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Mechanism of Combustion Reactions in Hydrogen-Air Premixed Flames

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Simulation was performed by use of a chemical kinetic model built for flat hydrogen-air premixed flames in order to investigate the combustion mechanism taking place in flames through a wide range of equivalence ratio. The following results were obtained: the flame zone of the stoichiometric flame can be considered as having two different regions; the low-temperature region has, furthermore, three parts differing in reaction mechanism; since the reactions cannot proliferate hydrogen atoms by themselves in the low-temperature region, the acceleration of the reactions is necessarily governed by the hydrogen atoms diffused from the flame front; in the high-temperature region, the reactions produce an excess of hydrogen atoms which activate the reactions in this region or diffuse toward the low-temperature region; lean hydrogen flames possess smaller burning velocity than that of rich flames because the reactions in the low-temperature region have less reproducibility of hydrogen atoms.

The propagation mechanism of a laminar premixed flame is determined as the result of complicated interactions between almost all properties of the flame. It has been well-known that the propagation mechanism can be simply analyzed either on the basis of the thermal theory or the active-species-diffusion theory.[1) These theories are able to explain approximately the propagation mode and the structure of a flame; nevertheless both theories are not exact enough for a detailed investigation.

The thermal theory, for instance, divides the whole flame region into two zones: a preheating zone and a reaction zone. The temperature raise in the preheating zone is ascribed only to the accumulation of heat through conduction from the flame front, if the contribution of heat release from reactions is ignored. According to the definition of the two zones, the net increment of thermal energy due to conduction becomes zero at the boundary between them; there, heat release due to reactions must, therefore, be equilibrated with the convective heat outflow in a steady flame; since chemical reactions cannot be initiated immediately, reaction must have already started in the preheating zone, contradicting the theory. Hence, an accurate discussion on the propagation mode and the structure of a flame requires the solution of the full governing equations.

There is considerable difficulty to solve analytically the governing equations of a flame. Moreover, an actual flame propagation is governed partly by thermal conduction and partly by active species diffusion, and the problem becomes very complicated.

The purpose of this investigation is to elucidate in detail the mechanism of combustion reactions in hydrogen-air premixed flames by means of computer simulation using a chemical kinetic model. Although hydrogen-air flames are simple combustion systems, their elementary reactions are essential for almost all flames of fuels containing hydrogen atoms. In addition, hydrogen-air systems can burn fast, allowing the recognition of the necessary conditions for large burning velocities.

Simulation Model

The following assumptions were made in the construction of the simulation model.

1. The flame under consideration is an idealized flat flame, where any properties are described as functions of time and a one-dimensional position.
2. Since the flow velocity of the gas mixture is much smaller than the sound velocity, the pressure is constant throughout the flame and is set to be atmospheric pressure.
3. The effect of viscosity is neglected.
4. Heat loss from the flame to its surroundings is neglected. Consequently the temperature is asymptotically raised up to the adiabatic flame temperature, which is evaluated on the basis of the temperature, pressure and composition of the initial gas mixture. Radiational heat transfer is also neglected.
5. Chemical species present in the flame are OH, H, O, HO_2, H_2O_2, H_2O, H_2, O_2, and N_2. The twenty-one pairs of elementary reactions tabulated in Table 1 take place between those species. Nitrogen is considered as inert according to the following reasons: (1) the rate constant of the nitrogen oxidation by oxygen atoms,[6) which is the governing step of NO_x formation, is much smaller than that of the corresponding hydrogen oxidation;[2) (2) the reactions producing nitrogen oxides do not proceed in the main combustion reaction zones of hydrogen flames[7) so that they do not appreciably influence the hydrogen combustion process.

The above described assumptions simplify the governing equations as follows:

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

$$\frac{\partial}{\partial t}(\rho\omega_i)+\frac{\partial}{\partial x}(\rho\omega_i v)=\frac{\partial}{\partial x}\left(D_i\rho\frac{\partial \omega_i}{\partial x}\right)+\phi_i \qquad i=1,2,\ldots,9 \tag{2}$$

Table 1. Hydrogen-Oxygen Reaction Scheme
$k = AT^n \exp(-E/T)$[a)]

