Title	Two-stage ignition of DME/air mixture at low-temperature (< 500 K) under atmospheric pressure
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Citation	FUEL, 106, 241-248 https://doi.org/10.1016/j.fuel.2012.12.085
Issue Date	2013-04
Doc URL	http://hdl.handle.net/2115/52753
Type	article (author version)
File Information	fuel_corrected_manuscript_20130528.pdf

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Two-stage Ignition of DME/air Mixture at Low-temperature (<500K) under Atmospheric Pressure

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Abstract

Low-temperature ignition characteristics of dimethyl ether (DME)/air mixture were studied in an external heated, straight-shaped, plug-flow reactor under atmospheric pressure. Auto-ignition of the mixture was attained under a specific narrow range of temperature and equivalence ratio with relatively longer exposure time. Three kinds of ignition behaviors were identified accordingly as the equivalence ratio increased, such as (1) periodic hot flames, followed by (2) periodic two-stage ignitions (weak flame(s) and subsequent hot flame), lastly (3) chaotic weak flames. Time-sequential gas analyses were conducted for the case showing a typical periodic two-stage ignition in order to investigate the mechanism of the observed low-temperature auto-ignition under 500 K. The results revealed that the formation of CH_4 and C_2H_2 was promoted prior to the hot flame ignition, suggesting that the chain-branching reaction pathway might exist. The transition from weak flame to hot flame was clearly observed as the mixture equivalence ratio decreased, implying the oxygen could be responsible to trigger this transition. It is suspected that the chain-branching precursor $\text{CH}_2\text{OCH}_2\text{OOH}$ radicals should be relatively stable in the examined temperature range here, thus can gradually accumulate through a longer exposure time, and eventually give rise to the chain-branching explosion.

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Keywords: dimethyl ether, low-temperature oxidation, low-temperature auto-ignition, flames with repetitive extinction and ignition (FREI), two-stage ignition, cool flame.

Highlights

- ▶ Auto-ignition of DME/air mixture was captured in a specific narrow range in temperature and equivalence ratio.
- ▶ Weak flame is transited to hot flame as equivalence ratio decreases.
- ▶ CH_4 and C_2H_2 formed due to the chain-branching reaction pathways.

Graphical abstract:

1. Introduction

Dimethyl ether (DME: CH_3OCH_3) has been considered as a promising alternative fuel due to its merits of favorable compression ignition property and little soot formation in combustion field [1]. On the other hand, because of its higher reactivity at low-temperature, the leakage of DME in transportation or storage may cause an accidental fire and the harmful species might be produced associated with incomplete combustion [2]. A better understanding of DME low-temperature oxidation under atmospheric condition is, therefore, of a scientific as well as practical interest.

A number of experimental [3-13] and theoretical [14-17] studies have been accomplished to elucidate the detailed processes of DME oxidation at low-temperature. The atmospheric chemistry of DME has been studied with attention to the reactions of methoxymethyl radical (CH_3OCH_2) with itself, chlorine (Cl_2), and oxygen (O_2) [3-7]. Sehested et al. [3] and Maricq et al. [4] suggested that the reaction between CH_3OCH_2 radicals and O_2 proceeded along two distinct pathways between 230 and 350 K. For instance, At 296 K, the formation of methoxymethyl-peroxy radicals ($\text{CH}_3\text{OCH}_2\text{OO}$) dominated at pressures above 10 Torr, while the formation of formaldehyde (HCHO) and hydroxyl radicals (OH) dominated at pressures less than 10 Torr. Jenkin et al. [5] found that the self-reaction of $\text{CH}_3\text{OCH}_2\text{OO}$ radicals could lead to the formation of methyl formate (CH_3OCHO) and hydroperoxy radicals (HO_2) at 298 K. Japar et al. [6] indicated that the consumption of DME was accompanied by the formation of CH_3OCHO at 700 Torr and 295 K.

Detailed chemical models of DME oxidation at low-temperature were proposed by Dagaut et al. [8] and Curran et al. [10, 11], which have been validated by the experimental results of jet-stirred reactors [8], flow reactors [11], shock tubes [18] and

