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Fuel Mixing Effects on Propagation of Premixed Flames. II. Hydrogen+Methane Flames

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Fuel mixing effects on flame propagation were investigated with hydrogen and methane, whose flames, respectively, propagate through two different kinds of mechanisms. The calculated burning velocities did not show linearity with the hydrogen content in the fuel. The addition of only 5% of methane to hydrogen reduces the burning velocity by 20%, notoriously inhibiting the combustion of the mixture. This is caused by obstruction of the harmonious progression of two key chain-branching reactions, resulting in a decrease in hydrogen atom production at the flame front. However, the upstream flux, at the ignition point, of chemical energy due to diffusion of hydrogen atoms from the flame front and the integrated amount of heat released in the low-temperature region did show linearity with the burning velocity. Therefore, it was found that even for flames of mixed fuels whose components burn individually through different propagation mechanisms, the burning velocity can be expressed as a simple linear function of the upstream chemical energy flux or of the amount of heat released in the low-temperature region.

Hydrogen- and methane-air premixed flames propagate according to different mechanisms,[1] and have consequently different burning velocities. Propagation of hydrogen-air premixed flames is supported by chemical energy carried into the low-temperature regions by hydrogen atoms diffusing from the flame fronts, and this propagation mode, the active species-diffusion mechanism, affords fairly large burning velocities.[2] Methane-air premixed flame propagation, in contrast, is governed by thermal energy transported into the low-temperature regions by conduction and flames propagating with this so-called thermal propagation mechanism do not have, in general, large burning velocities.[2]

As methane content increases in flames of the mixed fuel hydrogen+methane, their propagation mechanism shifts continuously from the first type to the second one; therefore analyses of the chemical reactions occurring in them are expected to give instructive information on the relation between combustion reactions and propagation mechanisms. The purpose of the second paper of the present studies on the fuel-mixing effects is to elucidate the factors influencing the propagation mechanisms and the burning velocity of hydrogen+methane premixed flames from chemical points of view by investigating the transition process from one propagation mechanism to the other by means of a computer simulation.

Simulation Model

Flat premixed flames burning under stoichiometric conditions were simulated here by using the same governing equations and reaction scheme as those of the first paper.[3] The reaction scheme includes only fourteen species, but it has been previously proved to reproduce well the structure of stoichiometric methane premixed flames.[4]

Results and Discussion

Figure 1 shows the predicted burning velocities of stoichiometric hydrogen+methane flames as a function of the initial content of hydrogen in the mixed fuel. In the hydrogen-rich flames the burning velocity decreases very steeply as methane is added to the fuel. Substitution of hydrogen with methane by 20%, for instance, reduces the burning velocity down to about a half of that of the pure hydrogen flame. On the other hand, methane should be substituted with hydrogen by 70% in

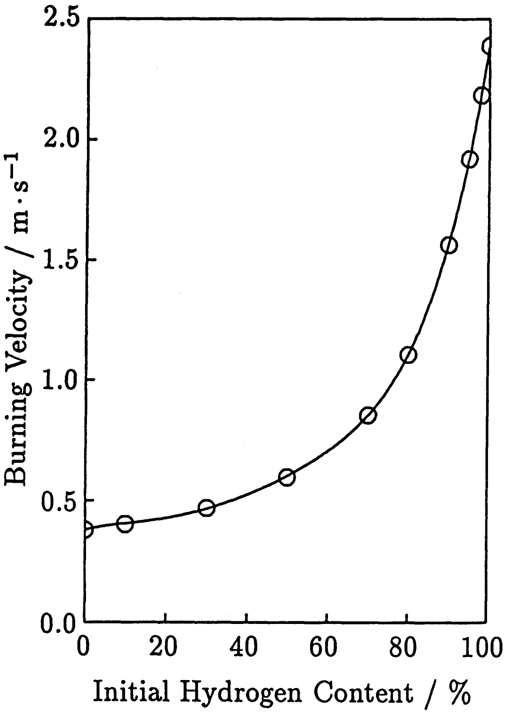

Fig. 1. Burning velocities of stoichiometric hydrogen + methane premixed flames.

order to raise the burning velocity up to twice as large as that of the pure methane flame. Figure 1 thus indicates that methane strongly inhibits the combustion of hydrogen.

