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# Study of Low-Pressure Premixed Dimethyl Ether/Hydrogen/Oxygen/Argon Laminar Flames with Photoionization Mass Spectrometry

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Laminar premixed fuel-rich (equivalence ratio of 1.5) dimethyl ether/hydrogen/oxygen/argon flames with different hydrogen fractions (0%, 20%, 40%, 60%, and 80%) were investigated with tunable synchrotron vacuum-ultraviolet photoionization and molecular-beam mass spectrometry. The flame temperature profile was measured. Through measurement of the signal intensities at different distances from the burner surface, the mole fraction profiles of major intermediates are derived. A comparison of the flame temperature profiles or mole fraction profiles is made among these flames. The influences of hydrogen addition on the flame temperature and mole fractions of major species and intermediates are analyzed. The results show that the flame temperature in the flame zone decreases with an increase of hydrogen addition. The mole fractions of major species and intermediates are decreased with an increase of the hydrogen fraction. This might be attributed to the decrease of the C/H ratio of the fuel blend by hydrogen addition. The mole fraction ratios of CO to $CO_2$ are decreased with an increase of the hydrogen fraction, and this indicates that hydrogen addition can promote oxidation of CO and realizes complete combustion of dimethyl ether.

## 1. Introduction

With increasing concern about fossil fuel shortage and stringent emission regulations, studies on alternative fuels gain more and more attention in the combustion community and engine development society. As renewable energy sources, dimethyl ether (DME) and hydrogen ($H_2$) have received considerable attention and are regarded as the most promising alternative fuels because of their excellent characteristics. DME is regarded as one of the potential alternative fuels and fuel additives for compression ignition (CI) engines because of its high cetane number and smokeless combustion.[1−3] It can be mass-produced from a variety of resources such as natural gas, coal, and so on. $H_2$ is also being extensively studied as an excellent alternative fuel and fuel additive to spark-ignited

engines for its high flame speed, wide flammability range,[4−7] and low required ignition energy. Recent studies on fundamental combustion and internal combustion engines with $H_2$-enriched fuels showed that hydrogen addition could accelerate the flame speed, increase the engine thermal efficiency, and decrease emissions.[8−10] The ignition behaviors of DME and $H_2$ are different. Adjusting the proportion of two fuels with different ignition properties has been reported as a technology to control the ignition timing and load in homogeneous-charge CI (HCCI) combustion,[11] and experimental studies have proven that $H_2$ is an effective ignition controller for HCCI combustion of DME.[11]

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Experimental and numerical studies of DME/air[12−20] or $H_2$/air premixed flames have been extensively carried out. However, except for a few works on the fundamental studies of DME/$H_2$ mixtures,[21] few studies reported the measurement of combustion intermediates of DME/$H_2$ blended fuel flames. To understand the details of hydrogen addition to the DME flames, the measurement of combustion intermediates of a DME/$H_2$ blend is needed. These data and their mole fractions will be helpful for the establishment and validation of the kinetic model for DME/$H_2$ blended fuel combustion.

In this study, fuel-rich ($\phi = 1.5$) DME/$H_2$/oxygen ($O_2$)/ argon (Ar) premixed flames with different hydrogen fractions (volumetric volumes of $H_2$ to the total of DME and $H_2$ were 0%, 20%, 40%, 60%, and 80%) were investigated. The effect of hydrogen addition on DME/$H_2$/$O_2$/Ar combustion was evaluated by analyzing the mole fraction profiles of the main species and major intermediates of the flames. Molecular-beam mass spectrometry and synchrotron radiation photo-ionization technology were used to identify the intermediate species and derive their mole fraction profiles.

## 2. Experimental Setup and Procedure

The experiments were carried out at the Combustion and Flame Endstation of the National Synchrotron Radiation Laboratory in Hefei, China. The instrument has been reported in the literature.[22] In brief, it consisted of a low-pressure flame chamber, a differentially pumped chamber with a molecular-beam sampling system, and a photoionization chamber with a reflection time-of-flight spectrometer, as displayed in Figure 1. Laminar premixed DME/$H_2$/$O_2$/Ar flames were stabilized on a 6.0-cm-diameter flat-flame burner (McKenna) at a pressure of 30 Torr. Flame species were sampled by a quartz conelike nozzle with an included angle of 40° and an orifice of about 500 $\mu$m at the tip. The sampled gases formed a molecular beam into the differentially pumped chamber and were collimated by a nickel skimmer upon entering the photoionization chamber. Then the collimated molecular beam was crossed by tunable synchrotron light, and the species were photoionized. The photoions were collected and analyzed by the reflection time-of-flight mass spectrometer with an approximate mass resolution of 1400. The McKenna burner was driven by a step motor. Movement of the burner toward or away from the quartz nozzle allowed mass spectra to be taken at different positions in the flame. Signal profiles of the flame species
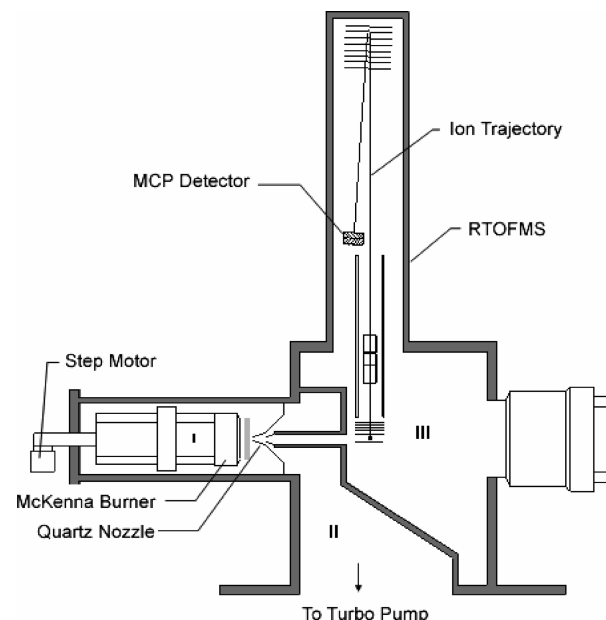
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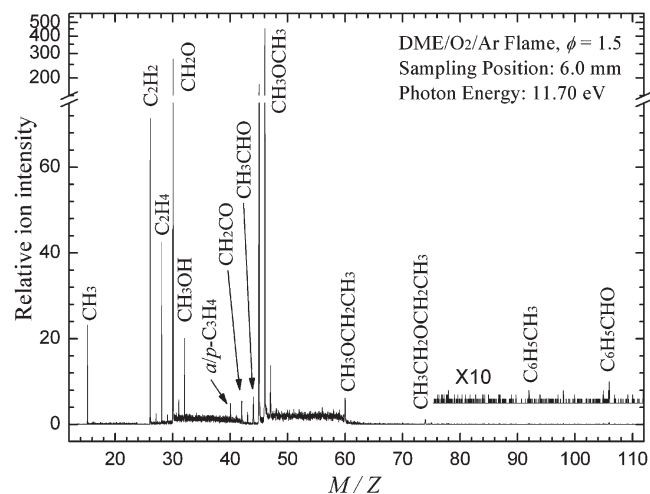
**Figure 1.** Scheme diagram of the combustion endstation.

