© 1991 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 64, 3098—3104 (1991) [Vol. 64, No. 10

Exothermic Reactions in C_2 Hydrocarbon Flames

Seishiro FUKUTANI,[*] Nílson KUNIOSHI, Keizo SAKAGUCHI, and Hiroshi JINNO[†]
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University,
Yoshida-honmachi, Sakyo-ku, Kyoto 606
[†]Department of Chemistry, Faculty of Science and Engineering,
Sophia University, Kioicho 7-1, Chiyoda-ku, Tokyo 102
(Received June 7, 1991)

Premixed stoichiometric flames of acetylene, ethylene, and ethane with air were investigated using a chemical scheme composed of eighty-two pairs of elementary reactions to illustrate the dependence of the propagation mechanisms of C_2 hydrocarbon flames on the heat release distribution. The general role of heat release distribution through flames was depicted by means of an analytical treatment of the governing equations with the thermal properties of the gases being constant and the temperature profile given by an appropriate function of the position in the flame. It was found that the amount of heat released by chemical reactions at low-temperature regions of a flame is of fundamental importance for its propagation and that the main trigger of exothermic reactions at those zones is hydrogen atoms, which diffuses from the flame front; in the acetylene flame reactions consuming hydrogen atoms at the low-temperature region were found to yield all the heat released at that zone. Heat release distribution extended down to low-temperature regions was found to be able to lead to large burning velocities even though the amount of heat released at each position was small.

Since in the low-temperature region of a premixed flame thermal energy must increase only by the supply from the high-temperature region, the propagation mechanism of a premixed flame can be classified into two types according to the way by which the supply of energy occurs:[1] Thermal propagation and diffusion-controlled propagation. In the latter mode chemical enthalpy is carried by diffusion of active species such as hydrogen atoms and transformed to thermal energy by exothermic reactions occurring in the low-temperature region. Hydrogen–air premixed flames propagate mainly through this mode at least near stoichiometric conditions[2] and methane flames through the former mode.[3]

Acetylene, ethylene, and ethane contain two carbon atoms but different number of hydrogen atoms in their molecules. A hasty consideration may lead to the conclusion that the propagation of ethane flames is governed by the diffusion of hydrogen atoms and that of acetylene by thermal conduction. Experimental measurements of the burning velocity of those three flames,[4] however, have clarified that ethane flames possess burning velocities similar to that of methane, and acetylene flames have velocities which are less than those of hydrogen flames but considerably large among premixed flames. Those facts may warn us not to conclude rashly that the propagation mechanism of a premixed flame is simply deduced on the basis of the chemical composition of the fuel molecule.

The purposes of this paper are to elucidate the following two points by means of computer simulation using a detailed chemical reaction model: (1) What is the decisive factor to determine the propagation mechanism in the three C_2 hydrocarbon premixed flames; and (2) How heat release by chemical reactions controls the burning velocity.

Simulation Model

Some usual assumptions for models of flat flames[2] derive the following governing equations, which were used in the model in this investigation:

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

$$\frac{\partial}{\partial t}(c_p\rho T)+\frac{\partial}{\partial x}(c_p\rho Tv)= \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right)+\sum_i D_i\rho\frac{\partial h_i}{\partial x}\frac{\partial \omega_i}{\partial x}-\sum_i h_i\phi_i, \tag{2}$$

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

$$p=\rho RT\sum_i\frac{\omega_i}{m_i}, \tag{4}$$

where ρ is the density, v the flow velocity, T the temperature, p the pressure, c_p the specific heat, and λ the thermal conductivity of the gas mixture; ω_i is the mass fraction, ϕ_i the net production rate, h_i the enthalpy, m_i the molar mass and D_i the diffusion coefficient of the i-th species; and R is the gas constant.

The reaction scheme which was proposed in a previous paper[3] comprises eighty-two pairs of elementary reactions among twenty-five chemical species of C_1 and C_2 hydrocarbons and hydrogen–oxygen-containing species. The model gives valid burning velocities for methane flames with a wide range of equivalence ratio.[3]

Table 1. Stoichiometric Hydrocarbon–Air Premixed Flames

Hydrocarbons	C_2H_2	C_2H_4	C_2H_6
Burning velocity/m s^{-1}	1.56	0.76	0.49
Adiabatic flame temperature/K	2550	2380	2260
Experimental burning velocity[4]/m s^{-1}	1.56	0.78	0.48

As for the C_2 flames, however, it gives burning velocities agreed with the experimental values only for the stoichiometric and lean conditions (see Table 1); for rich conditions the calculated burning velocities are larger than the corresponding experimental velocities since the decrease in the burning velocity due to the waste of a small part of the fuel in the soot-forming process is neglected in the reaction scheme. In this work, stoichiometric flames of the C_2 hydrocarbons are, therefore, investigated by using the proposed scheme.

