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A Reaction Scheme Applicable to Combustion of C_1 - and C_2 -Hydrocarbons

By

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Abstract

A reaction scheme is constructed for the combustion of simple fuels. It comprises C_1 and C_2 species and does not contain higher hydrocarbons. The rate constants are mainly determined on the basis of Westbrook's and Warnatz's reaction schemes, but some of them must be changed to make the scheme comprehensive. This reaction scheme and a mathematical model for one-dimensional premixed flames are applied to methane/air flames under various equivalence ratios and acetylene, ethylene and ethane flames under their stoichiometric conditions. The validity of the proposed scheme is verified by comparing the predicted burning velocities with this scheme and the experimental ones under the corresponding conditions.

The mechanism of the combustion reactions in the above hydrocarbon flames are analyzed. In the methane flames, the reaction paths through C_2 species cannot simply be neglected. The reaction scheme where the C_2 species are omitted cannot reproduce the satisfactory burning velocities for these flames. In the acetylene flame, active C_2H_3 radicals are produced at low temperatures and are converted again to C_2H_2 at higher temperatures. In the ethylene flame, C_2H_4 reacts through C_2H_2 . In the ethane flame, more than half of C_2H_6 is oxidized through C_1 -species reaction paths.

1. Introduction

There are two alternative approaches to the detailed investigation on chemical reactions taking place in a steady flame. One way is to analyze the experimental profiles of concentrations of species or temperature in the flame and to determine individual reaction paths. This is the most fundamental investigation. The other way is to construct an overall combustion reaction on the basis of a set of elementary reactions and their kinetic data, and to predict the apparent profiles of temperature and the concentrations of species. This synthetic approach has been used mainly for computer simulation. It can also estimate unknown elementary reactions by comparing the predicted and the corresponding experimental results using a trial-

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and-error method. In this investigation, proposed reaction schemes will be applied to methane/, acetylene/, ethylene/ and ethane/air premixed flames according to the latter technique.

A reaction scheme should be as precise as possible in order to simulate combustion reactions taking place in flames. Reaction schemes including C₁, C₂, and higher hydrocarbons have been intensively investigated, and several schemes have been proposed by Westbrook *et al.*¹⁾, Warnatz *et al.*²⁾, Miller *et al.*³⁾ and so on. However, the combustion reactions of higher hydrocarbons have not yet been clear. Moreover, all of the proposed reaction schemes are not necessarily valid for the combustion of the above four hydrocarbons. One of the necessary conditions which must be satisfied by a reaction scheme is that it can represent combustion reactions of different kinds of fuels under various conditions.

First, we shall make a so-called comprehensive reaction scheme comprising only C₁ and C₂ hydrocarbons. This reaction scheme cannot elucidate the reaction mechanisms of the rich flames of C₂ hydrocarbons. Then, we shall apply this scheme to acetylene, ethylene and ethane premixed flames in their stoichiometric conditions and methane flames under various conditions.

2. Mathematical Model

The following assumptions were made for constructing a mathematical model.

1. The flames under consideration are one-dimensional premixed flames.
2. Flow velocity of a gas mixture is small so that the pressure is constant throughout the flame and is equal to atmospheric pressure.
3. Heat loss from the flame to its surroundings is neglected and the temperature is, therefore, raised up to the adiabatic flame temperature at an infinite distance. Radiative heat transfer between any parts inside the flame is also neglected.

These assumptions simplify the governing equations like Eqs. (1) to (4).

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho v) = 0 \quad (1)$$

$$c_p \rho \left(\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial x} \right) = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) + \sum_i D_i \rho \frac{\partial h_i}{\partial x} \cdot \frac{\partial \omega_i}{\partial x} - \sum h_i \phi_i \quad (2)$$

$$\rho \left(\frac{\partial \omega_i}{\partial t} + v \frac{\partial \omega_i}{\partial x} \right) = \frac{\partial}{\partial x} \left(D_i \rho \frac{\partial \omega_i}{\partial x} \right) + \phi_i \quad (3)$$

$$p = \rho R T \sum_i \frac{\omega_i}{m_i} \quad (4)$$

In these equations, t denotes time; x , distance; ρ , the density of a gas mixture; v , the flow velocity; c_p , the specific heat; T , temperature; λ , the thermal conductivity; h , the enthalpy; ω , the mass fraction; D , the diffusion coefficient; m , the molecular weight; ϕ , the net production rate due to reactions; R , the universal gas constant;

Table 1. C₂ Hydrocarbon-O₂ Reaction Scheme
 $k = A \cdot T^n \cdot \exp(-E/T)$

No.	Reaction	A	n	E	Ref
1.	CH ₄ + M → CH ₃ + H + M	1.41E10	0.0	44500.0	1
2.	CH ₄ + OH → CH ₃ + H ₂ O	3.47E-3	3.08	1010.0	1
3.	CH ₄ + H → CH ₃ + H ₂	2.20E-2	3.0	4400.0	2
4.	CH ₄ + O → CH ₃ + OH	1.20E01	2.1	3840.0	2
5.	CH ₃ + HO ₂ → CH ₃ O + OH	3.24E07	0.0	0.0	1
6.	CH ₃ + O ₂ → CH ₃ O + O	2.51E07	0.0	14600.0	1
7.	CH ₃ + OH → HCHO + H ₂	3.98E06	0.0	0.0	1
8.	CH ₃ + O → HCHO + H	7.00E07	0.0	0.0	2
9.	CH ₃ + CH ₃ → C ₂ H ₆	4.00E06	0.0	0.0	2
10.	CH ₃ + CH ₃ → C ₂ H ₅ + H	8.00E07	0.0	13400.0	2
11.	CH ₃ + CH ₃ → C ₂ H ₄ + H ₂	1.00E10	0.0	16100.0	2
12.	CH ₃ O + O ₂ → HCHO + HO ₂	1.00E06	0.0	3020.0	1
13.	CH ₃ O + M → HCHO + H + M	5.01E07	0.0	10600.0	1
14.	HCHO + OH → CHO + H ₂ O	7.59E06	0.0	85.5	1
15.	HCHO + H → CHO + H ₂	3.31E08	0.0	5280.0	1
16.	HCHO + O → CHO + OH	5.01E07	0.0	2310.0	1
17.	HCHO + M → CHO + H + M	3.31E10	0.0	40800.0	1
18.	CHO + OH → CO + H ₂ O	1.00E08	0.0	0.0	1
19.	CHO + H → CO + H ₂	2.00E08	0.0	0.0	1
20.	CHO + O → CO + OH	1.00E08	0.0	0.0	1
21.	CHO + O ₂ → CO + HO ₂	3.98E06	0.0	3520.0	1
22.	CHO + M → CO + H + M	5.00E09	0.0	8460.0	2
23.	CO + OH → CO ₂ + H	4.40E00	1.5	-373.0	2
24.	CO + O + M → CO ₂ + M	5.89E09	0.0	2060.0	1
25.	CO + HO ₂ → CO ₂ + OH	1.51E08	0.0	11900.0	1
26.	CO + O ₂ → CO ₂ + O	3.16E05	0.0	18900.0	1
27.	C ₂ H ₆ + OH → C ₂ H ₅ + H ₂ O	1.12E07	0.0	1230.0	1
28.	C ₂ H ₆ + H → C ₂ H ₅ + H ₂	5.37E-4	3.5	2620.0	1
29.	C ₂ H ₆ + O → C ₂ H ₅ + OH	2.51E07	0.0	3200.0	1
30.	C ₂ H ₆ + CH ₃ → C ₂ H ₅ + CH ₄	5.50E-7	4.0	4170.0	1
31.	C ₂ H ₅ + O ₂ → C ₂ H ₄ + HO ₂	1.00E06	0.0	2520.0	1
32.	C ₂ H ₅ + M → C ₂ H ₄ + H + M	2.00E09	0.0	15100.0	1
33.	C ₂ H ₄ + OH → C ₂ H ₃ + H ₂ O	4.79E06	0.0	619.0	1
34.	C ₂ H ₄ + H → C ₂ H ₃ + H ₂	1.51E01	2.0	3020.0	1
35.	C ₂ H ₄ + M → C ₂ H ₃ + H + M	6.31E12	0.0	54700.0	1
36.	C ₂ H ₄ + M → C ₂ H ₂ + H ₂ + M	9.33E10	0.0	38800.0	1
37.	C ₂ H ₄ + OH → CH ₃ + HCHO	2.00E06	0.0	483.0	1
38.	C ₂ H ₄ + O → CH ₃ + CHO	3.31E06	0.0	569.0	1
39.	C ₂ H ₄ + O → HCHO + CH ₂	2.51E07	0.0	2520.0	1
40.	C ₂ H ₃ + H → C ₂ H ₂ + H ₂	2.00E07	0.0	1260.0	1
41.	C ₂ H ₃ + O ₂ → C ₂ H ₂ + HO ₂	1.00E06	0.0	5030.0	1
42.	C ₂ H ₃ + M → C ₂ H ₂ + H + M	7.94E08	0.0	15900.0	1