No.	Reaction	A	n	E	Ref.
R1	$H_2 + O_2 \rightarrow OH + OH$	2.50E06	0.0	19600.0	2
R2	$H + O_2 \rightarrow OH + O$	2.20E08	0.0	8450.0	2
R3	$O + H_2 \rightarrow OH + H$	1.80E04	1.0	4480.0	2
R4	$OH + OH \rightarrow O + H_2O$	6.30E06	0.0	550.0	2
R5	$OH + H_2 \rightarrow H + H_2O$	2.20E07	0.0	2590.0	2
R6	$H + H + M \rightarrow H_2 + M$	2.60E06	−1.0	0.0	2
R7	$O + O + M \rightarrow O_2 + M$	1.90E01	0.0	−900.0	2
R8	$H + O + M \rightarrow OH + M$	3.60E06	−1.0	0.0	3
R9	$OH + H + M \rightarrow H_2O + M$	4.06E10	−2.0	0.0	2
R10	$H + O_2 + M \rightarrow HO_2 + M$	5.00E03	0.0	−500.0	2
R11	$H + HO_2 \rightarrow H_2 + O_2$	2.50E07	0.0	350.0	2
R12	$H + HO_2 \rightarrow OH + OH$	2.50E08	0.0	950.0	2
R13	$H + HO_2 \rightarrow O + H_2O$	9.00E05	0.5	2000.0	2
R14	$OH + HO_2 \rightarrow H_2O + O_2$	5.00E07	0.0	500.0	4
R15	$O + HO_2 \rightarrow OH + O_2$	6.30E07	0.0	350.0	5
R16	$HO_2 + H_2 \rightarrow H + H_2O_2$	7.30E05	0.0	9400.0	2
R17	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	8.50E06	0.0	500.0	2
R18	$OH + H_2O_2 \rightarrow HO_2 + H_2O$	1.00E07	0.0	910.0	2
R19	$H + H_2O_2 \rightarrow OH + H_2O$	2.20E09	0.0	5900.0	2
R20	$O + H_2O_2 \rightarrow OH + HO_2$	2.80E07	0.0	3200.0	2
R21	$H_2O_2 + M \rightarrow OH + OH + M$	1.20E11	0.0	22900.0	2

a) The rate constants are expressed in m · mol · s units.

$$\frac{\partial}{\partial t}(c_p \rho T) + \frac{\partial}{\partial x}(c_p \rho T v) = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) + \sum_i D_i \rho \frac{\partial h_i}{\partial x}\frac{\partial \omega_i}{\partial x} - \sum_i h_i \phi_i \tag{3}$$

$$p = \rho R T \sum_i \frac{\omega_i}{m_i} \tag{4}$$

where the independent variables t and x are the time and position, 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 by reactions, h_i the enthalpy, m_i the molar mass and D_i the diffusion coefficient of the i-th species in the gas mixture; and R is the gas constant. The partial differential terms in the governing equations were discretized into the corresponding finite difference terms using the control-volume method.[8)]

At the boundary of the unburned side, the temperature is 298 K and the combustible gas mixture is composed of only the fuel and air. By means of a trial-and-error method the flow velocity is so given that it agrees with the burning velocity, which is univocally determined by the combustion conditions. At the boundary of the burned side, adiabatic flame temperature and the correspondent equilibrium composition are assumed. The finite difference equations were solved by use of a time-dependent method; this method yields steady-state solutions independently of the initial conditions when the flow velocity given as the cold boundary condition agrees with the burning velocity.

Results and Discussion

Validity Verification of the Simulation Model. We verified the validity of the model by comparison of the predicted burning velocities of various hydrogen-air

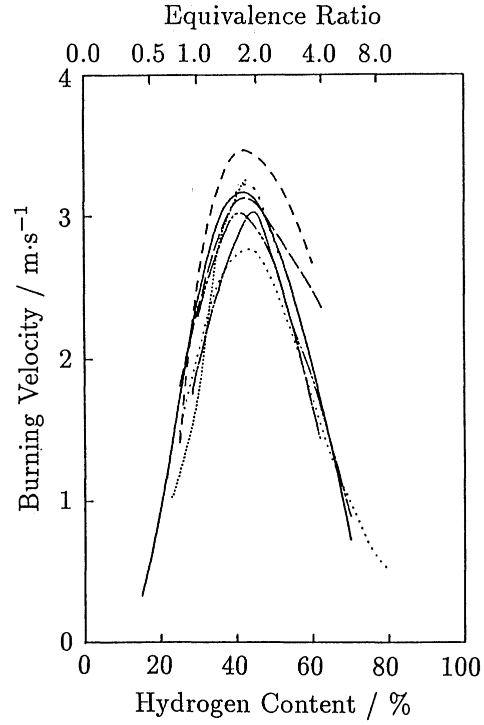

Fig. 1. Burning velocities of hydrogen-air premixed flames. The solid line denotes the burning velocity calculated in this investigation, and the other lines represent experimental values.[7)]

premixed flames with experimental values of the literature. Figure 1 shows the burning velocities obtained by simulation over a wide range of fuel content and the experimental velocities summarized by Andrews and Bradley.[9)]

