the bimolecular

termination rates. It can be shown, using the complete set of differential equations describing a flame, that the eigenvalue for the burning velocity is rigorously independent of the pressure if all reactions are bimolecular. However, according to the most-recent measurements,[2] the $p^{-1/2}$ pressure dependence of methane–air burning velocities persists even down to 0.25 atm, the lowest investigated pressure.
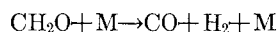
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1. VanDooren, J. and Van Tiggelen, P. J.: unpublished results.
2. Bradley, D. and Hundy, G-F.: *Thirteenth Symposium (International) on Combustion*, p. 575, The Combustion Institute, 1971.

‡

J. Troe, Institut de Chimie-Physique de l'EPF-Lausanne, Avenue des Bains 31 1007 Lausanne, Switzerland. From our investigation[1] of HO_2 profiles in the thermal dissociation of H_2O_2 near 1400°K, we had to conclude that the rate constant of

$$OH + HO_2 \rightarrow H_2O + O_2$$
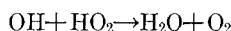
is about $10^{13.0 \pm 0.3}$ cm^3 mole^{-1} sec^{-1}. With your high value of $k_5 \simeq 10^{13.7}$ cm^3 mole^{-1} sec^{-1}, we would have seen much smaller HO_2 concentrations than actually observed. Since your apparent rate constant for

$$CH_2O + M \rightarrow CO + H_2 + M$$

differs considerably from the rate constant of the unimolecular dissociation,[2]

$$CH_2O + M \rightarrow HCO + H + M,$$
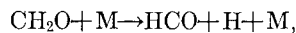
it rather corresponds to a complex dissociation path.

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1. J. Troe: Ber. Bunsenges. Physik. Chem. *73*, 946 (1969).
2. H. G. Schecker and W. Jost: Ber. Bunsenges. Physik. Chem. *73*, 521 (1969).

Authors' Reply. Our value of $k(OH + HO_2)$ is estimated to be good within a factor of 2. Kaufman[1] estimates a value of $k(OH + HO_2) \geq 6 \times 10^{12}$ cm^3 mole^{-1} sec^{-1} at 300°K; combination with our results at 1600°K yields a reasonable activation energy ≤ 1.5 kcal/mole.

It should be emphasized that we have not directly observed decomposition of CH_2O. Rather, we ascribe the mole change observed in the flame to the specific process

$$CH_2O(+M) \rightarrow CO + H_2(+M),$$
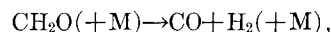
as this reaction appears to satisfy the experimental results. Possible reasons for our high value of the rate constant are given in the paper.

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1. Kaufman, F.: Ann. Geophys. *20*, 106 (1964).

F. L. Dryer, Guggenheim Laboratories, Princeton University, Princeton, N.J. Would the authors care to comment on the limits of error associated with their reported rate constant for the reaction

$$CH_4 + OH \xrightarrow{k_1} CH_3 + H_2O. \qquad (1)$$
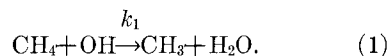
You have noted throughout the region of methane consumption, equal concentrations of oxygen atoms and hydroxyl radicals; furthermore, in the initial stages of reactions, the concentration of H atoms was not negligible compared to [O] or [OH].

If one accepts recent literature values for k_1,[1] k_2,[2] and k_3,[3]

$$CH_4 + O \rightarrow CH_3 + OH, \qquad (2)$$

$$CH_4 + H \rightarrow CH_3 + H_2, \qquad (3)$$
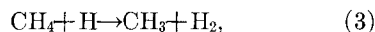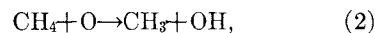
it is apparent that Reaction (1) should account for no more than 60%, and as little as 40% of your observed methane consumption rate, depending upon the position in the flame. If this is the case, your evaluation of (1) intrinsically contains errors associated with Reactions (2) and (3). Herron[2] has suggested that the evaluation of k_2 is good to within a factor of 1.5 at your temperatures, while Kurylo and Timmons[3] suggest the value of k_3 is determined to within a factor of 2.