The exothermic rate profiles for the hydrogen+methane flames are plotted in Fig. 2 as a function of temperature. As methane is added to the pure hydrogen flame the heat-release rates at low temperatures decrease steeply. The heat-release rate becomes maximum at 1000 K in the pure hydrogen flame, at 1410 K in the 80% hydrogen flame and at 1550 K in the pure methane flame. Thus, in the pure hydrogen flame the rate reaches its maximum at a fairly low temperature compared with methane-rich flames.

In the pure hydrogen flame thermal energy is mostly released through reactions

$$H+O_2+M \rightarrow HO_2+M, \tag{R32}$$

$$H+HO_2 \rightarrow OH+OH, \tag{R34}$$

$$OH+H_2 \rightarrow H+H_2O, \tag{R27}$$

and

$$H+HO_2 \rightarrow H_2+O_2 \tag{R33}$$

in a wide temperature range.[5] In the pure methane flame about a half of thermal energy is released by the reaction

$$CH_3+O \rightarrow HCHO+H, \tag{R8}$$

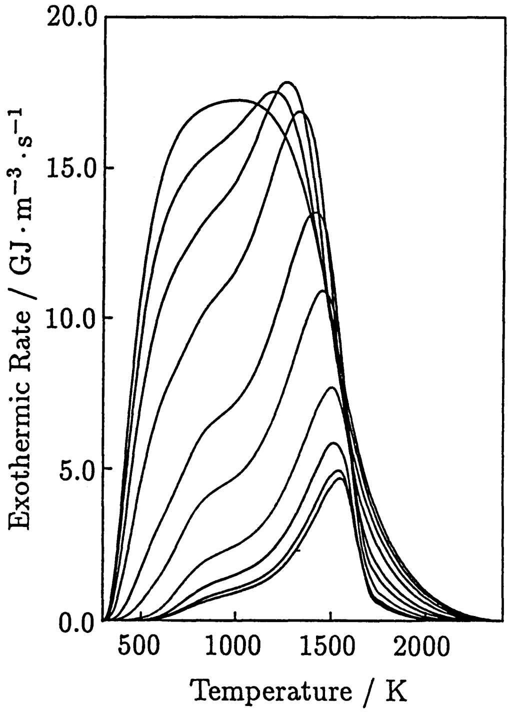

Fig. 2. Exothermic rates of hydrogen + methane flames. The curves corresponds to the flames of 100%, 98%, 95%, 90%, 80%, 70%, 50%, 30%, 10% H_2 and the flame of 100% CH_4. The maximum value shifts to the right as the methane content in the fuel increases.

and the rest by

$$CH_4+OH \rightarrow CH_3+H_2O, \tag{R2}$$

$$CH_3+OH \rightarrow HCHO+H_2, \tag{R7}$$

$$CHO+H \rightarrow CO+H_2, \tag{R16}$$

$$HCHO+H \rightarrow CHO+H_2, \tag{R12}$$

and so on.

The mechanism of activation of exothermic reactions at low temperatures in pure hydrogen flames[5] and the reason for retardation of combustion reaction up to around 1100 K in pure methane flames[4,6] have been already elucidated. We have also pointed out that thermal energy evolved through reactions within low-temperature regions can accelerate the burning velocity;[2,7] such exothermic reactions at low temperatures are triggered by hydrogen atoms diffusing from high-temperature regions. The considerable increase in the burning velocities observed in hydrogen-rich flames is explained on the basis of this viewpoint.

In this investigation, therefore, our attention is focused on the burning velocity change between the 100% H_2 and the 95% H_2+5% CH_4 flames (hereafter the initial composition of the mixed fuel will be designated only with the hydrogen content like 95% H_2 flame), and on the analyses of the reaction mechanisms for elucidating such notorious changes; the burning velocity of the latter flame decreases to about 80% of that of the first flame with addition of methane by only 5%.