The burning velocity obtained through simulation techniques should result from the contributions of all the constituents of the model such as chemical reaction terms and transport terms of species and enthalpy. The agreement between the calculated and the measured velocities shown in Fig. 1 leads us to the conclusion that the model employed in this investigation can reproduce accurately the combustion processes of actual hydrogen-air premixed flames.

Reaction Mechanism of a Stoichiometric Hydrogen Flame. Figures 2 and 3 show the mole fraction profiles of the reactants and products, and those of the intermediate species, respectively, in a stoichiometric hydrogen-air premixed flame together with the temperature profile. Since the flames considered in this investigation are ideally flat, the burning velocities are eigenvalues for the given combustion conditions; a simulated flame is stable only when the flow velocity of the unburned gas is equilibrated with the burning velocity; the flame can be stabilized at an arbitrary spatial position and therefore the abscissas in Figs. 2 and 3 indicate only relative positions within the flame. The mole fractions of hydroperoxyl radicals and hydrogen peroxide become maxima at about 400 K and 500 K, respectively. In addition, the mole fraction of hydroxyl radicals, increasing at temperatures as low as 400 K, once becomes almost constant at about 600 K and increases again from 900 K. The two-staged increase in hydroxyl radicals reveals that reactions have already taken place in low-temperature regions, and at about 1000 K chemical reactions are intensified.

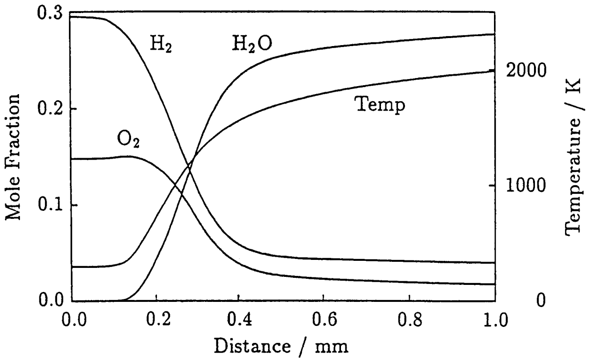

Fig. 2. Profiles of the temperature and the concentrations of stable species in the stoichiometric hydrogen-air premixed flame.

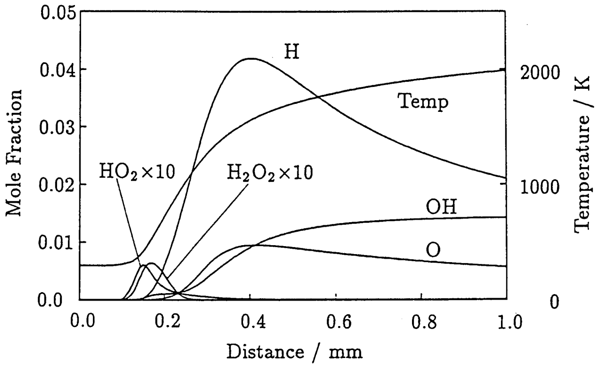

Fig. 3. Profiles of the temperature and the concentrations of active and intermediate species in the stoichiometric hydrogen-air premixed flame.

Figure 4 shows the heat increase rates due to the respective terms in the conservation equation of thermal energy, Eq. 3: convection, conduction, heat transfer accompanying species diffusion, and heat evolution by reactions. The rate of thermal conduction increases remarkably at a temperature a little higher than room temperature and decreases to zero at 980 K after reaching its maximum at 410 K. Heat evolution from chemical reactions occurring in this flame is large even at a very early stage of combustion, exceeding the thermal conduction at 450 K. Such large heat release forms a reaction zone about 0.2 mm thick, beyond which temperature approaches asymptotically the adiabatic flame temperature, 2380 K. The thermal conduction term does not make considerable contribution to the balance of thermal energy except in the low-temperature region but the heat-release term, on the other hand, plays a major role over a wide range of temperature.