The boundary conditions were given as follows: at the unburned side the temperature is 298 K and the gas mixture contains only the fuel and air, and at the burned side the temperature is raised up to the adiabatic flame temperature, which is obtained by the chemical equilibrium calculation based on the total enthalpy at the unburned side, and the gas has the corresponding equilibrium composition at that temperature. A simulated flame can be kept in the steady state only when the flow velocity just agrees with the burning velocity, and this value was obtained by the trial-and-error method.

Results and Discussion

Structures of the Flames. Figure 1 shows the temperature profiles of the three C_2 hydrocarbon premixed flames. The temperature gradients increase in the order of the increasing burning velocity. In the ethane flame the temperature is elevated gradually at low temperatures just like an exponential function. In the acetylene flame, on the contrary, the temperature gradient increases steeply. The ethylene flame keeps an intermediate temperature gradient between those of the acetylene and ethane flames over the whole region.

Figure 2 shows the exothermic rates of the three flames as functions of temperature. Distinguished differences among those rates are: (1) the rate of the ethane flame is much smaller than that of the acetylene flame; (2) in the acetylene flame heat evolution starts increasing at such a low temperature as 450 K and rises with a large slope particularly at low temperatures, but in the ethane flame it increases from 700 K and keeps almost a constant gradient.

Analytical solution of the thermal energy conservation equation, Eq. 2, neglecting chemical reactions occurring at low temperatures yields the following results: if the thermal properties of the gas mixture can be treated as being constant, (1) the reaction-zone thickness of a premixed flame is inversely proportional to the burning velocity and (2) the burning velocity is proportional to the square root of the averaged reaction rate.[1] Those two predictions seem to be valid in the three C_2 flames as suggested by Figs. 1 and 2. Strictly speaking, however, the simulated burning velocity of the acetylene flame is larger than the value of the analytical prediction. The deviation comes from the indifference to the reaction-rate distribution or, correspondingly, to the exothermic rate distribution in the analytical treatment. The distribution of heat release throughout the flame, particularly at low temperatures, should be considered in order to estimate precisely the burning velocity of a premixed flame.

The inflow of chemical enthalpy into the low-temperature region of a premixed flame is substantially supported by hydrogen atoms diffused from the flame front. The second term in the right-hand side of Eq. 2

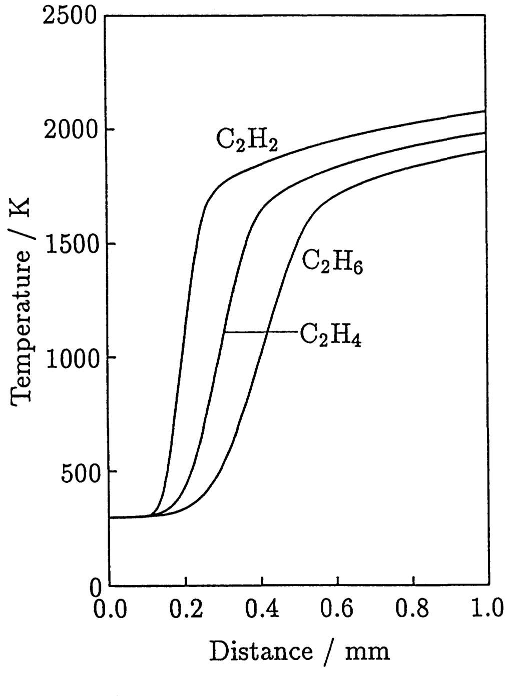

Fig. 1. Profiles of temperature in the stoichiometric C_2 hydrocarbon premixed flames.