43.	C ₂ H ₂ +OH→C ₂ H+H ₂ O	6.03E06	0.0	3520.0	1
44.	C ₂ H ₂ +H→C ₂ H+H ₂	2.00E08	0.0	9560.0	1
45.	C ₂ H ₂ +O→C ₂ H+OH	3.24E09	-0.6	8550.0	1
46.	C ₂ H ₂ +M→C ₂ H+H+M	1.00E08	0.0	57400.0	1
47.	C ₂ H ₂ +OH→CH ₂ CO+H	3.24E05	0.0	101.0	1
48.	C ₂ H ₂ +O→HCCO+H	3.55E-2	2.7	699.0	1
49.	C ₂ H ₂ +O→CH ₂ +CO	6.76E07	0.0	2010.0	1
50.	C ₂ H ₂ +O ₂ →CHO+CHO	3.98E06	0.0	14100.0	1
51.	C ₂ H+O ₂ →CHO+CO	1.00E07	0.0	3520.0	1
52.	C ₂ H+O→CH+CO	5.01E07	0.0	0.0	1
53.	CH ₂ CO+OH→HCCO+H ₂ O	1.00E07	0.0	0.0	1
54.	CH ₂ CO+H→HCO+H ₂	1.00E07	0.0	0.0	1
55.	CH ₂ CO+O→HCCO+OH	1.00E07	0.0	0.0	1
56.	CH ₂ CO+OH→HCHO+CHO	2.82E07	0.0	0.0	1
57.	CH ₂ CO+H→CH ₃ +CO	1.10E07	0.0	1710.0	1
58.	CH ₂ CO+O→CHO+CHO	1.00E07	0.0	1210.0	1
59.	CH ₂ CO+M→CH ₂ +CO+M	2.00E10	0.0	30200.0	1
60.	HCCO+OH→CHO+CHO	1.00E07	0.0	0.0	1
61.	HCCO+H→CH ₂ +CO	5.01E07	0.0	0.0	1
62.	HCCO+O→CO+CHO	3.39E07	0.0	1010.0	1
63.	CH ₂ +OH→CH+H ₂ O	2.69E05	0.67	12900.0	1
64.	CH ₂ +H→CH+H ₂	2.69E05	0.67	12900.0	1
65.	CH ₂ +O→CH+OH	1.91E05	0.68	12600.0	1
66.	CH ₂ +O ₂ →CHO+OH	1.00E08	0.0	1860.0	1
67.	CH+O ₂ →CHO+O	1.00E07	0.0	0.0	1
68.	CH+O ₂ →CO+OH	1.35E05	0.67	12900.0	1
69.	H+O ₂ →OH+O	2.20E08	0.0	8450.0	4
70.	O+H ₂ →OH+H	1.80E04	1.0	4480.0	4
71.	OH+OH→O+H ₂ O	6.30E06	0.0	550.0	4
72.	OH+H ₂ →H+H ₂ O	2.20E07	0.0	2590.0	4
73.	H+H+M→H ₂ +M	2.60E06	-1.0	0.0	4
74.	O+O+M→O ₂ +M	1.90E01	0.0	-900.0	4
75.	H+O+M→OH+M	3.60E06	-1.0	0.0	5
76.	OH+H+M→H ₂ O+M	4.06E10	-2.0	0.0	4
77.	H+O ₂ +M→HO ₂ +M	5.00E03	0.0	-500.0	4
78.	H+HO ₂ →H ₂ +O ₂	2.50E07	0.0	350.0	4
79.	H+HO ₂ →OH+OH	2.50E08	0.0	950.0	4
80.	H+HO ₂ →O+H ₂ O	9.00E05	0.5	2000.0	4
81.	OH+HO ₂ →H ₂ O+O ₂	5.00E07	0.0	500.0	6
82.	O+HO ₂ →OH+O ₂	6.30E07	0.0	350.0	7

k is expressed in m-mol-s units.

p , pressure. The subscript i denotes the i -th species.

It is also assumed that a gas mixture comprises twenty-five species and that eighty-two elementary reactions take place among these species as tabulated in

Table 1. Nitrogen is assumed to be inert and works as one of the third bodies in recombination reactions. Most of the rate coefficients were chosen on the basis of the values proposed by Westbrook *et al.*¹³ and by Warnatz *et al.*¹². Some of the frequency factors, however, must be modified in order to make the reaction scheme comprehensive.

The governing equations were converted into the corresponding differential-difference equations according to the method of line⁸. The interval of distance is nonuniform, and is settled to be roughly proportional to the product of the temperature gradient and the temperature itself at that mesh point.

The boundary conditions at an unburnt side is that the temperature be 298K and the combustible gas mixture be composed of fuel and air. Those at a burnt side is that the burnt gas is heated up to the adiabatic flame temperature, and has an equilibrium composition at that temperature.