Figure 3 depicts the heat release rates of the predominating reactions in the 100% and the 95% H_2 flames. The steep decrease in the heat release rate observed in the low-temperature region of the latter flame results from the reduction in the rates of the two low-temperature reactions (R32) and (R34). Both of these reactions are promoted by hydrogen atoms diffusing from high-temperature regions as described in the previous paper.[3] Therefore the decrease in the heat release in the methane-added flame is directly related to the decrease in the supply of hydrogen atoms.

At high temperatures, the decrease in the heat release due to reduction in reaction (R27) in the methane-added flame is compensated by reactions (R8) and (R16).

As already pointed out,[4] oxygen atoms play a particularly important role in the sequential methane combustion $CH_4 \rightarrow CH_3 \rightarrow HCHO \rightarrow CHO \rightarrow CO \rightarrow CO_2$. We will discuss here why in the methane-added flames hydrogen atoms diffuse in amounts smaller than in the pure hydrogen flame, starting from the analysis of the balance of oxygen atoms.

The rates of production and consumption of oxygen atoms in the two flames in question and the rates of reactions contributing to those processes are plotted in Fig. 4. The production and consumption rates have the same magnitudes in both flames. The production of oxygen atoms is ascribed, for both conditions, to the reaction

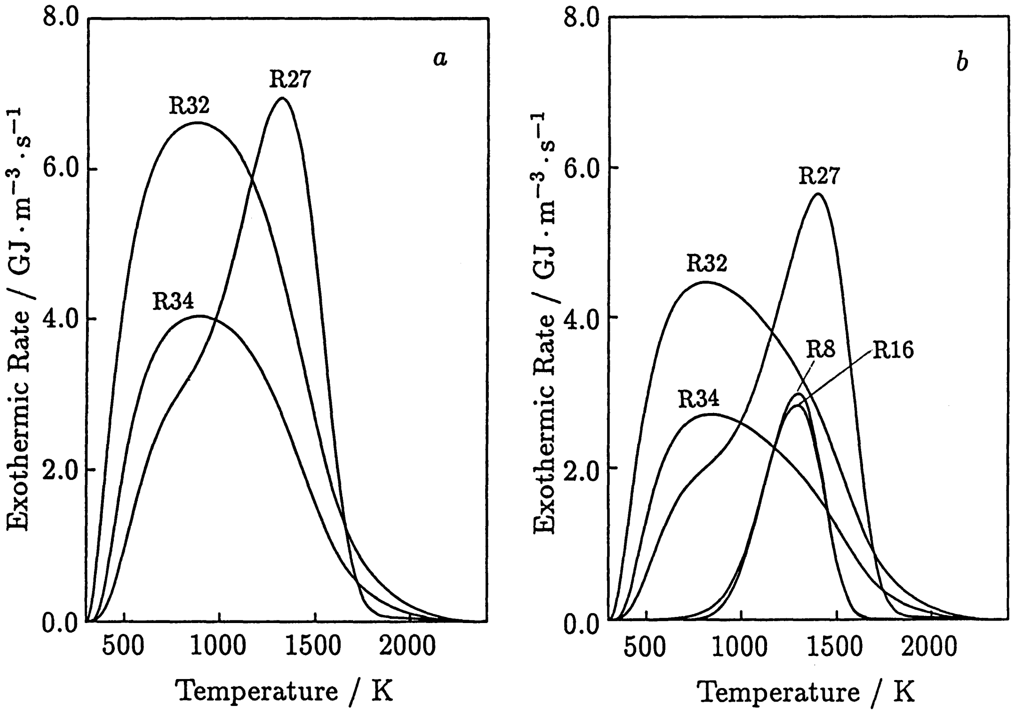

Fig. 3. Exothermic rates of the predominant reactions in the 100% H_2 flame (*a*) and the 95% H_2 +5% CH_4 flame (*b*). The plotted reactions are:

R8 $CH_3+O \rightarrow HCHO+H$
R16 $CHO+H \rightarrow CO+H_2$
R27 $OH+H_2 \rightarrow H+H_2O$
R32 $H+O_2+M \rightarrow HO_2+M$
R34 $H+HO_2 \rightarrow OH+OH$.