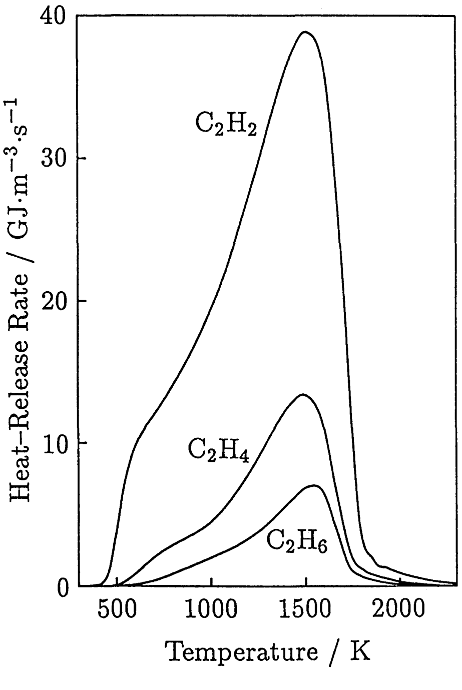

Fig. 2. Distributions of exothermic rates in the stoichiometric C_2 hydrocarbon premixed flames.

is called enthalpy transfer accompanying species diffusion. This popular designation, however, is not correct and that term does not strictly express the rate of enthalpy accumulation by species diffusion. The original enthalpy-conservation equation prescribes the conservation of total enthalpy (thermal enthalpy+chemical enthalpy):

$$\frac{\partial h}{\partial t}+\frac{\partial}{\partial x}(hv)=\frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right)+\sum_{i}\frac{\partial}{\partial x}\left(D_i\rho h_i\frac{\partial \omega_i}{\partial x}\right), \quad (5)$$

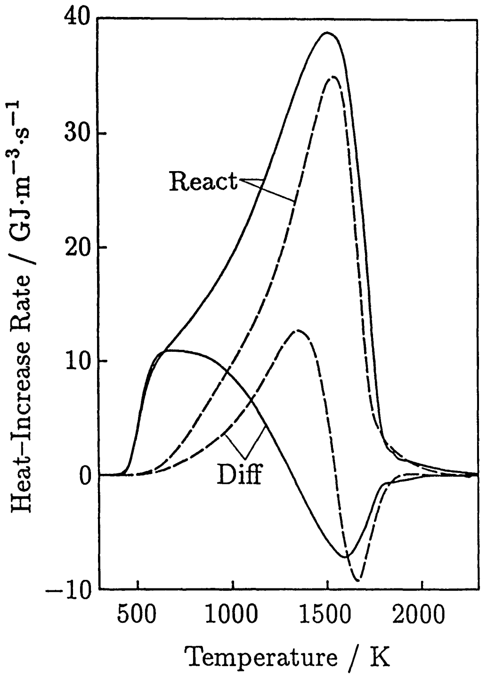

Fig. 3. Rates of the increase in enthalpy accompanying diffusion of hydrogen atoms (Diff) and those of heat release (React) in the acetylene (solid line) and ethane (dashed line) flames; the rates of the ethane flame are multiplied by a factor of 5.

where h is the total enthalpy per unit volume of the gas mixture. The second term in the right-hand side of Eq. 5 does designate the enthalpy carried by diffused species. This equation, however, does not involve explicitly an exothermic term and hence is usually transformed into the conservation equation of thermal enthalpy, Eq. 2. The so-called diffusion term appearing in Eq. 2, moreover, gives only a small contribution to the heat transfer toward low-temperature regions of premixed flames.[2,3]

Figure 3 depicts the rates of the increase in enthalpy due to diffusion of hydrogen atoms calculated according to Eq. 5 and the exothermic rates in the acetylene and ethane flames, as typical examples. In the low-temperature region of the acetylene flame the exothermic rate agrees very well with the enthalpy-increase rate due to diffused hydrogen atoms; it should be noted that the intense heat release observed between 450 K and 600 K is thoroughly ascribable to the exothermic reactions which consume all the diffused hydrogen atoms. In the ethane flame, on the other hand, diffused hydrogen atoms do not work as a direct source of the heat release but work only as a trigger for reactions occurring at low temperatures; the role as a reaction trigger is also essential because combustion reaction cannot be easily initiated in an unburned gas mixture within a short time if they are activated only by rising temperature.

The temperature-increase mode in the low-temperature region of a premixed flame, therefore, does not simply depend on the amount of hydrogen atoms contained in the fuel molecule but on the mechanisms of the reactions occurring in the high- and low-temperature regions.