The thermal theory divides the whole flame zone into two regions based on the contribution of thermal conduction,[1)] and assumes that (1) at the preheating zone heat evolution by reactions is negligibly small and the combustible gas mixture is heated by thermal energy transferred by conduction, and (2) conduction carries away thermal energy from the reaction zone toward the upstream region. The temperature at the point where the heat conduction rate crosses zero was calculated to be 980 K in this flame. It should be

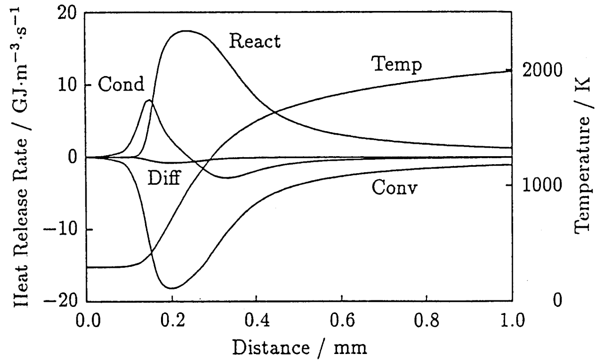

Fig. 4. Rates of the heat increase due to convection (Conv), conduction (Cond), heat transfer accompanying species diffusion (Diff), and heat release by chemical reactions (React) in the stoichiometric hydrogen-air premixed flame.

noted that chemical reactions are activated and release a large amount of thermal energy even at much lower temperatures than the above boundary temperature.

From the viewpoint of combustion chemistry and propagation modes, the hydrogen premixed flame is one of the most representative flames. Its combustion reaction includes some essential elementary reactions appearing in the combustion of almost all of hydrogenated fuels. The results of the investigation of chemical reactions in hydrogen-air premixed flames, which have been accumulated in a series of works of Dixon-Lewis, for instance, can be summarized as follows:[10–13]

1. Hydrogen atoms are diffused into low-temperature regions from the flame front, and work as a trigger for low-temperature reactions. A large amount of heat is released by reactions. The propagation of hydrogen flames is, therefore, governed predominantly by the diffusion of hydrogen atoms.

2. Water molecules are produced exclusively by the reaction

$$\mathrm{OH + H_2 \rightarrow H + H_2O} \tag{R5}$$

at both low and high temperatures.

3. Hydroxyl radicals, the oxidizer of hydrogen, are supplied at low temperatures by the reaction

$$\mathrm{H + HO_2 \rightarrow OH + OH,} \tag{R12}$$

which follows the reaction

$$\mathrm{H + O_2 + M \rightarrow HO_2 + M.} \tag{R10}$$

In high-temperature regions, on the other hand, they are yielded by the pair of reactions

$$\mathrm{H + O_2 \rightarrow OH + O} \tag{R2}$$

and

$$\mathrm{O + H_2 \rightarrow OH + H.} \tag{R3}$$

Both reactions (R2) and (R3) are well-known and take on a prominent role as chain-branching reactions not only in hydrogen flames but also in almost all flames of hydrogen-containing fuels.

An important role assigned to the theories on propagation of premixed flames is to elucidate how temperature increases in low-temperature regions. When no heat release occurs at early stages of combustion, only thermal conduction works, and, as easily shown by analytical solution of the time-independent conservation equation of thermal energy with some assumptions such as constant specific heat and thermal conductivity,[1] the temperature increases exponentially. If it were not for the heat release at low temperatures, the temperature gradient would be large immediately before heat evolution through reactions and the flame front would be thin; the heat release rate should be large to make the temperature approach asymptotically the adiabatic flame temperature[14] particularly when the flame possesses large burning velocity as that of hydrogen flames. One of the conditions for a premixed flame to maintain large burning velocity is that chemical reactions take place even in the low-temperature region, evolving some amount of thermal energy there.

Figure 5 gives the rates of the six predominant reactions in the stoichiometric flame; reaction (R11) has the sixth largest rate in this flame, but this and the other reactions which are not plotted in this figure can be neglected without fundamental errors in comparison with the five main reactions.