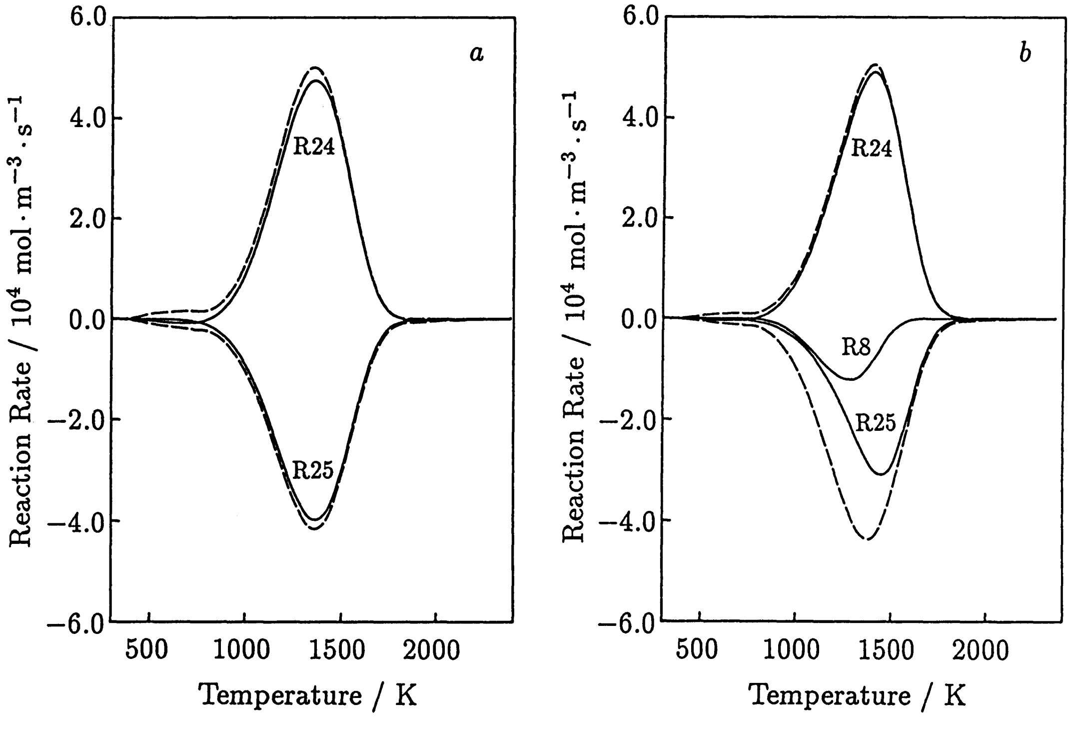

Fig. 4. Total production and consumption rates of oxygen atoms (broken lines), and the rates of some reactions involving that species (solid lines) in the 100% H_2 flame (*a*) and the 95% H_2+5% CH_4 flame (*b*). The plotted reactions are:

R8 $CH_3+O \rightarrow HCHO+H$
R24 $H+O_2 \rightarrow OH+O$
R25 $O+H_2 \rightarrow OH+H$.

$$H + O_2 \rightarrow OH + O, \qquad (R24)$$

while the consumption is due to the reactions

$$O + H_2 \rightarrow OH + H \qquad (R25)$$

and (R8) in the methane-containing flame; the contribution of reaction (R8) increases considerably with increasing initial content of methane. Both reactions (R25) and (R8) yield hydrogen atoms. The amount of the hydrogen atoms produced through these two reactions are therefore almost the same in the 100 and 95% H_2 flames.

Reaction (R25) is one of the most effective chain-branching reactions in hydrogen-containing combustion and produces hydroxyl radicals. Figure 5 shows the production and consumption rates of hydroxyl radicals. The decrease in the production rate at temperatures higher than 1000 K in the methane-containing flame is ascribed to the decrease in the rates of reactions (R25) and (R34). Reaction (R34) belongs to the low-temperature mechanism and is promoted by diffusing hydrogen atoms. The presence of a smaller amount of hydroxyl radicals in the high-temperature region reduces the production of hydrogen atoms through reaction (R27) in the 95% H_2 flame. Since reaction (R27) is responsible for about 70% of the hydrogen atom production, the amount of this active species considerably decreases in the methane-containing flame.