others [13, 19, 20]. These models have been developed based on the typical two-stage oxidation mechanisms for long-chain hydrocarbons [21]. Fig. 1 shows the overall reaction scheme for DME oxidation proposed by Curran et al. [11]. The mechanism starts with the abstraction of a hydrogen atom (H) from a DME molecule by a highly reactive radical, like OH radical, to form a CH_3OCH_2 radical, followed by the formation of a $\text{CH}_3\text{OCH}_2\text{OO}$ radical after a barrier-less reaction with O_2 , and then the $\text{CH}_3\text{OCH}_2\text{OO}$ radical isomerize to form a hydroperoxy-methoxymethyl radical ($\text{CH}_2\text{OCH}_2\text{OOH}$). In the temperature range of 530-600 K, $\text{CH}_2\text{OCH}_2\text{OOH}$ radicals combine with O_2 to lead chain-branching pathways, which often results in a “cool flame”. The term “cool” implies that this so-called flame does not reach its adiabatic flame temperature and the reacting mixture is not completely consumed. As temperature increases, the reaction rate decreases in the temperature range of 600-725 K due to the β -scission of $\text{CH}_2\text{OCH}_2\text{OOH}$ radicals, where there is a negative temperature coefficient (NTC) zone; the DME consumption is suppressed by the chain-propagation pathway of decomposition of $\text{CH}_2\text{OCH}_2\text{OOH}$ into two HCHOs and one OH radical. Lastly, when the temperature becomes higher than 730 K, the reactivity of the system increases again to induce rapid consumption of the remained fuel due to the breaking of the HO-OH bond in hydrogen peroxides. This is the second stage ignition with the non-chain-branching ignition mechanism.

This staged oxidation behavior has been captured by Liu et al. [22] and Oshibe et al. [19] at atmospheric pressure. Liu et al. [22] investigated the oxidation of DME at atmospheric pressure using a laminar flow reactor. Considered range of the temperature was from 513 K to 973 K and the residence time was set at 2-4 s. The products of reaction were determined by Fourier transform infrared spectrometer (FTIR). The

results showed that the reaction rate of DME oxidation was enhanced with increasing of temperature from 533 K and reached a maximum at approximately 633 K, after which the negative temperature coefficient (NTC) zone was encountered. More importantly, based on their observation, it was concluded that the formic acid (HCOOH) should be a major intermediate of the low-temperature oxidation. Oshibe et al. [19] reported a three-stage oxidation phenomenon of DME/air mixture using a micro flow reactor with a controlled temperature profile. Stable double weak flames were observed when the supplied rate was low (i.e., small velocity was imposed). The existence of low-temperature oxidation was conjectured by the production of HCHO occurring upstream the experimental first weak flame.

It should be noticed that the reported ignition temperatures under atmospheric pressure were always higher than 500 K except for our previous experimental report [23]. In our previous study [23], DME oxidation was conducted by a U-shape reactor below 550 K, and unexpected auto-ignition was observed at 483 K (< 500 K). U-shape reactor was somewhat uncertain in terms of uniformity so that we updated the reactor shape from U-shape to straight, which enabled us to make more careful observations and gas analyses in the present study. Besides the normal hot flame captured in [23], weak flame and two-stage ignition were first observed with a further attention. Different ignition behaviors as a function of mixture gas equivalence ratio were summarized accordingly. Time sequential gas sampling analyses were conducted along a typical two-stage ignition behavior by gas chromatograph (GC) system in order to discuss the potential chemical pathways that describe the observed low-temperature ignition.

2. Experimental

Fig. 2 shows the schematic of the experimental setup used in this study. Premixed DME/air mixture was supplied into a straight 1400 mm long Pyrex tube (referred as reactor, hereafter) with the inner and outer diameter of 12 mm and 15 mm. Ribbon heater was surrounded in order to control the temperature of the whole reactor. Several small slits were intentionally made for visual access to the luminous emission by the inner reacting flow. A digital video camera (Sony HDR-XR500, 30 frames per second) was used to record the auto-ignition events.

K-type thermocouples (junction diameter of 1.0 mm) were inserted at 400 and 900 mm from the inlet (later, we may call these points are simply “400 mm” or “900 mm”). The thermocouple junction (sensor part) was placed on the axis of the reactor in order to monitor the temperature of the flowing gas. Preliminary, we measured multi-points temperature and confirmed that the temperature along the reactor was uniform within an error of 2.0 K at the objective temperature of 500 K. Flow rate of DME was controlled by a mass flow controller (Kofloc model-5100), while flow rate of air was controlled by an orifice flow rate controlling system, which had been calibrated by a bubble flow meter (the accuracy is over 99%).

Gas sampling points were fixed at 400 mm and 900 mm as well. Gas in the reactor was sampled by a 2.0-ml-volume Pyrex syringe (TOP type-0310) and analyzed by direct injection of 1.0 ml sample into a gas chromatograph (Shimadzu GC-14B) with a thermal conductivity detector (TCD). The Syringe was preheated to 383 K to prevent possible condensations of the sample prior to injection. Hydrogen (H_2), oxygen (O_2), nitrogen (N_2), methane (CH_4) and carbon monoxide (CO) were separated by a molecule sieve 5A 80/100 column, and carbon dioxide (CO_2), acetylene (C_2H_2), formaldehyde

(HCHO), dimethyl ether (DME), water (H₂O), methyl formate (CH₃OCHO), and formic acid (HCOOH) were separated by a Proapak T 50/80 column. Calibrations for HCHO, H₂O, CH₃OCHO, and HCOOH were conducted by using the vaporization gases of corresponding solutions.