Reaction Mechanisms of Production and Consumption of Hydrogen Atoms. The mechanisms of combustion reactions in the C_2 hydrocarbon flames have been discussed by many authors based on computer simulation using various reaction schemes.[5–9] Figures 4a and

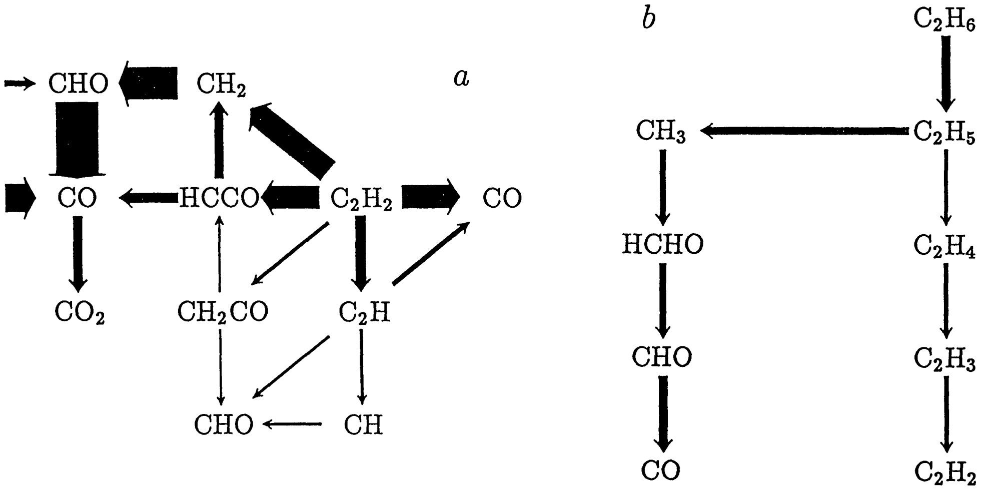

Fig. 4. Reaction pathways in the acetylene flame at 1510 K (a) and in the ethane flame at 1550 K (b). The width of the arrows is proportional to the rate of the corresponding route.

4b show the reaction pathways at the positions of the maximum exothermic rates in the acetylene and ethane flames obtained in this investigation. Carbon monoxide is slowly oxidized even at temperatures higher than 1500 K; only after conversion of all the hydrocarbons to carbon monoxide its oxidation proceeds fast.

A characteristic of the combustion reaction of the acetylene flame is that the reaction pathway from the fuel to carbon monoxide is short. Such a short span in the reaction pathway can lead to easy acceleration of the whole fuel oxidation without congestion of intermediate species. In the ethane flame, on the contrary, the main combustion route proceeds unexpectedly along the so-called C_1 route after the leap from ethyl radicals to methyl radicals through the reaction

$$C_2H_5 + H \rightarrow CH_3 + CH_3 \qquad (R10)$$

at high temperatures. This is a reason why ethane flames have burning velocity similar to that of methane flames. At temperatures lower than 1200 K, however, ethyl radicals are predominantly dehydrogenated to ethylene by the reaction

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2. \qquad (R31)$$

The ethylene flame holds the same mechanism as that of the acetylene flame since the fuel is once dehydrogenated to acetylene and reacts along the same route; the burning velocity settles down at an intermediate value between those of the acetylene and ethane flames.

In order to pursue the production and consumption of hydrogen atoms the rates of the elementary reactions in which hydrogen atoms participate are shown in Figs. 5a and 5b. Differences between the reactions of the acetylene and ethane flames are: (1) the reaction rates in the acetylene flame are much larger, as a whole, than those in the ethane flame; and (2) hydrogen atoms are consumed in a great amount in the low-temperature region of the acetylene flame.

The consumption of hydrogen atoms at low temperatures in the acetylene flame is due to the reactions