Admittedly, linear extrapolation of Greiner's results from 500°K to $\sim$1200°K on an Arrhenius plot must be met with some skepticism. However, it appears that no reasonable pre-exponential temperature dependence of k_1 can reconcile your reported measurements of k_1 with those of Greiner, especially when one considers that Reactions (2) and (3) must have some pre-exponential temperature dependence themselves.

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1. N. R. Greiner: J. Chem. Phys. *53*, 1070 (1970).
2. J. T. Herron: Intern. J. Chem. Kinetics *1*, 527 (1969).
3. M. J. Kurylo and R. B. Timmons: J. Chem. Phys. *50*, 5076 (1969).

Authors' Reply. Our value of $k(CH_4+OH)$ depends primarily on the shape and position of the profiles of the methane disappearance rate and of the OH concentration. Combined systematic errors amount here to at most 25%. Taking the respective rate constants and their error limits from the sources quoted by Dr. Dryer, the combined rates of CH_4+O and CH_4+H are, on the average, $20\pm10\%$ of the total observed CH_4-disappearance rate. In the worst case, therefore, our smoothed $k(CH_4+OH)$ value might be too high or too low by a factor of 1.5. In fact, in our derivation, we have neglected the small ($\pm6\%$) contribution of CH_4+H.

Even when the upper limits of the respective rate constants are used to evaluate the contributions of CH_4+O and CH_4+H, Greiner's value of $k(CH_4+OH)$ is still too low, by a factor of 3.5, to account for the remainder (70%) of the observed CH_4-disappearance rate. In his paper, Greiner notes that the extrapolation above 500°K of his Arrhenius lines predicts $k(CH_4+OH)$ and also $k(H_2+OH)$ values that are a factor of 3 lower than the combustion data, and therefore further experimental work may be necessary.

It is worthwhile to point out that the recent data of Horne and Norrish[1] support our higher value of $k(CH_4+OH)$.

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1. Horne, D. G. and Norrish, R. G. W.: Nature, *215*, 1373 (1967).

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J. E. Dove, Dept. of Chemistry, University of Toronto, Toronto, Ontario, Canada. The authors' application of the "pool" concept of Kaskan and Schott is very interesting. When trying to elucidate the kinetic behavior of an over-all reaction whose mechanism is incompletely known, the use of the pool concept may well be more immediately fruitful than, e.g., computer calculations based on large systems of rate equations.

It should be borne in mind that, in the pool law, many species which could be present in this system, such as HO_2, CH_3O, and CH_3O_2, have negative values of m. Formation of these species would allow the concentrations of other reactive species to increase without violating the pool law. Presumably, the concentrations of species with negative m are much too small to account directly for the observed apparent rapid increase in the pool. However, the formation and subsequent rapid decomposition of a species such as CH_3O_2 might still be important in forming the pool.

Authors' Reply. The maximum sum of the observed mole fluxes of HO_2 and CH_3O_2 (both with $m=-1$) is 2 to 3 orders of magnitude less than the value of the pool flux. Therefore, these species could indeed be neglected.

It should be emphasized that the total observed rate of decomposition is very large in the flame: on the average, about 40% of the CH_4-destruction rate. Therefore, only fast processes need be considered. It is highly unlikely that CH_3O_2 is formed in a fast reaction; moreover, the small observed amount of CH_3O_2 is most probably formed in a reaction that decreases the pool,

$$CH_3+O_2 \rightarrow CH_3O_2.$$
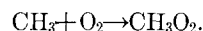
In this respect, matters might be different for CH_3O: one could indeed have

$$CH_3+OH \rightarrow CH_3O+H.$$
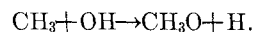
The rate constant of CH_3+OH, however, as measured by Fenimore,[1] is about 6 times too low to account for the observed pool-flux growth, even when one assumes that CH_3O and H are the sole products and that all CH_3O decomposes (into CH_2O+H).

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1. Fenimore, C. P.: *Twelfth Symposium (International) on Combustion*, p. 463, The Combustion Institute, 1969.