In the stoichiometric hydrogen flame, there are two different reaction mechanisms, the low-temperature and the high-temperature mechanisms, according to Fig. 5. The series of reactions (R10), (R12), and (R5) take place predominantly in the low-temperature region defined, based on the profiles of the reaction rates, as the region with temperatures lower than 1100 K. Assuming the relative rates of the above three reactions to be 1 : 1 : 2, the overall reaction derived by addition of these three elementary reactions in consideration of their reaction rates, becomes

$$\mathrm{2H_2 + O_2 \rightarrow 2H_2O.} \tag{5}$$

Consequently, the low-temperature reactions cannot proliferate the active species such as hydrogen atoms by themselves. Rising temperature reduces the overall reaction rate since the activation energy of reaction (R10), the chain-initiation reaction in this mecha-

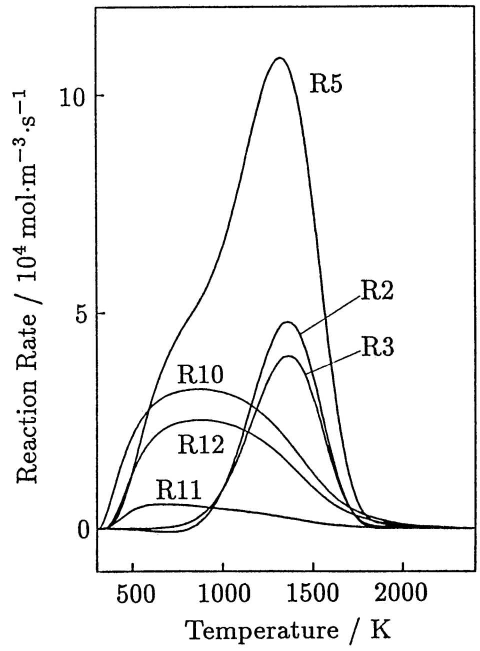

Fig. 5. Rates of the predominant reactions in the stoichiometric hydrogen-air premixed flame.
R2 : $\mathrm{H + O_2 \rightarrow OH + O}$
R3 : $\mathrm{O + H_2 \rightarrow OH + H}$
R5 : $\mathrm{OH + H_2 \rightarrow H + H_2O}$
R10 : $\mathrm{H + O_2 + M \rightarrow HO_2 + M}$
R11 : $\mathrm{H + HO_2 \rightarrow H_2 + O_2}$
R12 : $\mathrm{H + HO_2 \rightarrow OH + OH}$

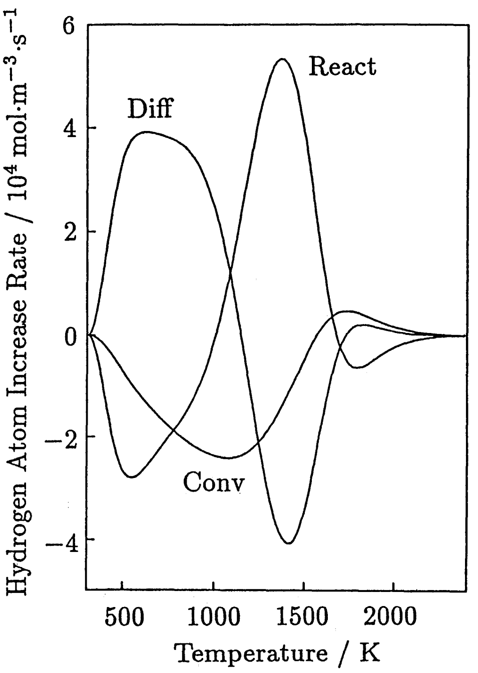

Fig. 6. Rates of the increase in hydrogen atoms due to convection (Conv), diffusion (Diff), and reactions (React) in the stoichiometric hydrogen-air premixed flame.

nism, is negative. The increase in the rates of the low-temperature reactions should, therefore, be ascribed to hydrogen atoms diffused from the high-temperature region. Figure 6 indicates that the hydrogen atoms produced by reactions at high temperatures are diffused to the low-temperature region, where they are consumed by the low-temperature reactions.

In the high-temperature region of this flame, the rates of the two reactions in which hydroperoxyl radicals participate decay with the rising temperature, and the two chain-branching reactions are instead added to the reaction mechanism. The predominant three reactions, (R2), (R3), and (R5), in the high-temperature mechanism yield the overall reaction

$$3H_2 + O_2 \rightarrow 2H_2O + 2H \qquad (6)$$

under the assumption that the rates of the three reactions are also in the ratio 1 : 1 : 2. The excess of hydrogen atoms produced is responsible for the exponential increase in the overall reaction rate and for the promotion of the supply of hydrogen atoms toward the low-temperature region.

Activation of the above two mechanisms is simply controlled by the balance of the rate constants of reactions (R10) and (R2); a critical temperature for the activation of the high-temperature mechanism is defined so that the rates of those two reactions become equal. Although this temperature depends on the gas composition because of the third-body efficiency of reaction (R10),[2] it was estimated to be 1160 K in this investigation.