$$C_2H_2 + H + M \rightarrow C_2H_3 + M \qquad (R42)$$

and

$$C_2H_3 + H \rightarrow C_2H_2 + H_2. \qquad (R40)$$

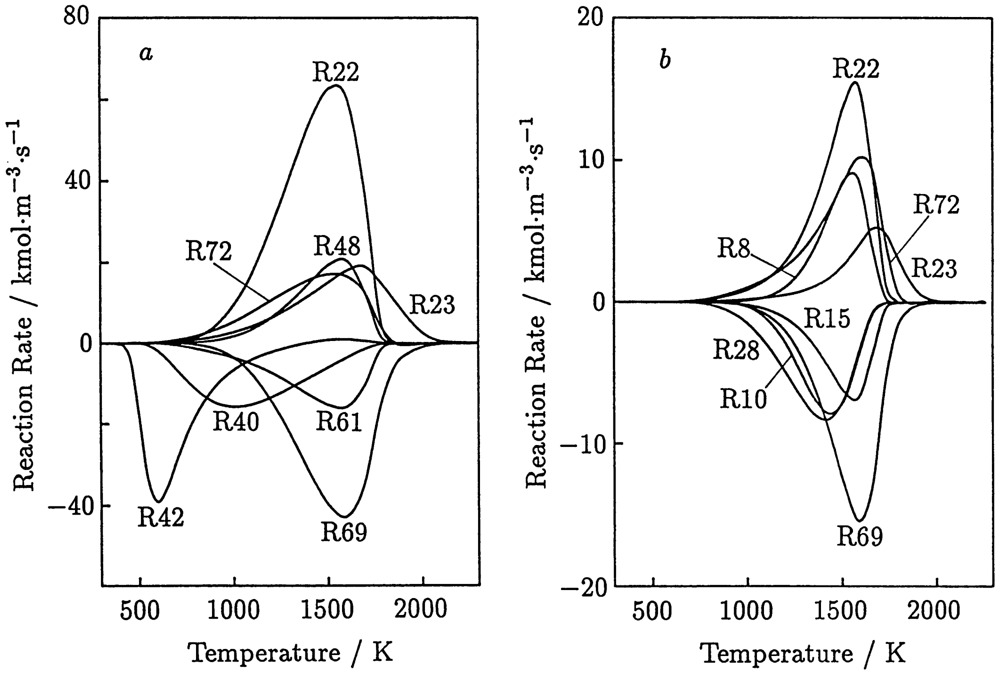

Fig. 5. Rates of the reactions in which hydrogen atoms participate in the acetylene (a) and ethane (b) flames. The negative rates express that the corresponding reactions consume hydrogen atoms.

R8: $CH_3 + O \rightarrow HCHO + H$
R10: $C_2H_5 + H \rightarrow CH_3 + CH_3$
R15: $HCHO + H \rightarrow CHO + H_2$
R22: $CHO + M \rightarrow CO + H + M$
R23: $CO + OH \rightarrow CO_2 + H$
R28: $C_2H_6 + H \rightarrow C_2H_5 + H_2$
R40: $C_2H_3 + H \rightarrow C_2H_2 + H_2$
R42: $C_2H_2 + H + M \rightarrow C_2H_3 + M$
R48: $C_2H_2 + O \rightarrow HCCO + H$
R61: $HCCO + H \rightarrow CH_2 + CO$
R69: $H + O_2 \rightarrow OH + O$
R72: $OH + H_2 \rightarrow H + H_2O$

The rate constant of reaction (R42) changes increasingly with decreasing temperature because of its negative activation energy. Hydrogen atoms diffused from the flame front, therefore, easily react with the fuel at low temperatures releasing a fairly large amount of heat, 193 kJ mol^{-1} at 500 K and 197 kJ mol^{-1} at 1000 K, for example. As temperature rises another possibility for their consumption, that is, reaction (R40) is added to the reaction mechanism. The rate constant of this reaction increases gradually with increasing temperature. This reaction also generates much heat, 249 kJ mol^{-1} at 500 K and 247 kJ mol^{-1} at 1000 K. The steep increase in exothermic rate of the acetylene flame shown in Fig. 2 is ascribed to these two reactions and the shoulder observed around 600 K comes from the intense exothermicity of reaction (R42).

The acetylene flame has thus a very effective source of heat release at low temperatures; the above described pair of reactions convert hydrogen atoms to molecular hydrogen and, at the same time, the fuel to vinyl radicals at the first stage and then the vinyl radicals back to acetylene at the second stage.

The production of hydrogen atoms is predominantly ascribable to the reaction

$$\mathrm{CHO} + \mathrm{M} \rightarrow \mathrm{CO} + \mathrm{H} + \mathrm{M} \qquad \text{(R22)}$$

at the flame fronts of hydrocarbon flames. As described above, the reaction path from the fuel to carbon monoxide is fairly short in the acetylene flame and, therefore, hydrogen atoms are yielded in a great amount at the flame front.