3. Results and Discussion

3.1 Validity of Proposed Reaction Scheme

The calculated burning velocities of the stoichiometric flames are listed in Table 2 together with their initial concentrations of fuel and the adiabatic flame temperatures. These burning velocities agree well with those obtained experimentally^{9,10}. Predicted burning velocity by means of a mathematical model is given as a result of complicated interactions among chemical and physical properties of a flame. Good agreement between the predicted and the experimental burning velocities permits us to conclude that the mathematical model proposed in this investigation is valid at least for the flames of the four hydrocarbons.

Table 2. Stoichiometric Hydrocarbon/Air Premixed Flames.

Hydrocarbon	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	CH ₄
Burning Velocity/m·s ⁻¹	1.56	0.76	0.49	0.39
Initial Mole Fraction of Fuel/%	7.73	6.53	5.65	9.48
Adiabatic Flame Temperature/K	2550	2380	2260	2230

3.2 Methane/Air Flame

3.2.1 Reaction Mechanism in Stoichiometric Flame

Figure 1a shows the profiles of the temperature and the mole fractions of stable species in a stoichiometric methane/air premixed flame. Water vapor is present even at a very early stage. Carbon dioxide, however, is not produced in a large quantity until the temperature is raised as high as 1300K, or until a fairly large amount of methane has been exhausted. The mole-fraction profiles of active or

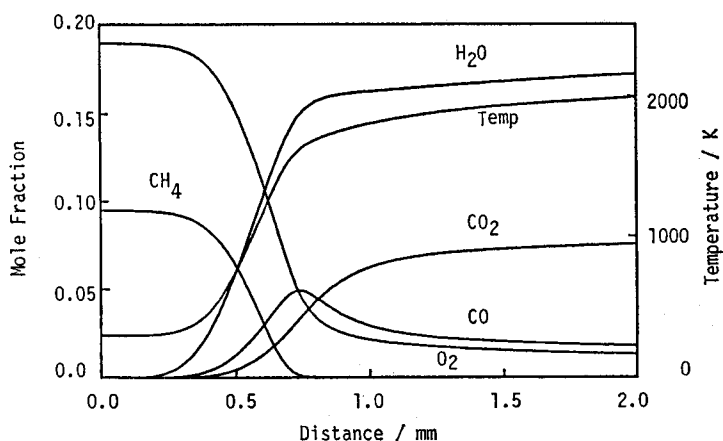


Fig. 1a. Profiles of temperature and the mole fractions of stable species in the stoichiometric methane flame.

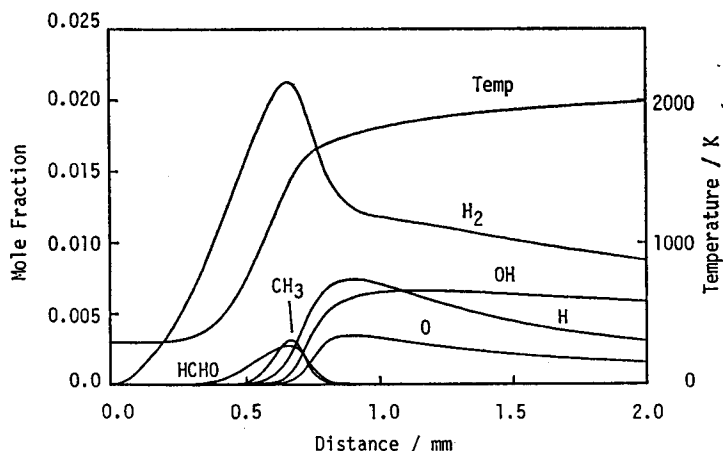


Fig. 1b. Profiles of temperature and the mole fractions of unstable and intermediate species in the stoichiometric methane flame.

intermediate species are given in Fig. 1b. The three active species, OH radicals and H and O atoms, increase at higher temperatures.

Figure 2 indicates the rates of heat increase due to convection, conduction, heat transfer accompanying species diffusion and heat release on account of chemical reactions. Heat release does not increase at low temperatures, suggesting that this flame is a typical example of the flames propagating thermally, where the temperature is raised chiefly by means of thermal conduction toward a low-temperature region. The heat-release rate decreases very steeply immediately after it reaches a maximum value. In other words, a sufficient amount of active species is not left any more to recombine

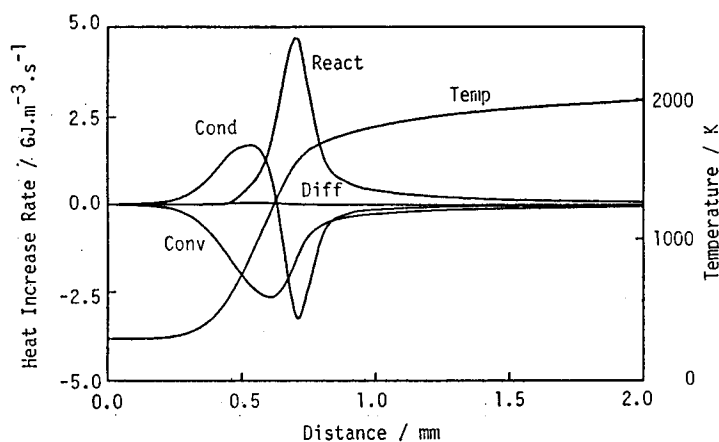


Fig. 2. Rates of heat increase due to convection (Conv), conduction (Cond), heat transfer accompanying species diffusion (Diff) and heat release (React) in the stoichiometric methane flame.

releasing some thermal energy when the gas mixture goes into a so-called recombination zone.

Figure 3a shows the ratio of the share of carbon atoms in CH_4 , CO , CO_2 and the other species. Figure 3b shows their detailed distributions in the other species except the fuel, CO and CO_2 . It is noteworthy that about 5% of the carbon atoms are shared with C_2H_6 at about 1200K, and the reaction paths through C_2 hydrocarbons cannot simply be neglected. The relative distributions of hydrogen atoms tell that quite a large quantity of hydrogen atoms are given to the final product, H_2O , even at the early stages of combustion. Water vapor contains about half of the hy-

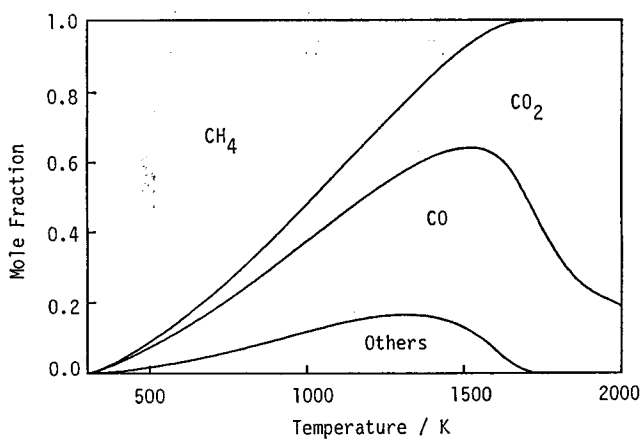


Fig. 3a. Distribution of carbon atoms in CH_4 , CO , CO_2 and the other species in the stoichiometric methane flame.