Dividing the whole reaction region into two, the high-temperature and the low-temperature reaction zones, we investigated the individual reaction mechanism in detail. The low-temperature reaction zone was partitioned furthermore into the three subdivisions: (1) from the unburned side to the position where the rate of heat release becomes equal to that of the heat increase due to thermal conduction (298—450 K in this flame); (2) between the first subdivision and the position where the rate of reaction (R2) becomes positive (450—810 K); (3) between the second subdivision and the limit of the low-temperature reaction zone (810—1160 K). The reaction mechanisms in each subdivision will be described in the following.

First Subdivision: Hydrogen atoms are scarcely produced by chemical reactions in the range of temperature from 298 to 450 K; although their production can be ascribed to reaction (R5) at temperatures lower than 810 K, the low temperature and the lack of hydroxyl radicals hinder the activation of that reaction. Hydrogen atoms are, therefore, supplied to this region only by diffusion from the flame front. More than 60 % of the consumed hydrogen atoms are oxidized to hydroperoxyl radicals through reaction (R10) and the rest of them further react with the produced hydroperoxyl radicals through reaction (R12) and its competitive reaction

$$H + HO_2 \rightarrow H_2 + O_2. \qquad (R11)$$

Some of the hydroperoxyl radicals are accumulated in the gas. Most of them are, however, transformed into stable species such as hydrogen peroxide, molecular hydrogen and oxygen by reactions (R11) and

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \qquad (R17)$$

and the rest are converted to hydroxyl radicals through reaction (R12).

All of the reactions activated in this lowest temperature region have negative or small activation energy and yield stable or inactive species. The diffused hydrogen atoms are, consequently, degraded to stable species, such as molecular hydrogen or hydrogen peroxide, particularly via hydroperoxyl radicals. The secondary formation of hydrogen atoms or other reactions which directly affect the combustion at later stages do not take place in this subdivision.

This region is hence not much more than a preheating zone where enthalpy is transferred to mostly by thermal conduction from the flame front. At the same time, however, a small amount of heat comes with hydrogen atoms as chemical energy, released when the hydrogen atoms are combined to stable species. More than 80% of the released heat is due to reactions (R10), (R12), (R11) and

$$OH + HO_2 \rightarrow H_2O + O_2. \qquad (R14)$$

Second Subdivision: About half of the hydrogen atoms consumed in this subdivision are oxidized to hydroperoxyl radicals. With the increase in temperature, the proportion of the hydroperoxyl radicals converted further to hydroxyl radicals by reaction (R12) increases from 50% to 75% within this region. About 45% of the produced hydroxyl radicals at low temperatures and 90% at high temperatures are effectively used by the oxidation of hydrogen (R5). About 20% (at low temperatures) to 75% (at high temperatures) of the consumed hydrogen atoms are reproduced by this reaction. The chain-branching reactions (R2) and (R3), however, are not incorporated into the whole combustion reaction yet. The reactions cannot replace fully the amount of hydrogen atoms consumed in this region though the overall reaction in this subdivision is approximately expressed as Eq. 5.

At early stages in this subdivision, the reaction rates increase with the increasing diffusion of hydrogen atoms. At later stages, however, the rate of such diffusion to this region becomes almost constant (see Fig. 6); the acceleration of the chemical reactions and the transition to the third subdivision are, therefore, ascribed to the reduction in the degradation of hydrogen atoms to stable species as temperature increases.

The formation and consumption rates of hydroperoxyl radicals reach maxima at about 830 K. Although the concentration profiles of hydrogen peroxide and hydroperoxyl radicals are similar, both production and consumption reactions of the former species are much smaller than those of the latter. Since hydrogen peroxide is present in small amounts and works only as a temporary storage of active species, it can be neglected in hydrogen-air premixed flames.

Third Subdivision: At low temperatures, reaction (R2) proceeds backward and produces hydrogen atoms:

$$OH + O \rightarrow H + O_2. \qquad -(R2)$$

The third subdivision starts from the position where this reaction turns forward and consumes hydrogen atoms. The pair of reactions (R2) and (R3) produce abundantly hydroxyl radicals, and reactions (R3) and (R5) compensate 70% to 100% (near the limit with the high-temperature reaction zone) of the consumed hydrogen atoms. Diffusion of hydrogen atoms, on the contrary, declines steeply (see Fig. 6).