**Table 1. Gas Flow Rates in the Experiments**

| flame no. | $R(H_2)$ (%) | gas flow rate (SLM) | | | |
| --- | --- | --- | --- | --- | --- |
| | | DME | $H_2$ | $O_2$ | Ar |
| 1 | 0 | 0.600 | 0.000 | 1.200 | 1.200 |
| 2 | 20 | 0.554 | 0.138 | 1.154 | 1.154 |
| 3 | 40 | 0.491 | 0.327 | 1.091 | 1.091 |
| 4 | 60 | 0.400 | 0.600 | 1.000 | 1.000 |
| 5 | 80 | 0.257 | 1.029 | 0.857 | 0.857 |

relative to the distance from the burner could be obtained from the spectra. Species mole fractions could be derived from the signal profiles according to the methodology reported in the literature.[22,23]

The flame temperature profile was measured by a 0.100-mm-diameter Pt−60% Rh/Pt−30% Rh thermocouple coated with BeO/$Y_2O_3$ ceramic to prevent catalytic effects, with the uncertainty of the maximum flame temperature estimated as ±100 K.

In the experiment, the fuel-rich ($\phi = 1.5$) DME/$H_2$/$O_2$/Ar flames at different hydrogen fractions (0%, 20%, 40%, 60%, and 80%) were investigated. The hydrogen fraction is defined as the volumetric fraction of $H_2$ in the DME/$H_2$ fuel blends, i.e., $R(H_2) = V(H_2)/[V(H_2) + V(DME)]$. The total flow rates of the gases were kept constant as 3.000 SLM (standard liter per minute), and the pressure of the chamber was kept at about 4.0 kPa. The purity of DME used in the experiment was 99.9%, that of $H_2$ 99.99%, that of $O_2$ 99.5%, and that of Ar 99.9%. The flow rates of the gases at different experimental conditions are listed in Table 1.

## 3. Results and Discussion

**3.1. Mass Spectra of the Flames.** A mass spectrum of the DME/$O_2$/Ar flame is shown in Figure 2 with a photon energy of 11.70 eV and a sampling position (distance from the burner surface) of 6.0 mm. At this distance, most flame intermediates reach their maximum concentrations. The photon energy of 11.70 eV is high enough to ionize those intermediates, especially acetylene with an ionization energy (IE) of 11.40 eV.

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**Figure 2.** Mass spectrum of the DME/$O_2$/Ar flame ($\phi$ = 1.5; photon energy = 11.70 eV; sampling position = 6.0 mm).

Signals at $m/z$ (mass-to-charge ratio) 15, 26, 28, 30, 32, 40, 42, 44, and 46 are readily observed. Through measurement of the IE, these intermediates are identified as methyl, acetylene, ethylene, formaldehyde, methanol, propyne/allene, ketene, acetaldehyde/ethanol, DME, methyl ethyl ether, and diethyl ether, respectively. Besides, weak peaks of toluene ($m/z$ 92) and benzaldehyde ($m/z$ 106) can also be determined from this spectrum.

Mass spectra of the DME/$O_2$/Ar flame at sampling positions ranging from 4.5 to 6.0 mm with 0.5 mm intervals are plotted in Figure 3. The signal of DME decreases continuously with an increase of the sampling position. This indicates that DME is consumed gradually. Signals of the intermediates demonstrate an increasing trend with an increase of the sampling position near the burner surface and a subsequent decreasing trend with an increase of the sampling position apart from the burner surface. This indicates the production and consumption of intermediates.