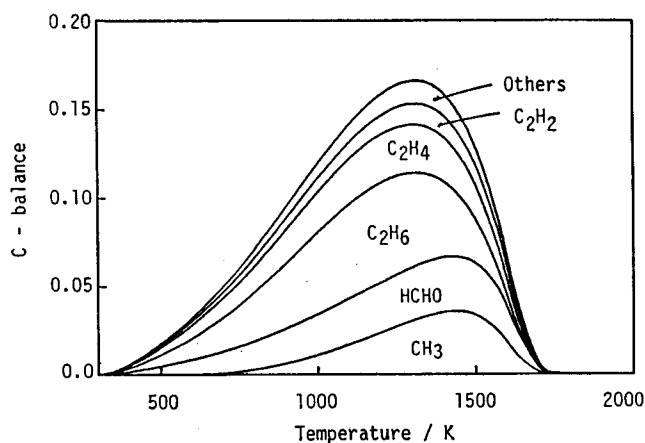


Fig. 3b. Distribution of carbon atoms in the intermediate species in the stoichiometric methane flame.

drogen atoms at a temperature as low as 1000K.

The mechanism of the combustion reaction in the stoichiometric methane flame is rather complicated when reaction pathways via C₂ hydrocarbons are taken into consideration. Its reaction mechanism was investigated both at a low temperature and a high temperature. The low temperature is assumed to be the one where the heat-release rate is equal to the rate of heat increase due to conduction, 1120K. The contributions of chemical reactions cannot be neglected at temperatures higher than this temperature. Therefore, this can reasonably be the temperature where chemical reactions are actually initiated in the flame. On the other hand, the high temperature is chosen to be the one where the heat-release rate becomes maximum (1550K). The reaction mechanism at the high temperature is given in Fig. 4. The arrow in the figure denotes the direction of the net reaction between the concerned two species. The width of the line is proportional to the rate of change in the carbon atoms passing through that reaction path.

The ratio of the carbon atoms reacting through C₂ hydrocarbons via reaction



to those reacting to CH₃O or HCHO is about three at low temperatures. However, half of C₂H₆ does not further react, and is accumulated as that very species in the gas mixture. Some of the ethane is decomposed to CH₃ radicals again via C₂H₅. On the contrary, the CH₃ radicals reacting through the C₁-hydrocarbon routes can be oxidized down to carbon monoxide. The role of CH₃O is now in discussion, and, for example, Westbrook *et al.* have taken it into account¹³, but Warnatz *et al.* have not²³. About 40% of the CH₃ radicals pass through reaction



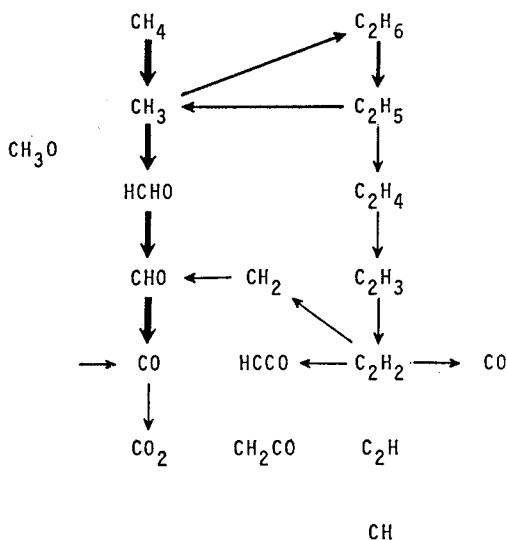


Fig. 4. Reaction mechanism of the stoichiometric methane flame at 1550 K.

and the rest of them through



at 1120K. The contribution of the latter reaction increases with an increasing temperature. The methoxy radicals are further decomposed at once through reactions



and



At 1550K, most of the methane is oxidized sequentially as $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{HCHO} \rightarrow \text{CHO} \rightarrow \text{CO}$ through the following reactions, respectively:



The percentage of the rates of reactions (C2. R2) and (C2. R3) is 55% and 35% for the total dehydrogenation of methane, respectively; that of reaction (C2. R8) is 65%; that of reactions (C2. R15) and (C2. R14) is 65% and 20%; and almost all formyl radicals are decomposed to carbon monoxide through reaction (C2. R22). About 20% of the CH_3 is recombined to C_2H_6 via reaction (C2. R9), but most of it comes back again passing C_2H_5 through reaction



The reaction mechanism of the oxidation of C₂ hydrocarbons will be analyzed in the following subsection.

About 85% of the carbon monoxide cannot yet be oxidized into CO₂ even at this temperature. Its oxidation is activated only after the methane has been exhausted. Almost all carbon monoxide reacts with hydroxyl radicals via reaction



The slow oxidation of carbon monoxide is explained as follows. There are several reactions consuming OH radicals such as reactions (C2. R2), (C2. R72), (C2. R14) and (C2. R23) at high temperatures. The oxidation step of carbon monoxide, however, has the smallest rate constant among them, though it has a negative activation temperature. It can be activated for the first time after all the other consumption reactions of OH radicals have actually been completed.

Heat release due to chemical reactions is caused predominantly by the following reactions: reaction (C2. R1) at low temperatures, reaction (C2. R9) at 950-1350K, reaction (C2. R8) at 1400-1650K, reaction (C2. R23) at 1700-1800K, and reactions (C2. R76) and (C2. R77) at higher temperatures. The contribution of reaction (C2. R8) is the most important. The fairly steep decrease in the heat-release rate after passing its maximum value as shown in Fig.2 is ascribable to the decrease in the rate of the above reaction. It is noteworthy that reaction



proceeds in the reverse direction and releases some thermal energy in a low-temperature region, while this reaction is generally considered one of the initiation reactions. The evaluation of the rate constant of its reverse reaction must be exact from the viewpoint of the heat release at low temperatures.

3.2.2. Reaction Mechanism under Various Equivalence Ratios

It is expected that the combustion reaction in methane/air premixed flames proceeds in various reaction mechanisms depending on their equivalence ratios. The reaction paths which pass through the C₂ hydrocarbons are not important under the stoichiometric condition as described above, though its contribution cannot be evaluated to be negligibly small. They are, however, of importance as a starting step of soot formation under rich conditions. Here, we shall simulate three more methane flames with various equivalence ratios, and investigate their reaction mechanisms by comparing them with one another.

The equivalence ratios of the flames added here are 1.56, 1.18 and 0.61. The calculated burning velocities are 0.11 m/s, 0.41 m/s and 0.14 m/s, respectively. Those velocities are in good agreement with experimental values, which are summarized by Andrews and Bradley¹¹⁾.