Moreover, the acetylene flame has advantages for fast transport of hydrogen atoms to the low-temperature region because of the thin reaction zone shown in Fig. 1 though this condition is naturally satisfied in a flame having large burning velocity since the reaction-zone thickness is inversely proportional to burning velocity.

Consequently, when the three conditions for supply of a sufficient amount of chemical enthalpy toward the low-temperature region, that is, production of hydrogen atoms at high temperatures, their diffusion toward low-temperature region and their consumption with heat release at low temperatures, are satisfied, the amount of chemical enthalpy easily exceeds that of thermal energy carried by thermal conduction, and therefore the flame is stably maintained according to the so-called diffusion-controlled propagation mechanism.

Role of Heat Release at Low Temperatures on Flame Propagation. As pointed out in the previous subsection the effects of heat release on the burning velocity must be discussed based on the magnitude of its rate and the shape of its distribution as well. The role of the distribution of exothermic rate, particularly at low temperatures, will be investigated here.

The temperature distribution in a flame must satisfy Eq. 2. The second term in the right-hand side of that equation gives the rate of heat transfer related to species diffusion and is negligibly small as described above, and the time-dependent term in the left-hand side equals zero at steady state; therefore Eq. 2 is reduced to an ordinary differential equation

$$\frac{\mathrm{d}}{\mathrm{d}x}(c_p \rho T v) = \frac{\mathrm{d}}{\mathrm{d}x}\left(\lambda \frac{\mathrm{d}T}{\mathrm{d}x}\right) - \sum_i h_i \phi_i. \qquad (6)$$

In the steady state ρv=const., and c_p and λ can be assumed to be constant in a first-order approximation, and thus Eq. 6 becomes

$$\lambda \frac{\mathrm{d}^2 T}{\mathrm{d}x^2} - c_p \rho v \frac{\mathrm{d}T}{\mathrm{d}x} - \sum_i h_i \phi_i = 0. \qquad (7)$$

In a low-temperature region, Eq. 7 is further simplified by neglect of the exothermic term and gives an analytical solution

$$T = \alpha \exp\left(\frac{c_p \rho v}{\lambda} x\right) + T_{\mathrm{u}}, \qquad (8)$$

where T_{u} is the temperature of the unburned gas mixture and α is an arbitrary constant fixing the position of the flame along the x-axis. Equation 8 shows that the temperature rises exponentially in the region preceding the exothermic region in a steady premixed flame, and the temperature gradient grows as the burning velocity increases.

On the other hand the temperature of a premixed flame cannot be raised higher than its adiabatic flame temperature. The temperature, therefore, must approach asymptotically the adiabatic flame temperature and have an inflection point in its distribution. The decline of the temperature gradient toward zero should consequently be actualized by the exothermic term, that is, the last term in Eq. 7.

When exothermic reactions start at a high temperature the heat release must reduce the temperature gradient within the small temperature interval remaining before the adiabatic flame temperature; therefore chemical reactions should emit heat with a large rate. On the contrary, when they occur at low temperatures even a small rate of heat release can shift the temperature gradient toward zero. These effects of the heat release are discussed by solving Eq. 7.

Unfortunately Eq. 7 cannot be solved analytically. The subject to elucidate in this subsection is, however, how burning velocity is influenced by heat release at low temperatures. Here, in contrast with the usual method, the temperature distribution in the exothermic region is assumed, at first, as a function of position and substituted into Eq. 7, and then the exothermic term is evaluated for the given temperature distribution.

The temperature distribution is given by using a logistic function:

$$T = \frac{T_0}{1 + \beta \exp(-bx)} + T_{\mathrm{u}}, \qquad (9)$$

where T_0, T_{u}, β and b are four arbitrary constants; such a function asymptotically approaches T_{u}, the temperature of the unburned gases, at $x = -\infty$, $T_0 + T_{\mathrm{u}} \equiv T_{\mathrm{ad}}$ at