Mass spectra of the DME/$H_2$/$O_2$/Ar flame with different hydrogen fractions are compared in Figure 4. The sampling position is 5.5 mm and the photon energy is 11.70 eV for the five flames. Direct comparisons of the signals of any intermediate among the five flames are meaningless because of the difference in photon fluxes. However, a comparison of the relative signal intensity variations can be provided. When the hydrogen fraction is within 40%, the signal ratios of methyl, acetylene, ethylene, and formaldehyde to DME gradually increased with an increase of the hydrogen fraction. When the hydrogen fraction is larger than 40%, an increase in these ratios is significant. The increase in the signal ratios may be due to the lower bond energy of the C−H bond in DME than that of the H−H bond in $H_2$. The hydrogen-abstraction reaction of DME will occur more easily than that of $H_2$. This indicates that DME will be oxygenized preferentially. Hydrogen addition is beneficial to the decomposition and oxidation of DME and the formation of methyl and formaldehyde. Moreover, the formation of ethylene and acetylene greatly relies on the mole fraction of methyl. Therefore, the signal ratios of methyl, acetylene, ethylene, and formaldehyde to DME increase with an increase of the hydrogen fraction.

**3.2. Flame Temperature in the Flame Zone.** Flame-temperature profiles of the five DME/$H_2$/$O_2$/Ar flames are shown in Figure 5. The monotonous decrease in the flame
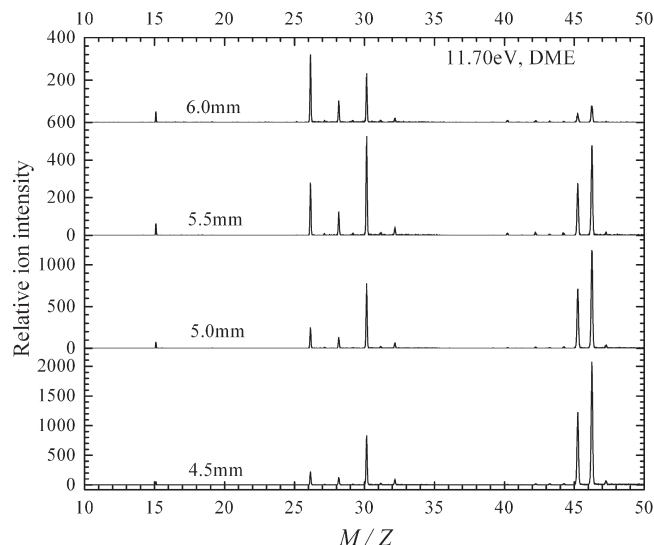


**Figure 3.** Comparison of the DME/$O_2$/Ar flame at different sampling positions ($\phi$ = 1.5; photon energy = 11.70 eV.).
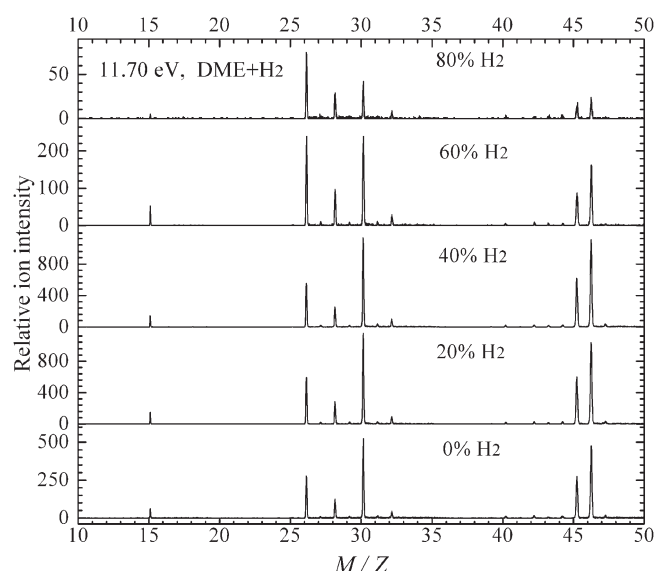


**Figure 4.** Comparison of the DME/$H_2$/$O_2$/Ar flame at different hydrogen fractions (photon energy = 11.70 eV; sampling position = 5.5 mm).

temperature is presented as the hydrogen fraction. The same effect on the flame temperature of hydrogen addition in the low-pressure, fuel-rich, premixed, burner-stabilized methane (CH$_4$)/$O_2$/nitrogen ($N_2$) flame was proven by Sepman et al.[24] In this experiment, the total flow rates of the gases were kept constant as 3.000 SLM and the pressure of the chamber was kept about 4.0 kPa. The volume calorific value of $H_2$ was much lower than that of DME. As the hydrogen fraction in the premixed mixture was increased, the heat release of the unit volume mixture decreased. Meanwhile, the burning velocities of $H_2$/DME blend fuels increased with an increase of the hydrogen fraction.[21] The higher flame velocity resulted in more heat transfer to the burner. The above two facts

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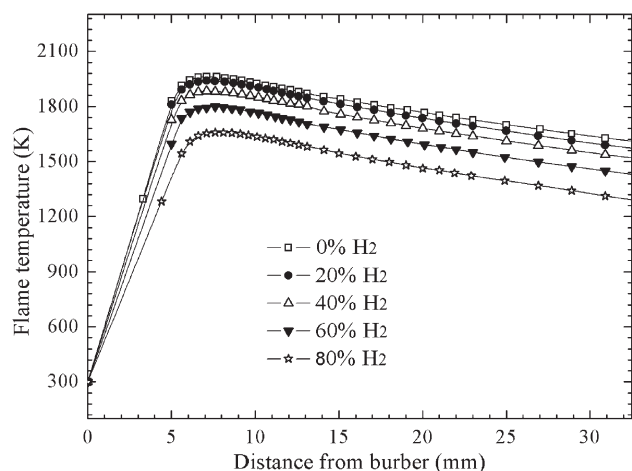
**Figure 5.** Flame-temperature profiles of the five DME/H$_2$/O$_2$/Ar flames.