As the equivalence ratio increases, the oxidation of CO is naturally suppressed and more carbon monoxide is left unburnt even at the adiabatic flame temperature. Figures 5a, 5b and 5c present the distributions of carbon atoms to the species except CH_4 , CO and CO_2 in the three methane flames (see also Fig. 3b). Those distributions in the flames with the equivalence ratios of 1.18 and 1.0 are fairly similar, though the distribution in the C_2 hydrocarbons is large in the former flame. More than 5% of the carbon atoms are contained temporarily in the C_2 hydrocarbons even in the methane flame with the equivalence ratio of 0.61. In the richest methane flame in this investigation, the ratio of the carbon atoms shared with C_2 hydrocarbons increases, and it is indicated that those C_2 hydrocarbons react toward C_2H_2 .

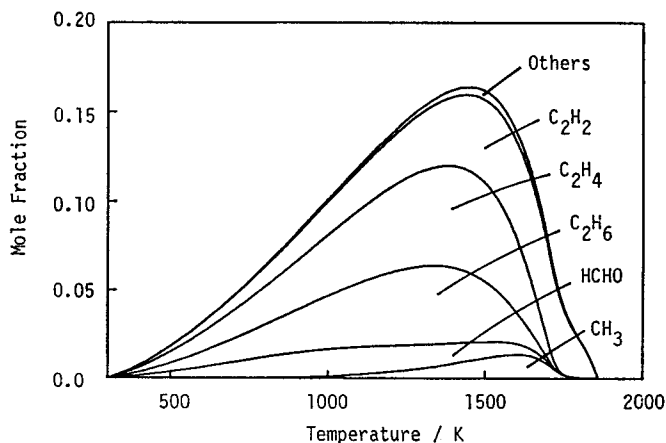


Fig. 5a. Distribution of carbon atoms in the intermediate species in the methane flame with the equivalence ratio of 1.56.

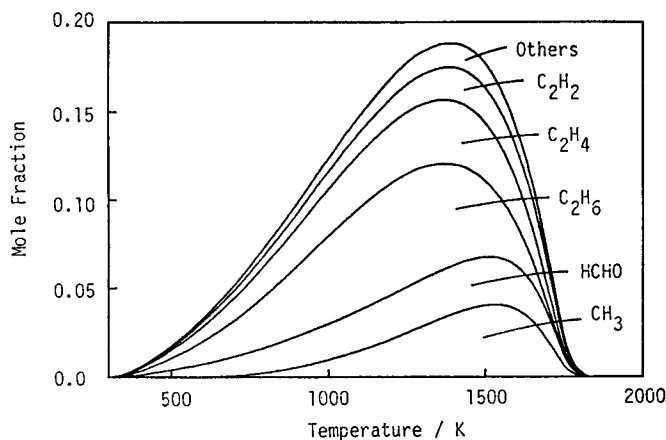


Fig. 5b. Distribution of carbon atoms in the intermediate species in the methane flame with the equivalence ratio of 1.18.

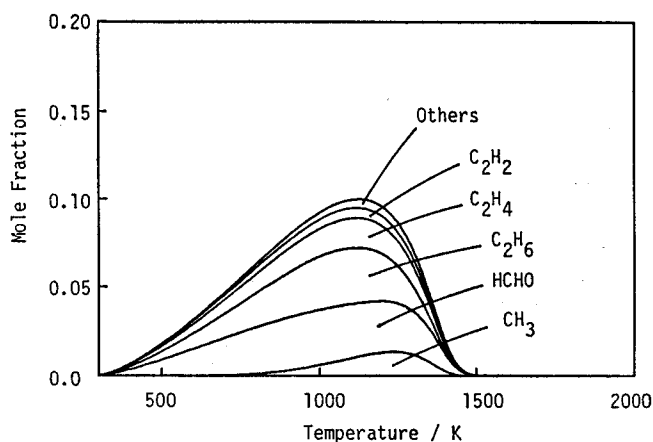


Fig. 5c. Distribution of carbon atoms in the intermediate species in the methane flame with the equivalence ratio of 0.61.

3.2.3. Application of Simple Reaction Scheme

As described above, the reaction paths through the C_2 hydrocarbons cannot be neglected for the combustion of methane even under the stoichiometric condition in order to investigate its reaction mechanism in detail. However, the above reaction paths are not major ones at least under the stoichiometric and lean conditions. There may be some combustion phenomena which can be investigated without considering the detailed reaction mechanism. A simple reaction scheme among C_1 compounds and oxygen will, therefore, be proposed. Also the criterion for its application and the difference in the results obtained by means of both reaction schemes will be discussed.

A reaction scheme for the combustion of methane was made on the basis of the reaction scheme for the combustion of C_1 hydrocarbons (Table 3) where the reactions including C_2 compounds were naturally omitted. Furthermore, the frequency factor of reaction (C2. R22) must be multiplied by a factor of 0.284. Otherwise, the burning velocity of the stoichiometric methane/air premixed flame increases up to 0.49 m/s. The routes via the C_2 hydrocarbons are approximately equivalent to the suppression of the rate of the sequential oxidation of CH_4 . In other words, those routes have inhibiting effects on the methane combustion.

The predicted burning velocity for the stoichiometric methane flame is 0.38 m/s, while that obtained using the C_2 -hydrocarbon reaction scheme is 0.39 m/s. Figure 6 shows the profiles of the temperature and the heat-release rate of the stoichiometric methane flame calculated by using both reaction schemes. Figures 7a and 7b show the mole-fraction profiles of the stable and active or intermediate species, respectively. These profiles are in good agreement except those of H_2O and H_2 . The comparison