The third subdivision is consequently a transient stage where the low-temperature reaction mechanism consisting of reactions (R10), (R12), and (R5) shifts to the high-temperature mechanism, composed of reactions (R2), (R3), and (R5). The boundary between this subdivision and the high-temperature reaction zone agrees very well with the position where the net production rate of hydrogen atoms becomes positive, and, in addition, with the position where the diffusion rate of hydrogen atoms becomes negative as shown in Fig. 6.

Heat release by chemical reactions is overwhelmingly ascribed to reaction (R10). As temperature rises, however, the contribution of reaction (R5) to the total heat release increases, exceeding 30% at the end of this subdivision. The predominant endothermic reactions are (R2) and (R3).

High-Temperature Reaction Zone: In this zone the high-temperature reaction mechanism whose overall reaction is approximately expressed as Eq. 6, gradually becomes predominant. The production rate of hydrogen atoms reaches maximum at 1340 K and about 70% of their production is ascribed to reaction (R5) and the rest to reaction (R3). As for their decrease, on the other hand, 35% is due to the consumption by reaction (R2), 30 % to the diffusion toward the low-temperature region, 15 and 10 % to reactions (R10) and (R12), respectively. It should be noted that the low-temperature reactions remain even at such high temperatures (see Fig. 5); the ratios between the reaction rates of (R2) and (R10) are 2.0 at 1300 K, 2.6 at 1400 K, 2.8 at 1500 K and decreases again down to 1.0 at 1700 K. The combustion reaction enters into a so-called recombination stage above 1700 K and the overshoot of hydrogen atoms is relaxed toward the equilibrium composition at the adiabatic flame temperature by the recombination reactions such as reactions (R10) and

$$OH + H + M \rightarrow H_2O + M. \qquad (R9)$$

The gradual increase in temperature in this region is due to heat release by these recombination steps.

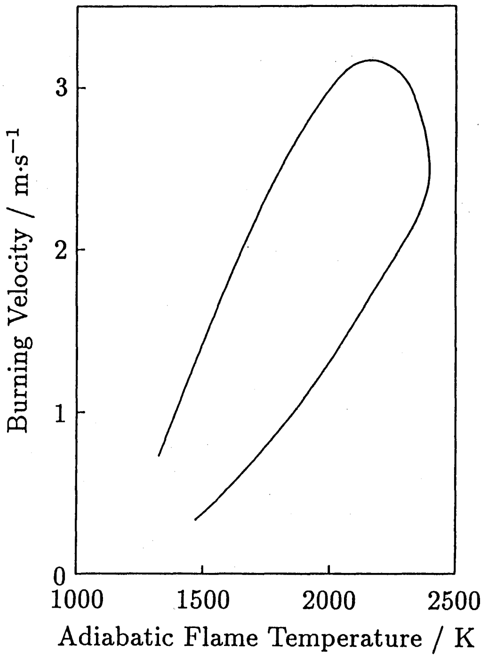

Fig. 7. Burning velocity of various hydrogen-air premixed flames as a function of their adiabatic flame temperature. The upper half corresponds to rich conditions.

Reaction Mechanism under Various Equivalence Ratios. We simulated hydrogen-air premixed flames through a wide range of fuel content. The equivalence ratio is defined as the ratio of the amount of fuel in a gas mixture to its stoichiometric amount. Figure 7 shows the relation between the adiabatic flame temperature and the burning velocity predicted in this investigation. Rich and lean flames having the same adiabatic flame temperatures do not necessarily possess the same burning velocities: the former flames burn about twice as fast as the latter indicating that the combustion reactions proceed more effectively in the former flames. Adiabatic flame temperature is determined univocally by the given initial gas composition and combustion conditions such as temperature and pressure. Burning velocity, on the other hand, depends chiefly on the propagation mode and the chemical characteristics of the combustible gas mixture.

The ratios of the total production rate of hydrogen atoms to their total consumption rate for the various flames are plotted in Fig. 8 as functions of temperature. This ratio is expected to be one of the simplest indices for the prediction of the reaction mechanism in hydrogen flames since it should be equal to unity when the low-temperature reactions (R10), (R12), and (R5) occur exclusively and three for the high-temperature reactions (R2), (R3), and (R5).