**Figure 6.** Mole fraction profiles of the main flame species in the DME/O$_2$/Ar flame.

could account for the decrease in the flame temperature of DME/H$_2$/O$_2$/Ar flames as the hydrogen fraction increased.

**3.3. Mole Fraction of Major Flame Species.** Mole fraction profiles of the major species ketene (C$_2$H$_2$O), O$_2$, carbon monoxide (CO), carbon dioxide (CO$_2$), water (H$_2$O), H$_2$, and Ar are plotted in Figure 6 Because the first sampling position was 1.0 mm apart from the burner surface to prevent the sampling nozzle from being destroyed, DME and O$_2$ were fractionally consumed and there were certain amounts of products of H$_2$, H$_2$O, CO, and CO$_2$ at the first sampling position. The mole fraction profiles of the species changed greatly in the zone from burner surface to a distance of 10 mm, and this indicates that the main reaction zone was within a distance of 10 mm. Ar was added to the mixture as the dilution gas; it did not take part in the reaction. However, the mole fraction of Ar changed from 0.4 at the burner surface to 0.29 at the postflame zone, and this was due to the decomposition reaction in the flames. With the oxidation and decomposition reactions of DME, a mass of small molecules were produced, increasing the total number of elements. Meanwhile, the total sum of major species was not equal to unity. It gave the smallest value at the position of 7 mm from the burner surface because a large number of combustion intermediates were produced in the combustion process.

The mole fractions of CO and CO$_2$ at different hydrogen fractions are presented in Figure 7a,b. CO is a common intermediate of all carbonaceous fuel combustion and will become the pollutant when the combustion reaction is terminated in real combustion devices.[25] CO$_2$ is the most prominent greenhouse gas in the Earth's atmosphere and leads to global warming. The mole fractions of CO and CO$_2$ decreased with an increase of the hydrogen fraction in the fuel blends. That resulted from the decrease of the DME mole fraction in the combustible mixture. When H$_2$ was added to the mixture, the mole fraction of DME decreased. Meanwhile, the C/H ratio of the mixture will decrease, resulting in decreases of the mole fractions of CO and CO$_2$.

The mole fractions of CO and CO$_2$ at different hydrogen fractions were normalized to that without hydrogen addition and are displayed in Figure 7c,d. In contrast to the mole
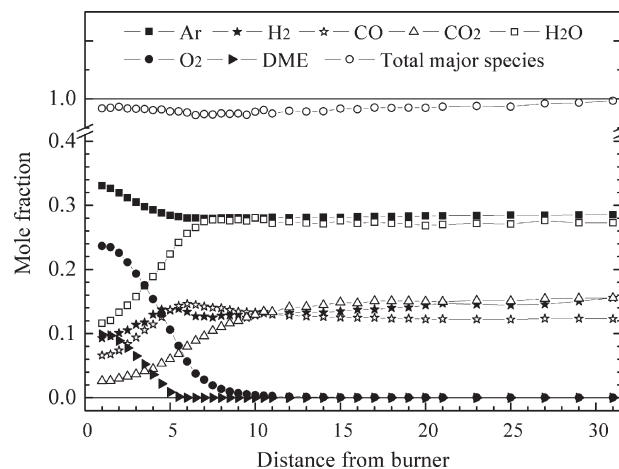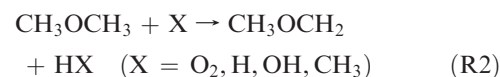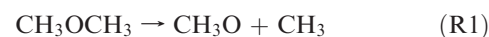
fractions of CO and CO$_2$, the normalized mole fractions of CO and CO$_2$ showed a clear increase with an increase of the hydrogen fraction. Also, the influence of hydrogen addition on the mole fraction of CO$_2$ was more remarkable than that on the mole fraction of CO. Those phenomena indicate that the addition of hydrogen to the DME/O$_2$/Ar flame can promote the decomposition and oxidation of DME, forming CO and finally CO$_2$.

CO is a common intermediate of hydrocarbon fuel combustion and will become a pollutant emission when the combustion reaction is terminated in real combustion devices. The mole fraction ratios of CO to CO$_2$ at different hydrogen fractions are displayed in Figure 7e. The mole fraction ratio of CO to CO$_2$ decreased with an increase of the hydrogen fraction, especially at the postflame zone. This indicates that hydrogen addition is beneficial to the oxidation of CO. The oxidation reaction of CO is an exothermic reaction, and a great part of the reaction release heat in combustion is released in this process. So, a decrease in the mole fraction ratio of CO to CO$_2$ by hydrogen addition can also contribute to complete combustion and improve the combustion efficiency of DME flames.

**3.4. Mole Fraction of Major C1 Species.** The mole fraction profiles of major C1 species CH$_2$O and CH$_3$ in the flames are shown in Figure 8a,b. The maximum mole fractions of CH$_2$O and CH$_3$ moved to the upstream with an increase of the hydrogen fraction, and the values changed slightly when the hydrogen fraction was within 40% but changed greatly when the hydrogen fraction was larger than 40%. The phenomena can be explained from analysis of the consumption of DME and H$_2$.