Table 3. C₁ Hydrocarbon-O₂ Reaction Scheme

$$k = A \cdot T^n \cdot \exp(-E/T)$$

No.	Reaction	A	n	E
1.	CH ₄ +M→CH ₃ +H+M	1.41E10	0.0	44500.0
2.	CH ₄ +OH→CH ₃ +H ₂ O	3.47E-3	3.08	1010.0
3.	CH ₄ +H→CH ₃ +H ₂	2.20E-2	3.0	4400.0
4.	CH ₄ +O→CH ₃ +OH	1.20E01	2.1	3840.0
5.	CH ₃ +HO ₂ →CH ₃ O+OH	3.24E07	0.0	0.0
6.	CH ₃ +O ₂ →CH ₃ O+O	2.51E07	0.0	14600.0
7.	CH ₃ +OH→HCHO+H ₂	3.98E06	0.0	0.0
8.	CH ₃ +O→HCHO+H	7.00E07	0.0	0.0
9.	CH ₃ O+O ₂ →HCHO+HO ₂	1.00E06	0.0	3020.0
10.	CH ₃ O+M→HCHO+H+M	5.01E07	0.0	10600.0
11.	HCHO+OH→CHO+H ₂ O	7.59E06	0.0	85.5
12.	HCHO+H→CHO+H ₂	3.31E08	0.0	5280.0
13.	HCHO+O→CHO+OH	5.01E07	0.0	2310.0
14.	HCHO+M→CHO+H+M	3.31E10	0.0	40800.0
15.	CHO+OH→CO+H ₂ O	1.00E08	0.0	0.0
16.	CHO+H→CO+H ₂	2.00E08	0.0	0.0
17.	CHO+O→CO+OH	1.00E08	0.0	0.0
18.	CHO+O ₂ →CO+HO ₂	3.98E06	0.0	3520.0
19.	CHO+M→CO+H+M	1.42E09	0.0	8460.0
20.	CO+OH→CO ₂ +H	4.40E00	1.5	-373.0
21.	CO+O+M→CO ₂ +M	5.89E09	0.0	2060.0
22.	CO+HO ₂ →CO ₂ +OH	1.51E08	0.0	11900.0
23.	CO+O ₂ →CO ₂ +O	3.16E05	0.0	18900.0
24.	H+O ₂ →OH+O	2.20E08	0.0	8450.0
25.	O+H ₂ →OH+H	1.80E04	1.0	4480.0
26.	OH+OH→O+H ₂ O	6.30E06	0.0	550.0
27.	OH+H ₂ →H+H ₂ O	2.20E07	0.0	2590.0
28.	H+H+M→H ₂ +M	2.60E06	-1.0	0.0
29.	O+O+M→O ₂ +M	1.90E01	0.0	-900.0
30.	H+O+M→OH+M	3.60E06	-1.0	0.0
31.	OH+H+M→H ₂ O+M	4.06E10	-2.0	0.0
32.	H+O ₂ +M→HO ₂ +M	5.00E03	0.0	-500.0
33.	H+HO ₂ →H ₂ +O ₂	2.50E07	0.0	350.0
34.	H+HO ₂ →OH+OH	2.50E08	0.0	950.0
35.	H+HO ₂ →O+H ₂ O	9.00E05	0.5	2000.0
36.	OH+HO ₂ →H ₂ O+O ₂	5.00E07	0.0	500.0
37.	O+HO ₂ →OH+O ₂	6.30E07	0.0	350.0

k is expressed in m-mol-s units.

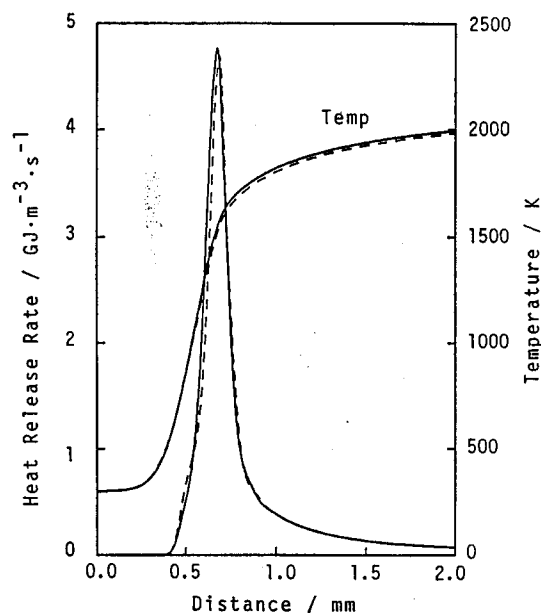


Fig. 6. Comparison of the profiles of temperature and the heat release rate in the stoichiometric methane flame predicted by means of the C_1 and the C_2 reaction scheme.

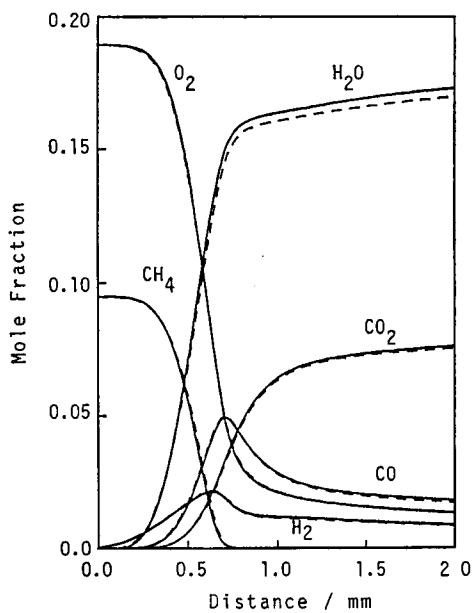


Fig. 7a. Comparison of the profiles of the mole fractions of the stable species in the stoichiometric methane flame predicted by means of the C_1 and the C_2 reaction scheme.

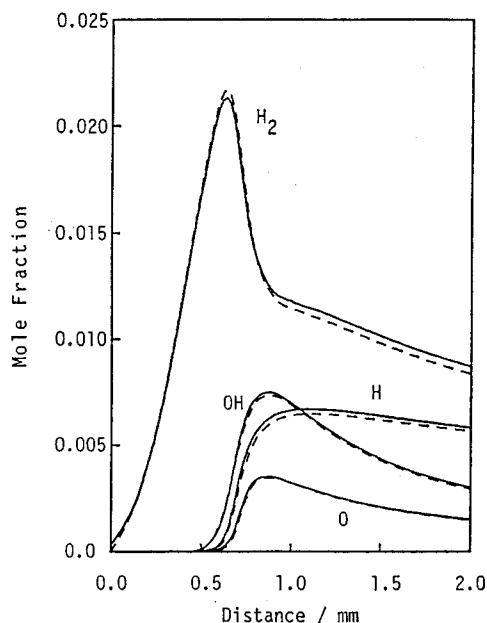


Fig. 7b. Comparison of the profiles of the mole fractions of the intermediate species in the stoichiometric methane flame predicted by means of the C_1 and the C_2 reaction scheme.

of the ratios of the carbon atoms shared in the other species excluding CH_4 , CO and CO_2 indicates that the ratio obtained by means of the C_2 -hydrocarbon scheme is about 1.5 times as large as that calculated by using the C_1 -hydrocarbon reaction scheme.

The fairly precise agreement between the results obtained by means of both reaction schemes permits us to use either reaction scheme for combustion of methane under the stoichiometric or lean conditions. The choice must depend on the problems to be solved.

3.3 Reaction Mechanisms in Stoichiometric Acetylene, Ethylene and Ethane Flame

The temperature profiles of the three flames are shown in Fig. 8, together with that of the stoichiometric methane flame for reference sake. The gradient of temperature increases in the order of the decreasing number of hydrogen atoms contained in a fuel molecule. The thickness of the flame front of the three flames are 0.11 mm, 0.19 mm and 0.27 mm, respectively, if a flame front is defined as the region where the temperature increases steeply. The temperature gradient becomes gentle in all the flames at temperatures 600–800K lower than their adiabatic flame temperatures.