About 90% of hydrogen atoms are consumed through reactions (R32), (R34), and (R24) at 1000 K (the ignition point) in the pure hydrogen flame. These reactions reproduce efficiently active species. The relative contribution of the above three reactions to the consumption of hydrogen atoms decreases as the initial content of methane increases, and instead, the contributions of reactions

$$CH_4 + H \rightarrow CH_3 + H_2 \qquad (R3)$$

and (R12), both of which consuming hydrogen atoms with conversion to molecular hydrogen, increase. The hydrogen atom consumption rate at the ignition point, 1320 K, in the pure methane flame is only 13% of that in the pure hydrogen flame at its ignition point.

The ratio of the production rate to the consumption rate of hydrogen atoms is 0.99 at 1000 K in the pure hydrogen flame, 0.77 at 1200 K in the 80% hydrogen flame and 0.67 at 1320 K in the pure methane flame. When the increase of hydrogen atoms by diffusion is taken into consideration, the above ratios are improved to 1.32, 1.09, and 1.03, respectively. The contribution of diffusion to the total increase rate of hydrogen atoms (production by reactions+diffusion) are around 30% at the ignition points in all the hydrogen+methane flames. The burning velocity of those flames is thus closely related to the diffusive flux of hydrogen atoms.

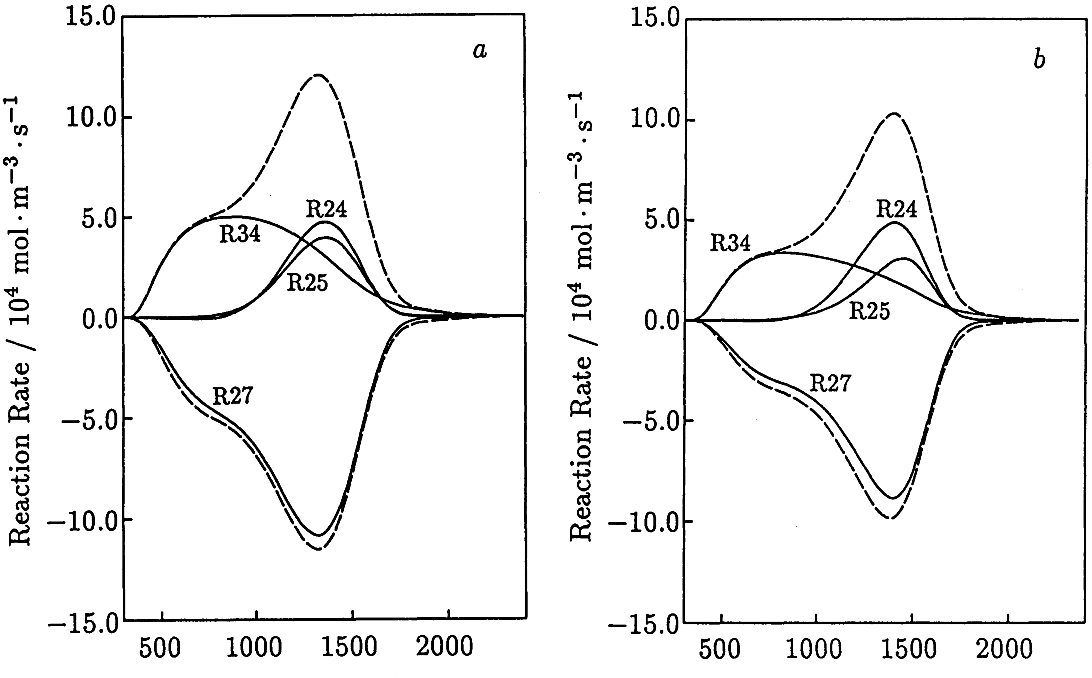

Fig. 5. Total production and consumption rates of hydroxyl radicals (broken lines), and the rates of some reactions involving that species (solid lines) in the 100% H_2 flame (*a*) and the 95% H_2+5% CH_4 flame (*b*). The plotted reactions are:

R24 $H+O_2 \rightarrow OH+O$
R25 $O+H_2 \rightarrow OH+H$
R27 $OH+H_2 \rightarrow H+H_2O$
R34 $H+HO_2 \rightarrow OH+OH$.