In the flame, DME is mainly consumed by two reactions, the thermal decomposition reaction and hydrogen-abstraction reaction:[26]

$$CH_3OCH_3 \rightarrow CH_3O + CH_3 \qquad (R1)$$

$$CH_3OCH_3 + X \rightarrow CH_3OCH_2$$
$$+ HX \quad (X = O_2, H, OH, CH_3) \qquad (R2)$$

Thermal decomposition of DME gives CH$_3$O and CH$_3$ by disconnection of the C−O bond (R1). CH$_3$O is unstable, which easily loses a H atom to produce CH$_2$O. The hydrogen-abstraction reaction of DME mainly gives CH$_3$OCH$_2$,

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(26) Curran, H. J.; Pitz, W. J.; Westbrook, C. K.; Dagaut, P.; Boettner, J.-C.; Cathonnet, M. A wide range modeling study of dimethyl ether oxidation. *Int. J. Chem. Kinet.* **1998**, *30*, 229–241.
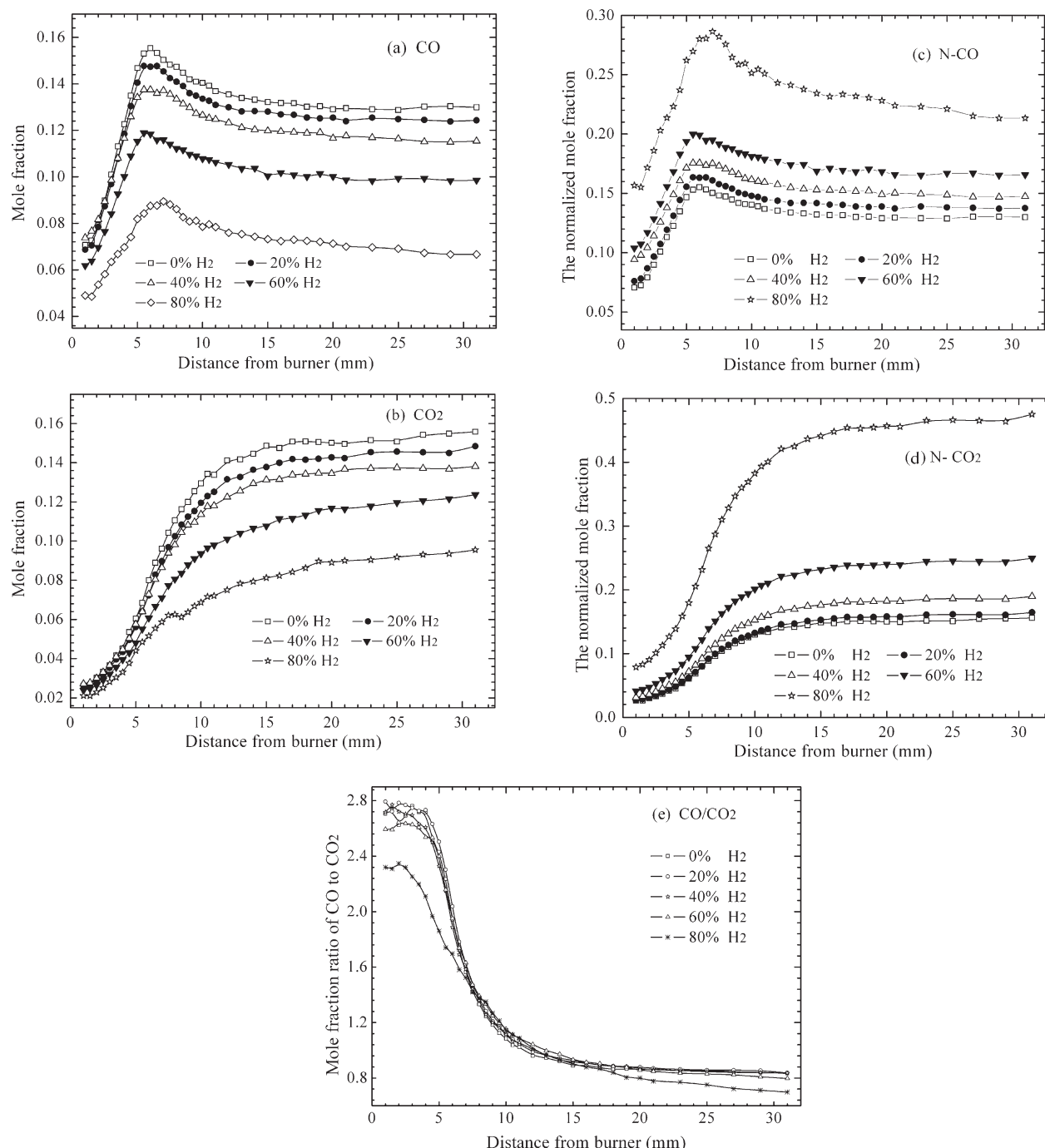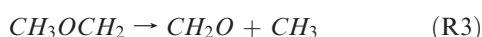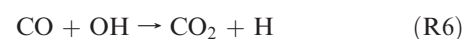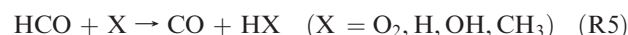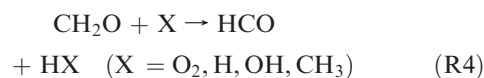
**Figure 7.** Mole fraction profiles of CO and $CO_2$ in the five $DME/H_2/O_2/Ar$ flames.

upon divestment of H by the free radicals in the flame, including OH, H, O, $CH_3$, $CH_3O$, and so on. However, $CH_3OCH_2$ is unstable and decomposes to $CH_2O$ and $CH_3$ by disconnection of the C−O bond (R3).