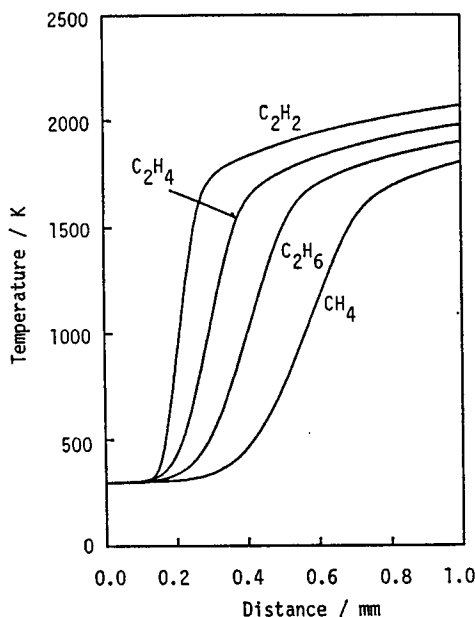


Fig. 8. Profiles of temperature in the stoichiometric acetylene, ethylene, ethane and methane flame.

The mole-fraction profiles of the fuel, the combustion products, O_2 and CO in the acetylene flame are shown in Fig. 9a as an example. There is a small dent in the profile of the C_2H_2 mole fraction around 500K, which cannot be observed in the other two flames. This indicates that the fuel is remarkably consumed in the low-temperature region. Figure 9b shows the mole-fraction profiles of the active species and H_2 in the acetylene flame. The maximum concentration of H_2 in the acetylene flame is about half of those in the other two flames. However, that in the methane flame is almost the same as those in the ethylene and the ethane flames. On the other hand, the mole fractions of the active species, especially those of the hydrogen and the oxygen atoms, are much larger in the acetylene flame.

The distribution of the carbon atoms in C_2H_2 , CO , CO_2 and the other species in the acetylene flame are given in Fig. 10. Acetylene is oxidized into CO or into the other species except CO_2 , even at very low temperatures. Then, the fuel and the species other than CO and CO_2 have been decomposed by the time when the temperature reaches about 1700K. At higher temperatures, these changes in the carbon balance are similarly observed in the other hydrocarbon flames including the methane flame as shown in Fig. 3a. However, the acetylene flame has the characteristic that the amount of carbon atoms contained in the intermediate species becomes maximum at a temperature as low as 700K. In the other three flames it has a peak at around

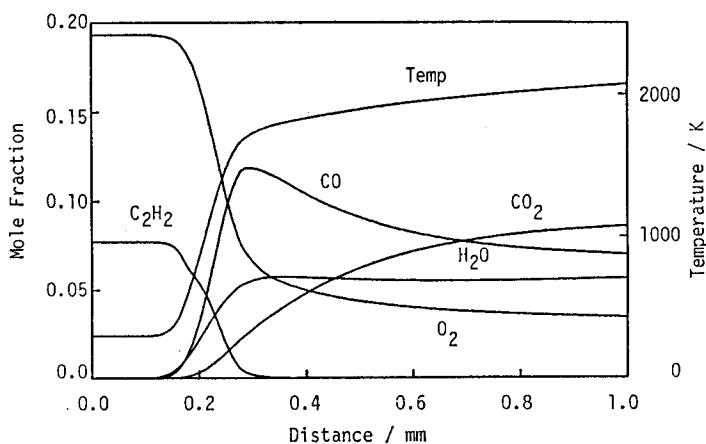


Fig. 9a. Profiles of temperature and the mole fractions of stable species in the stoichiometric acetylene flame.

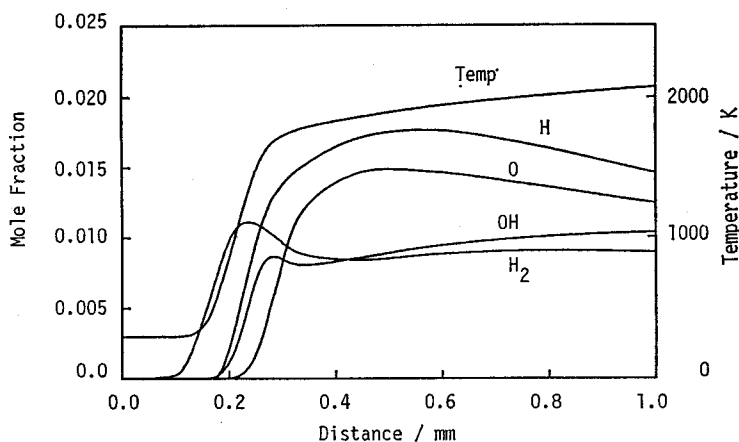


Fig. 9b. Profiles of temperature and the mole fractions of unstable and intermediate species in the stoichiometric acetylene flame.

1200K. The detailed discussion on the carbon-atom distribution to the intermediaries reveals the following: (1) In the acetylene flame, C_2H_3 radicals are produced in fairly large quantity at low temperatures. Also, more than 80% of the remaining carbon atoms except those contained in C_2H_2 , CO and CO_2 are distributed to the C_2H_3 radicals. (2) In the ethylene and the ethane flames, the amount of the remaining carbon atoms reaches 20%, but the ratio of those contained in the active species is fairly small, especially in the ethane flame. (3) In the ethane flame, the ratio of the fuel oxidized via C_2 hydrocarbons to that via C_1 hydrocarbons is almost unity, though some of the CH_3 radicals are recombined again to ethane.

The reaction mechanism of the three flames were investigated at two typical

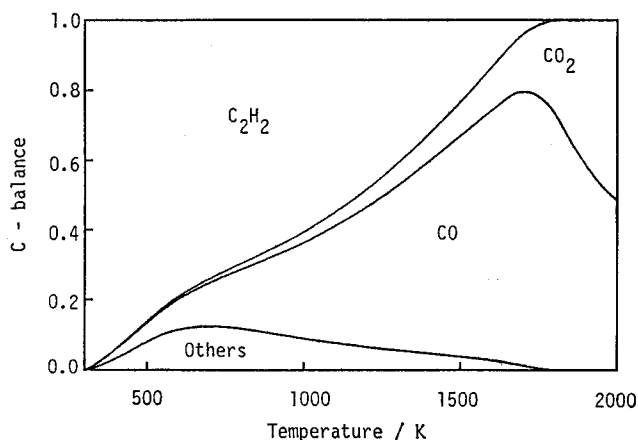


Fig. 10. Distribution of carbon atoms in C₂H₂, CO, CO₂ and the other species in the stoichiometric acetylene flame.

temperatures. The first temperature is where the heat-release rate becomes equal to the rate of increase in thermal energy on account of conduction as a representative of low temperature (800K for the acetylene flame, 1000K for the ethylene and 1030K for the ethane flame, respectively). The second temperature where the heat-release rate becomes maximum is a representative of high temperature (1510K for the acetylene flame, 1500K for the ethylene flame and 1550K for the ethane flame, respectively). The reaction mechanisms at these high temperatures are illustrated in Figs. 11a, 11b

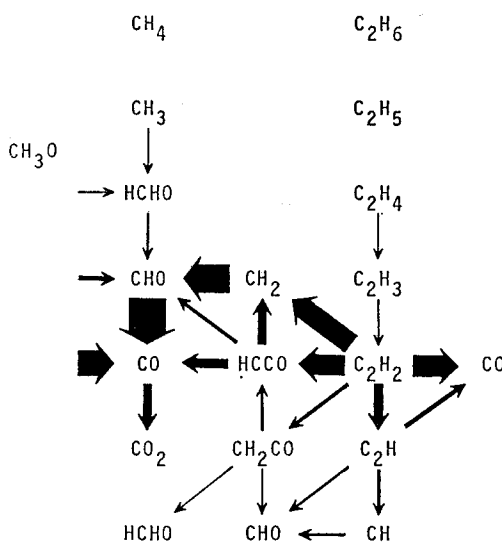


Fig. 11a. Reaction mechanism of the stoichiometric acetylene flame at 1510 K.