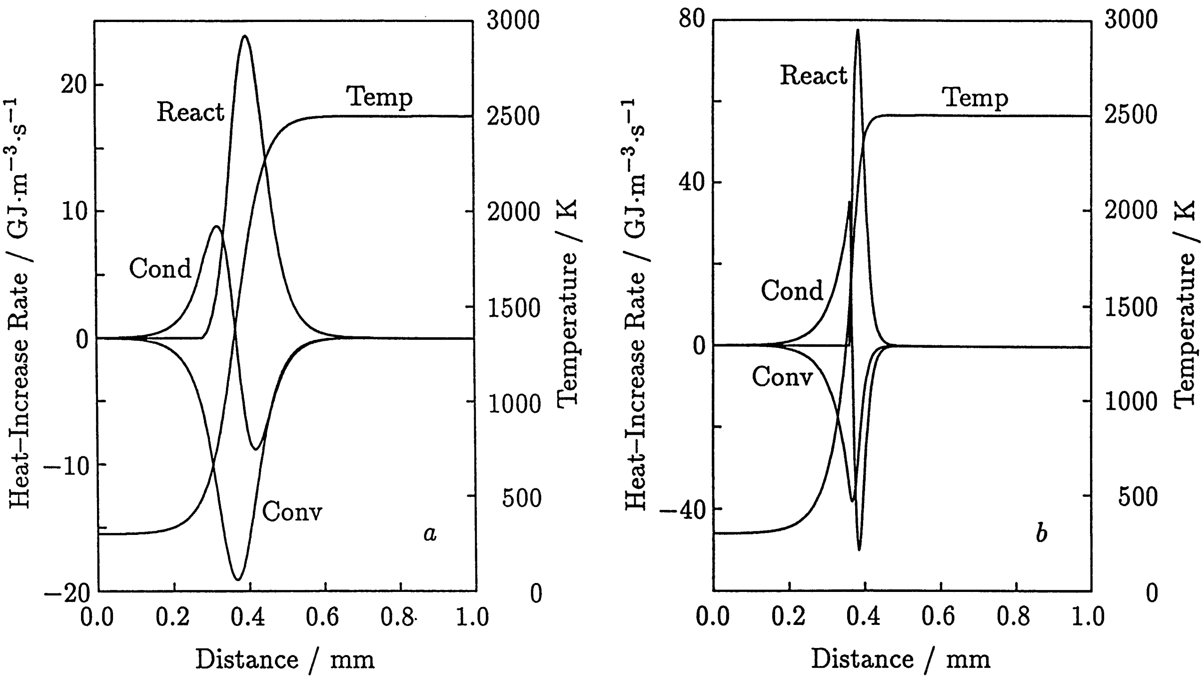

Fig. 6. Profiles of temperature (Temp) and the heat-increase rates due to convection (Conv), conduction (Cond), and the exothermic rate (React) in the flames with T_c=500 K (a) and 1500 K (b).

$x=\infty$, where T_{ad} corresponds to the adiabatic flame temperature, and has an inflection point at $x=\ln \beta/b$. The values of T determined by Eq. 9 are satisfactory for the temperature distributed in a premixed flame. The assumed logistic curve is connected with the exponential curve for the temperature distribution in the nonexothermic region, Eq. 8, in such a way that the temperature itself, and its first and second derivatives have the same values, respectively, at a certain point; the flames are distinguished by the connection temperature, which is designated as T_c. Those three conditions at the connecting point and a given T_{ad} can fix the four constants of the logistic curve.

Figures 6a and 6b show the distributions of the temperature and the heat balance in two flames with the same burning velocity, 1.0 m s^{-1}, and the same adiabatic flame temperature, 2500 K, but different connection temperatures, 500 K and 1500 K. The unburned gases of both flames have constant ρ, c_p, and λ equal to, respectively, 1.3 kg m^{-3}, 1000 J kg^{-1} K^{-1}, and 0.058 W m^{-1} K^{-1}. The two temperature distributions in the nonexothermic regions are expressed, as mentioned above, with the same exponential function of distance, but those in the exothermic regions are clearly different; the reaction zone of the flame with higher T_c is much thinner and its maximum exothermic rate is about four times as large as that of the flame with lower T_c, indicating that the flame front thickness is related to the exothermic-rate distribution.