$$CH_3OCH_2 \rightarrow CH_2O + CH_3 \qquad (R3)$$

$CH_2O$ and $CH_3$ are the main intermediates in the combustion of DME. $CH_2O$ is mainly consumed by the hydrogen-abstraction reaction in (R4), giving the free radical HCO. HCO is unstable, and it can also be consumed by the hydrogen-abstraction reaction (R5). As discussed above, successive dehydrogenation from formaldehyde ($CH_2O$) leads to the formation of CO. CO is oxygenized

by OH or other radicals to create $CO_2$ (R6). In a DME or $DME/H_2$ flame, these reactions compose the main way to form $CO_2$.

$$CH_2O + X \rightarrow HCO$$
$$+ HX \quad (X = O_2, H, OH, CH_3) \qquad (R4)$$

$$HCO + X \rightarrow CO + HX \quad (X = O_2, H, OH, CH_3) \quad (R5)$$

$$CO + OH \rightarrow CO_2 + H \qquad (R6)$$

It does not necessarily mean that methyl have the same amount as formaldehyde, as deduced from (R3). As a free radical, methyl is more active than formaldehyde. In flames,
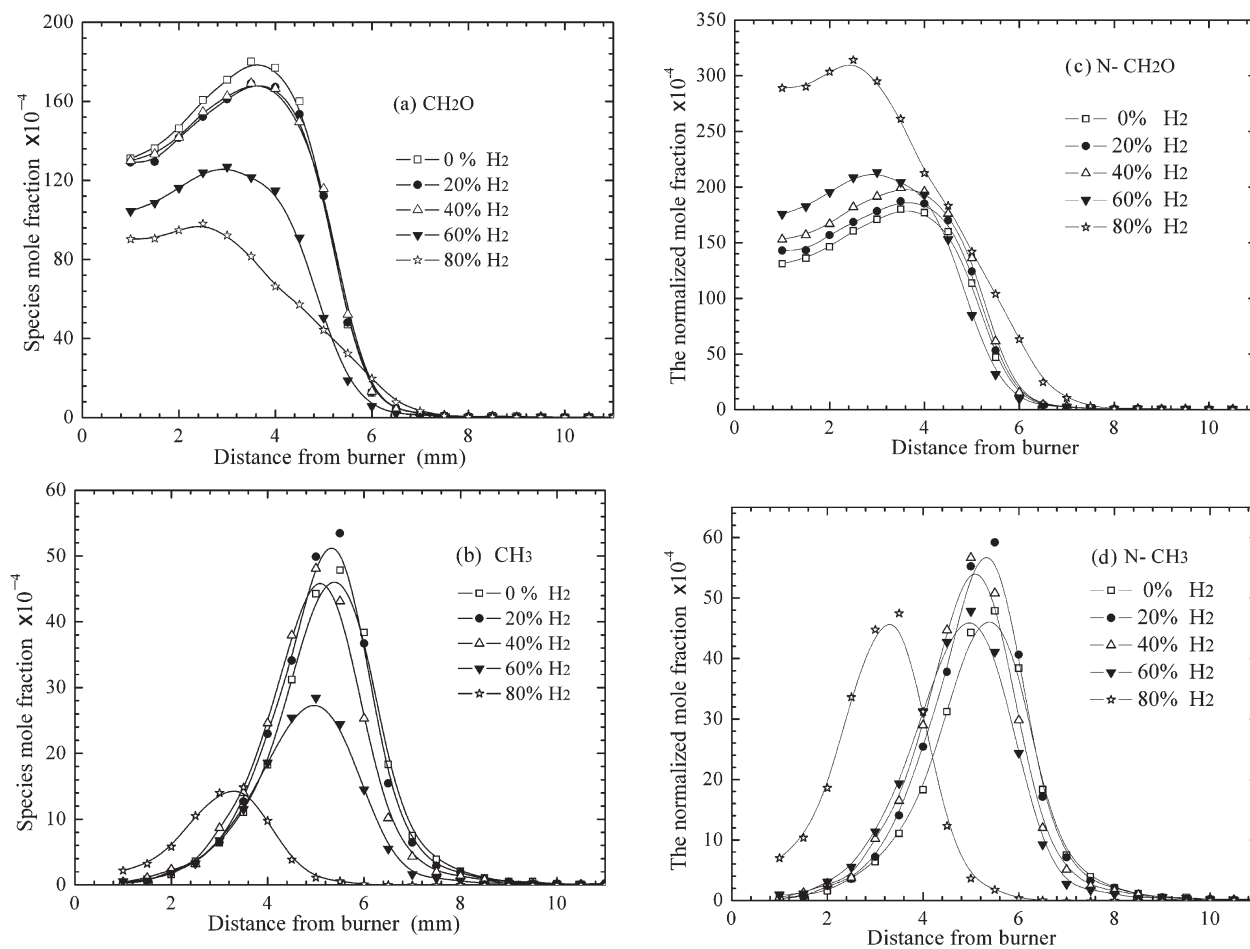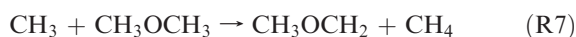
**Figure 8.** Mole fraction profiles of major C1 species in the five DME/$H_2$/$O_2$/Ar flames.