Figure 8 shows that the profiles for the flames with equivalence ratio less than 1.6 quite agree throughout the whole low-temperature reaction zone indicating that these flames have similar reaction mechanisms. However, in the flames with equivalence ratio greater than 2, those ratios increase with increasing equivalence ratio, allowing chemical reactions to proceed efficiently. There are virtually two alternative reaction pathways for consumption of hydroperoxyl radicals: reactions (R12) and (R11); the former reaction produces active hydroxyl radicals and is, then, indispensable for stable continuation of the combustion reaction at low temperatures; the latter reaction recombines hydroperoxyl radicals and hydrogen atoms into inactive molecular hydrogen and oxygen. Since both reactions have the same reactants, the ratio between their rates does not differ at an arbitrary temperature even in flames with different equivalence ratios. Hence these reactions cannot be responsible for the difference in the behavior of hydrogen atoms.

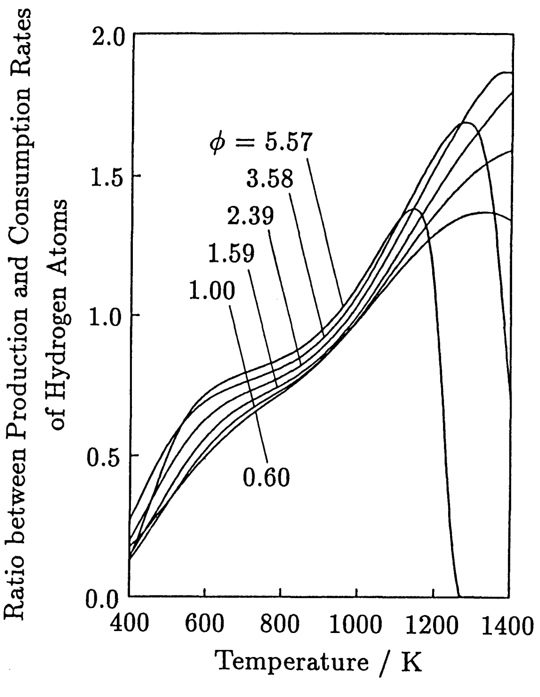

Fig. 8. Ratios of the hydrogen-atom production rate to its consumption rate in the hydrogen-air premixed flames with various equivalence ratios, ϕ.

As the equivalence ratio approaches unity, the concentration of hydroxyl radicals increases and another reaction

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad (R14)$$

contributes to the consumption of hydroperoxyl and hydroxyl radicals. The transformation of these two species into stable species obstructs the continuation of the combustion process in hydrogen flames having equivalence ratio less than 1.6. This is one of the reasons why the burning velocities of these flames are lower than those of flames with larger equivalence ratios for the same adiabatic flame temperatures.

Concluding Remarks

A chemical kinetic model for flat hydrogen-air premixed flames was proposed and its validity was verified by comparing the burning velocities predicted under various conditions with experimental values. Simulation using the model lead to the following conclusions:

1. According to the reaction mechanism, the reaction zone of the stoichiometric flame is divided into two parts at the temperature of 1160 K: the low-temperature and the high-temperature reaction zones. The low-temperature zone is furthermore partitioned, according to particular characteristics, into three subdivisions: the first subdivision, ranging from 298 to 450 K, the second subdivision, from 450 to 810 K, and the third subdivision, from 810 to 1160 K.

2. In the first subdivision, reactions are hardly activated and then the temperature is predominantly raised by the thermal energy transferred by conduction from the high-temperature region. This subdivision is simply a preheating zone, in agreement to the thermal propagation theory.

3. Most of the hydrogen atoms diffused from the flame front are oxidized to hydroxyl radicals via the produced hydroperoxyl radicals in the second subdivision. The hydroxyl radicals are consumed as the oxidizer of hydrogen molecules. A large amount of

thermal energy is released by reaction (R10).

4. In the third subdivision the low-temperature reactions (R10), (R12), and (R5), are gradually substituted with the high-temperature reactions (R2), (R3), and (R5) such that this subdivision becomes a transient stage to the high-temperature reaction zone.

5. The high-temperature reactions are activated at temperatures higher than 1160 K, but hydrogen atoms are still consumed by reactions (R10) and (R12). About 30 % of the hydrogen atom decreasing in this region are due to diffusion toward the low-temperature region.

6. Rich hydrogen-air premixed flames reproduce hydrogen atoms in their low-temperature regions through production of hydroxyl radicals by reaction (R12) from the hydroperoxyl radicals formed by reaction (R10). In the flames with equivalence ratio less than 1.6, however, a degradation of hydroxyl and hydroperoxyl radicals, reaction (R14), appears, lowering the reproducibility of hydrogen atoms at low temperatures.

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