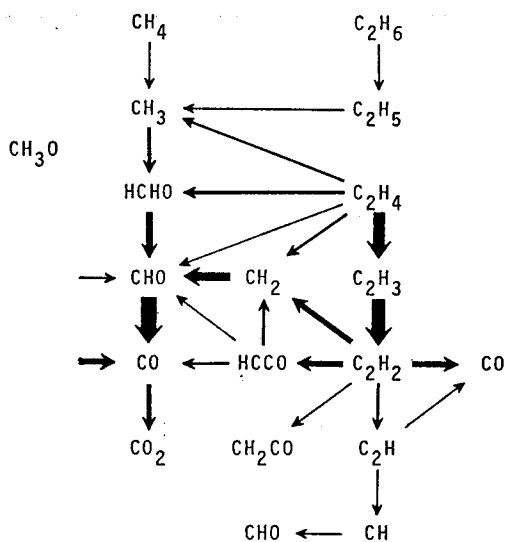


Fig. 11b. Reaction mechanism of the stoichiometric ethylene flame at 1500 K.

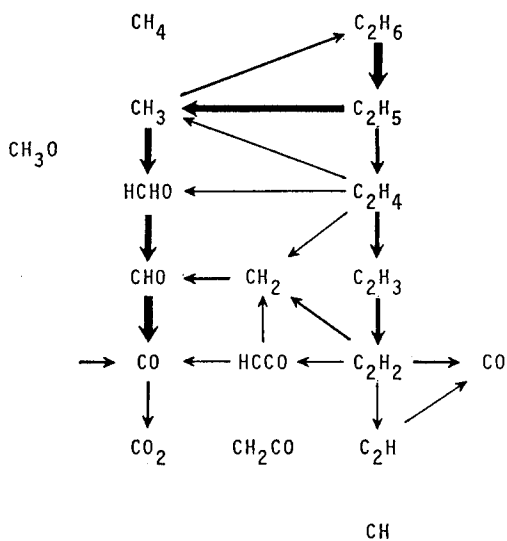
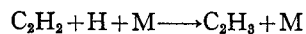


Fig. 11c. Reaction mechanism of the stoichiometric ethane flame at 1550 K.

and 11c.

In the acetylene flame, a large amount of C_2H_3 is produced at temperatures lower than 1000K, predominantly through reaction



—(C2. R42)

and it is reconverted again to C₂H₂ at 800-1500K via reaction



Some C₂H₃ is further reduced to C₂H₄. The dent observed in the mole-fraction profile of acetylene can be ascribed to the above reactions. No other remarkable reactions occur in the low-temperature region. At 1510K, about 55% of acetylene is directly transformed into CO and CH₂ through reaction



About 30% of acetylene is oxidized to HCCO through reaction



Most of the remainder is converted to C₂H via the following reactions alternatively;



and



As the second step, HCCO radicals react with H atoms yielding CH₂ and CO through reaction



Then the methylene radicals produced through reaction (C2. R49) and this species is further oxidized with O₂ to CHO via reaction



The produced C₂H radicals react with O atoms or O₂ through reactions



and



respectively.

In the ethylene flame, about 65% of the fuel is once converted to C₂H₃ and C₂H₂ through reactions



and



and then reaction (C2. R40) at a wide range of temperature. Reaction (C2. R34) is predominant at high temperatures, while reaction (C2. R33) has a larger rate at low temperatures. The following oxidation processes are the same as those of the acetylene flame. The remaining ethylene is directly oxidized to HCHO or CHO, or transformed to CH₂ radicals. A small amount of ethylene is decomposed into CH₃ radicals.

In the ethane flame, the fuel reacts with H atoms or OH radicals through reactions



and



The former reaction makes a larger contribution both in a low- and a high-temperature region. At low temperatures, most of C_2H_5 is dehydrogenated with O_2 yielding C_2H_4 via reaction



though the reaction rate is small. However, at temperatures higher than 1200K, more than half of C_2H_5 is decomposed into CH_3 through reaction -(C2. R10). In this temperature region, reaction



is added to the reaction path from C_2H_5 to C_2H_4 . Consequently, the ratio of the fuel oxidized through C_2 hydrocarbons to that through C_1 hydrocarbons is almost half. Some of the CH_3 radicals are recombined again to ethane.

4. Concluding Remarks

A reaction scheme expressing the combustion reactions of C_1 and C_2 hydrocarbons was proposed. This scheme was applied to one-dimensional methane, acetylene, ethylene and ethane premixed flames. The following conclusions were obtained:

1. In a methane premixed flame, the heat release on account of reactions rarely contributes to an increase in thermal energy at low temperatures. The reaction paths via C_2 hydrocarbons cannot be neglected even under the stoichiometric condition especially at low temperatures, but some ethane is accumulated without further oxidation. About 40% of the CH_3 radicals react via CH_3O radicals at around 1000K. At high temperatures, a predominant exothermic reaction is (C2. R8), while at low temperatures, reaction -(C2. R1) releases much thermal energy. The reverse reaction of this initiation reaction must be evaluated exactly. A simple reaction scheme for the methane combustion under lean or stoichiometric conditions was proposed. It is composed of thirty-seven elementary reactions. In that scheme, the rate constant of reaction (C2. R22) is reduced instead of removing the C_2 -hydrocarbon reactions, which depress the combustion reaction of methane.

2. In the stoichiometric acetylene premixed flame, the formation of C_2H_3 and its decomposition to C_2H_2 occur at low temperatures. Acetylene is directly decomposed to CH_2 and CO at high temperatures, or is oxidized via HCCO radicals, which are decomposed into CH_2 and CO reacting with H atoms. The methylene radicals are then oxidized to CHO radicals.

3. In the ethylene flame, the ratio of the carbon atoms contained in the active species becomes smaller than that in the acetylene flame. About 65% of C_2H_4 passes through C_2H_3 and C_2H_2 .

4. The C_1 -hydrocarbon reaction path becomes important at high temperatures

in the ethane flame. About 30% of the carbon atoms are transformed to CH₃ radicals via C₂H₅.

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