methyl can readily be consumed by other molecules, such as DME and $O_2$:

$$CH_3 + CH_3OCH_3 \rightarrow CH_3OCH_2 + CH_4 \tag{R7}$$

$$CH_3 + O_2 \rightarrow CH_2O + OH \tag{R8}$$

The addition of $H_2$ to the DME flame decreases of the mole fraction of DME and the C/H ratio in the mixture. This is the main factor that leads to a decrease of the mole fractions of carbonaceous intermediate radicals of $CH_2O$ and $CH_3$. The oxidation reaction of $H_2$ is a reaction in which the total amount of substances decreases. When the fuel amount is constant, the addition of $H_2$ to the flame leads to a decrease of the total amount of substance in the flame. Furthermore, the addition of $H_2$ to the flame can also affect the oxidation and decomposition and the mole fraction of intermediate radicals. These three factors are responsible for the change of the mole fractions of $CH_2O$ and $CH_3$.
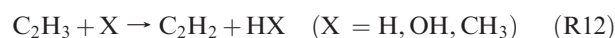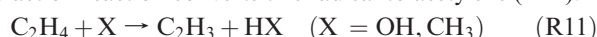
The hydrogen-abstraction reaction of DME occurs more easily than that of $H_2$ because of the lower bond energy of the C−H bond in DME than that of the H−H bond in $H_2$. This indicates that DME can be oxygenized preferentially. It can be imagined that hydrogen addition will make the mixture become "lean" for DME. Therefore, the addition of $H_2$ is beneficial to the oxidation and decomposition of DME. This is obviously demonstrated by the normalized mole fraction profile of $CH_2O$ and $CH_3$ in Figure 8c,d. When a slight amount of $H_2$ is added to the mixture, enhancement of the oxidation of DME and reduction of the total amount of mixture after the reaction partially

counteract the reduction of carbonaceous intermediate radicals caused by the decrease of the C/H ratio. Thus, the normalized mole fractions of $CH_2O$ and $CH_3$ are slightly changed. With a further increase of the hydrogen fraction, the decrease of the C/H ratio in the mixture becomes the dominate factor that affects the mole fraction of carbonaceous intermediate radicals in the flame. Consequently, the normalized mole fractions of $CH_2O$ and $CH_3$ increase greatly with a further increase in the hydrogen fraction.

**3.5. Mole Fraction of Major C2 Species.** Ethylene and acetylene are the major C2 species in the five flames. Mole fraction profiles of these two species are presented in Figure 9. Ethylene can be formed from the combination reaction of methyl in the flame: First, methyl radicals combine to form an ethyl radical (R9). Then the unstable ethyl radical produces ethylene by a dehydrogenation reaction (R10).

$$CH_3 + CH_3 \rightarrow C_2H_5 + H \tag{R9}$$

$$C_2H_5 + X \rightarrow C_2H_4 + HX \quad (X = H, O_2) \tag{R10}$$
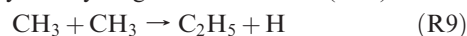
Successive dehydrogenation from ethylene leads to the formation of acetylene in flames: First, an H atom is abstracted from ethylene to form ethenyl (R11). Then, a second hydrogen-abstraction reaction converts this radical to acetylene (R12).

$$C_2H_4 + X \rightarrow C_2H_3 + HX \quad (X = OH, CH_3) \tag{R11}$$

$$C_2H_3 + X \rightarrow C_2H_2 + HX \quad (X = H, OH, CH_3) \tag{R12}$$

The maximum mole fraction of acetylene appears downstream to that of ethylene. This difference may originate
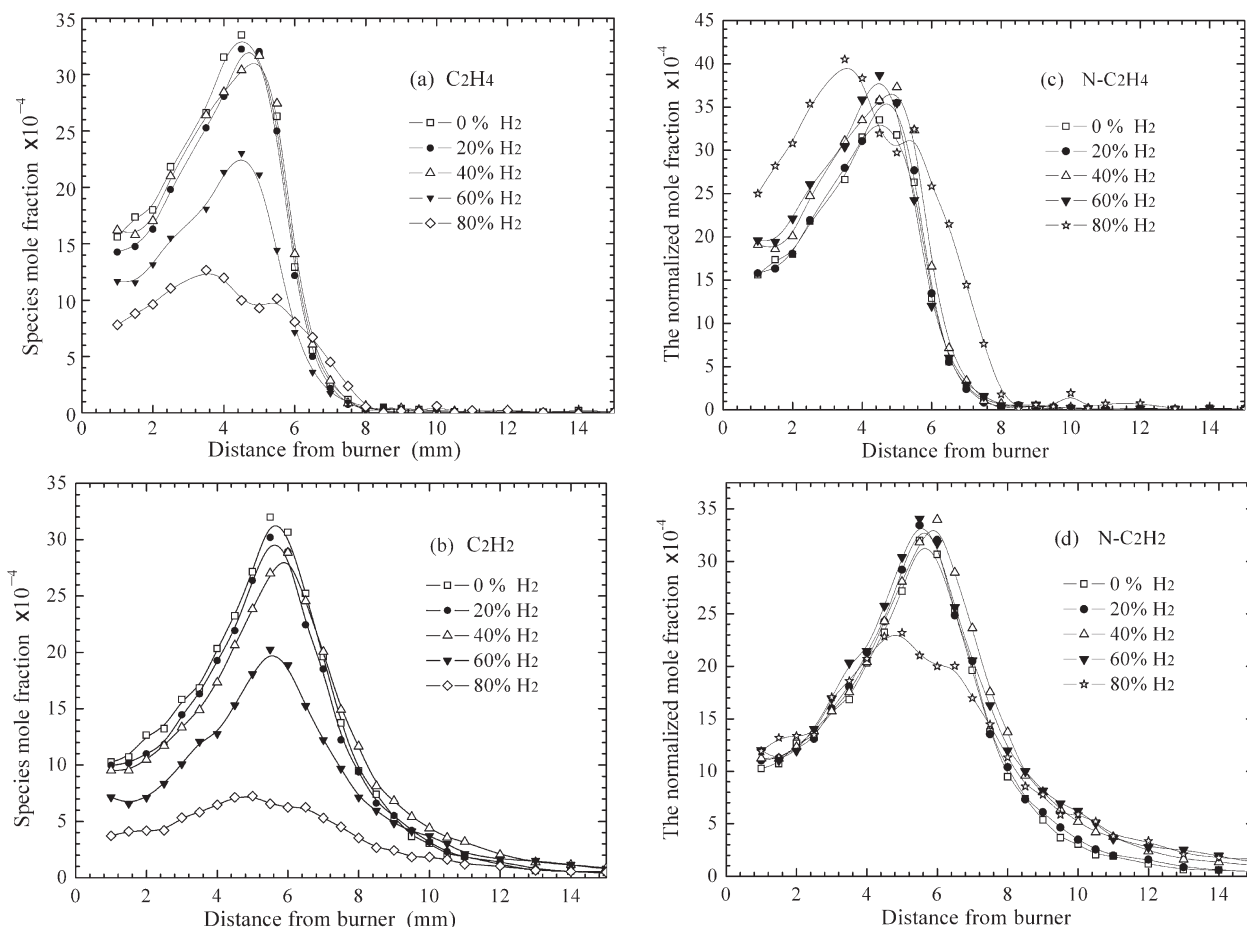
**Figure 9.** Mole fraction profiles of major C2 species in the five DME/H$_2$/O$_2$/Ar flames.