Figure 7 depicts the exothermic-rate distributions in the various flames with a wide range of T_c. The integration of the exothermic rate of the flames in the range of x from $-\infty$ to $+\infty$ gives the same value since this value corresponds to the thermal energy necessary for heating the unburned gases from room temperature to the adiabatic flame temperature, 2500 K. The maximum exothermic rate of the flame with the smallest T_c, however, is about 1/9 of that of the flame with the

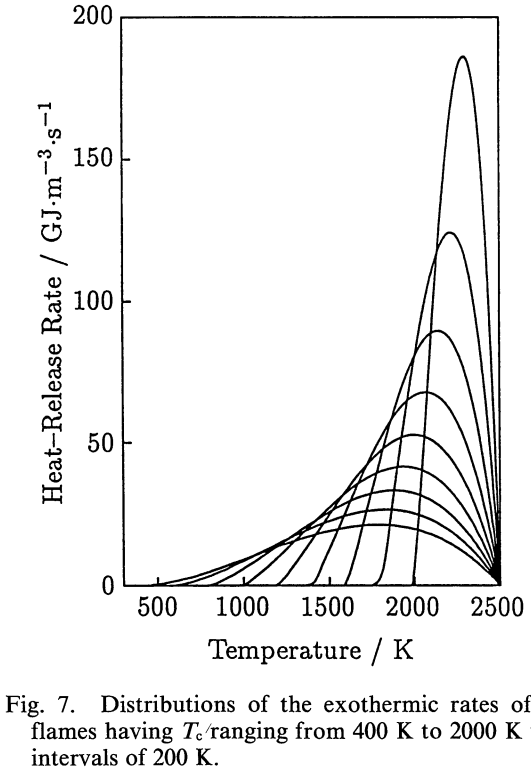

Fig. 7. Distributions of the exothermic rates of the flames having T_c ranging from 400 K to 2000 K with intervals of 200 K.

largest T_c; the temperature range of the exothermic region of the former flame is four times as large as that of the latter flame, and therefore the flame thickness of the former flame is larger. The result that a flame evolving heat at low temperatures can maintain stable flame propagation even if the exothermic rate is small indicates that the flame possibly possesses larger burning velocity when the exothermic rate has almost a similar magnitude.

Conclusions

Simulation of acetylene, ethylene, and ethane premixed flames was performed under the stoichiometric conditions using a detailed reaction scheme, which reproduces the combustion reactions of C_1 and C_2 hydrocarbons, and the following conclusions were obtained:

1. In the acetylene flame, enthalpy is carried into the low-temperature region as the chemical enthalpy of diffused hydrogen atoms, and converted there into thermal enthalpy by a pair of reactions which are substantially reduced to recombination of hydrogen atoms. The unburned gas is heated by those exothermic reactions. The flames where a large amount of hydrogen atoms are produced at high temperatures, diffused to the low-temperature region and consumed there with heat release can propagate according to the diffusion-controlled propagation mechanism. In the ethane flame, on the other hand, combustion reaction proceeds predominantly along the C_1 route and then this flame has the same propagation mechanism as that of a stoichiometric methane flame. In the ethylene flame the fuel is once dehydrogenated to acetylene.
2. When chemical enthalpy is carried by diffused hydrogen atoms and heat is liberated by reactions consuming them at low temperatures, the temperature distribution deviates from an exponential distribution, and the exothermic zone becomes thick. Then even small exothermic rate can maintain stably large burning velocity.

References

1) A. G. Gaydon and H. G. Wolfhard, "Flames," 4th ed, Chapman and Hall, London (1979), Chap. 5.

2) S. Fukutani, N. Kunioshi, and H. Jinno, *Bull. Chem. Soc. Jpn.*, **63**, 2191 (1990).

3) S. Fukutani, K. Sakaguchi, N. Kunioshi, and H. Jinno, *Bull. Chem. Soc. Jpn.*, **64**, 1623 (1991).

4) R. Guenther and G. Janische, *Chem. Ing. Tech.*, **43**, 975 (1971).

5) J. Warnatz, H. Bockhorn, A. Möser, and H. W. Wenz, "Nineteenth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh (1982), pp. 197—209.

6) J. Warnatz, "Twentieth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh (1984), pp. 845—856.

7) M. Cathonnet, F. Gaillard, J. C. Boettner, P. Cambray, D. Karmed, and J. C. Bellet, "Twentieth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh (1984), pp. 819—829.

8) R. J. Hennessy, C. Robinson, and D. B. Smith, "Twenty-First Symposium (International) on Combustion," The Combustion Institute, Pittsburgh (1986), pp. 761—772.

9) C. K. Westbrook, M. M. Thornton, W. J. Pitz, and P. C. Malte, "Twenty-Second Symposium (International) on Combustion," The Combustion Institute, Pittsburgh (1988), pp. 863—871.