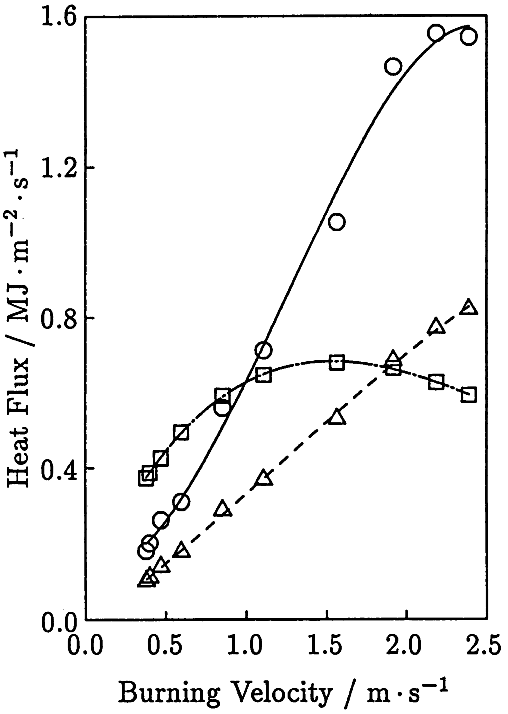

Fig. 6. Flux of thermal energy due to conduction (squares), that of the chemical energy carried by diffusing hydrogen atoms (triangles) at the ignition points, and the thermal energy release rate by exothermic reactions in the low-temperature regions (circles) of various hydrogen+methane flames, as functions of the burning velocity.

In the previous paper it was shown that the burning velocity is proportional to the amount of the chemical energy transported upstream across the ignition points and to the integrated heat release within the low-temperature regions.[3] Those relations were also checked in the hydrogen+methane flames under the same definition of the ignition point, and the obtained results are shown in Fig. 6. The ignition temperature was 1000 K in the pure hydrogen flame, 1200 K in the 80% hydrogen flame and 1320 K in the pure methane flame.

Both chemical energy fluxes and integrated exothermic rates give fairly linear relations against the burning velocity. The fluxes of thermal conduction, however, do not have a simple relation with the burning velocity. It should be noted that the burning velocity is governed by chemical factors even in the flames which propagate according to the thermal mechanism; the chemical energy flux accompanying active species diffusion is transformed into thermal energy by exothermic reactions in the low-temperature regions so that the hydrogen atom production at the high-temperature regions continues to be the key process even in the propagation modes governed by the thermal mechanism.

Concluding Remarks

Both burning velocity and propagation mechanism of methane–air premixed flames are quite different from those of hydrogen flames at stoichiometric conditions. Then substitution of hydrogen with methane leads to considerable changes in the propagation mechanism and the burning velocity; addition of 20% of methane to the pure hydrogen flame, for instance, reduces the burning velocity down to about a half. The considerable reduction of the burning velocity is mainly caused by steep decrease in the heat release rate at low temperatures. Most of the exothermic reactions at the low-temperature region require hydrogen atoms, which come by diffusion from the flame front. However, the addition of methane to the fuel leads to consumption of oxygen atoms at the flame fronts by reaction with methyl radicals, and the lack of oxygen atoms obstructs the progression of the chain-branching reactions which would lead, otherwise, to abundant production of hydrogen atoms. The importance of the heat release at low temperatures as a factor determining the burning velocity even in flames propagating through the thermal mechanism was evidenced by the obtained linearity between the burning velocity and the chemical energy flux toward the low-temperature regions.

References

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

2) S. Fukutani, N. Kunioshi, K. Sakaguchi, and H. Jinno, *Bull. Chem. Soc. Jpn.*, **64**, 3098 (1991).

3) S. Fukutani and N. Kunioshi, *Bull. Chem. Soc. Jpn.*, **65**, 2569 (1992).

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

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

6) S. Fukutani, T. Sasaki, and H. Jinno, *Nenryo Kyokai Shi*, **69**, 946 (1990).

7) S. Fukutani and H. Jinno, "Complex Chemical Reaction Systems," ed by J. Warnatz and W. Jäger, Springer-Verlag, Heidelberg (1987), pp. 233—242.