from the lower transition rate from ethenyl to acetylene compared to that from ethyl to ethylene because the C−H bond energy in ethenyl is higher than that in ethyl. Besides, the C−H bond energy in acetylene is higher than that in ethylene, thus resulting in the lower-consuming reactions of acetylene compared to that of ethylene. Acetylene is mainly consumed by reaction with hydroxyl and an O atom. Besides the hydrogen-abstraction reaction giving ethylene and acetylene, the ethyl radical and ethenyl can also be consumed by reaction with an O atom and give vinyl alcohol (C$_2$H$_4$O) and ketene (C$_2$H$_2$O).

As shown in Figure 9a,b, the peak values of the mole fractions of ethylene and acetylene shift to upstream with an increase of the hydrogen fraction. At a specific burner position, the mole fractions of each species decrease with an increase of the hydrogen fraction. Furthermore, the drop is more obvious at large hydrogen fractions than at small ones. Because the combination reaction of methyl is the leading reaction to the formation of ethylene and acetylene, the mole fractions of ethylene and acetylene in the flames are greatly dependent on the mole fraction of methyl. The C/H ratio is decreased when H$_2$ is added to the mixture, leading to a decrease of the mole fractions of methyl and C2 species.

Compared to C1 species, the normalized mole fractions of ethylene and acetylene give a slight change with an increase of the hydrogen fraction, as shown in Figure 9c,d. The normalized mole fraction of acetylene at a hydrogen fraction of 80% is decreased compared to those of low hydrogen fractions. As analyzed above, the addition of H$_2$ is beneficial to the oxidation and decomposition of DME. The normal-

ized mole fraction of methyl increases with an increase of the hydrogen fraction. It does not necessarily mean that the amount of ethylene and acetylene will increase with an increase of the methyl amount. As a free radical, methyl is more active and can easily react with other atoms or free radicals. These reactions compete with the combination reaction of methyl. Meanwhile, ethyl and ethylene radicals are not only consumed by the dehydrogenation reaction and form ethylene and acetylene but also consumed by reaction with an O atom and form C$_2$H$_4$O and C$_2$H$_2$O. Because the bond energy of the H−H bond in hydrogen is higher than that of the C−H bond in the mixture, the mixture becomes lean when H$_2$ is added to the mixture. This promotes reactions of methyl, ethyl, and ethylene radicals with an O atom and restrains the formation reactions of ethylene and acetylene. Thus, the normalized mole fractions of ethylene and acetylene are decreased.

## 4. Conclusions

Laminar premixed fuel-rich ($\phi = 1.5$) DME/H$_2$/O$_2$/Ar flames with different hydrogen fractions were investigated with tunable synchrotron vacuum-ultraviolet photoionization and molecular-beam sampling mass spectrometry techniques. Mole fractions of the main products and major intermediates are calculated based on measured ion signal intensity profiles. The influences of the hydrogen fractions on the flames are analyzed.

(1) The flame temperature in the flame zone decreases with an increase of hydrogen addition. This is mainly due to

the decrease in the volume calorific value of the mixture and increase in the heat transfer to the burner by hydrogen addition.

(2) Mole fractions of CO, $CO_2$, $CH_2O$, $CH_3$, $C_2H_2$, and $C_2H_4$ in the flames decrease with an increase of the hydrogen fraction, especially when the hydrogen fraction changes from 40% to 80%. This is mainly due to a decrease of the mole fraction of DME and a decrease of the C/H ratio in the mixture.

(3) At the post flame zone, the mole fraction ratio of CO to $CO_2$ decreases with an increase of the hydrogen fraction. This indicates that hydrogen addition can promote oxidation of CO and is beneficial to the complete combustion of DME.

(4) Normalized mole fractions of CO, $CO_2$, $CH_2O$, and $CH_3$ increase with an increase of the hydrogen fraction. Hydrogen addition is beneficial to the decomposition and oxygenation of DME.

(5) Normalized mole fractions of $C_2H_2$ and $C_2H_4$ change slightly with the hydrogen fraction. Hydrogen addition is beneficial to reactions of methyl, ethyl, and ethylene radicals with an O atom and restrains the formation reactions of ethylene and acetylene.