Here let us give the typical sequence to induce the first ignition in this study. First, the gas temperature was controlled at 483 K, mixture flow rate at 44.2 ml/min, and mixture equivalence ratio at 1.5-2.0. In that case, the oxidation process slowly proceeded without any subsequent auto-ignition to possibly reach equilibrium states ; this is called “mild oxidation” hereafter. The mild oxidation was remained for about two or three hours in order to ensure to stay the equilibrium states, then the temperature was increased or decreased with the heating rate of about 11 K/min within the range from 463 K to 513 K. The ignition could occur at certain temperature, which was considered as the “optimal auto-ignition temperature”. After tens of minutes of mild oxidation at the optimal auto-ignition temperature, the first ignition was finally achieved.

Once ignition was experienced, the flame was generated and propagates passing through the thermocouples. Then the flame was quenched at the inlet and temperature of gas in the reactor starts to decrease gradually until the controlled temperature as the fresh DME/air mixture flows into the reactor. Following some delays, re-ignition occurred periodically or chaotically. The temperature increment as well as the periodic duration (in the case of periodic behavior) depends on the flow velocity, temperature, and equivalence ratio of the mixture.

The supplied mixture flow rate was fixed at 78 ml/min throughout this study. At 488 K, the corresponding flow velocity was 18.8 mm/s, and the corresponding exposure time was about 21 s and 48 s at 400 mm and 900 mm, respectively. Adopting this flow

rate, the ignition was found at around 900 mm so that we could capture the temperature history at the ignition position.

3. Results and discussion

3.1 Low-temperature auto-ignition regime

Fig. 3 shows the obtained “auto-ignition” regime in temperature-equivalence ratio plane. Note that the definition of “auto-ignition” herein is the sudden temperature rise associated with observable luminous light emission. The auto-ignition could be only found in the limited range of temperature and equivalence ratio shown as blue shadow in the Figure, otherwise no apparent light emission or temperature rise was detected, mild oxidation slowly occurred instead. The auto-ignition regime obtained in the present study is consistent with our previous results by using a U-shape reactor [23] except for about 5 K differences in upper and lower boundary. These differences could result from the uncertainties of the K type thermocouples (± 2.5 K), temperature disunities along the reactor (2.0 K), and the irregular shape of the previous U-shape reactor.

After the auto-ignition was experienced, two kinds of flames were identified: one was a dim blue flame, which might partially consume the mixture gas, was defined as “weak flame”; the other one was a relatively bright flame, which might completely consume the mixture gas, was defined as “hot flame”. Appearances of these two modes of flame depend on the condition applied here. In the following, let us discuss this issue in detail.

3.2 Periodic ignition behaviors

3.2.1 Observed ignition behaviors against the equivalence ratio

Fig. 4 shows a series of temperature histories at different equivalence ratios of the mixture. The temperature was controlled at 488 K. Note that the measured temperature at the ignition becomes much lower than the actual field temperature due to insufficient residence time to reach thermal equilibrium, thus the thermocouple signal in this study is only used to detect the time when the generated flame passes through that location. Periodic hot flames were obtained at the equivalence ratio of 1.47, as shown in Fig. 4a. Under this condition, a luminous hot flame appears after the ignition at around 900 mm and then propagates both upstream and downstream, eventually is quenched at the inlet and outlet. The flame propagation was recorded by the video camera as shown in Fig. 5. The circles indicate the locations where the flames were captured. The hot flame propagates throughout the tube thus refreshes the whole reactor. Then the fresh mixture gas flows into the reactor, and re-ignition is experienced when and where the ignition condition meets. In this way, we have periodic ignition behaviors. The periodic duration is about 78 s, which is quite robust.

As the equivalence ratio increases from 1.47 to 1.65, the hot flame at 900 mm is “separated” into two flames, namely a weak flame and a subsequent hot flame. Fig. 4b shows the temperature history under this condition. As indicated by the cycle in the figure, the former peak corresponds to a dim blue flame (weak flame), while the latter one corresponds to a relatively bright flame (hot flame). Flame images taken by the video camera at 900 mm are shown in Fig. 6. Fig. 6a-2 and 6b-2 are the gray scale images, and the gray value of the hot flame (62.38 a.u.) is more than three times higher than that of the weak flame (17.22 a.u.), suggesting that the hot flame is much brighter than the weak flame. Since two distinct flames (weak and hot) were observed in this ignition behavior, we referred this as “two-stage ignition” behavior in this study. Fig. 7

depicts the typical periodic two-stage ignition behavior with the cycle duration of 60 s schematically.

When the equivalence ratio was set at 1.73, another periodic “two-stage ignition” behavior was obtained, the temperature history of which is shown in Fig. 4c. The frequency of the periodic behavior is also robust at about 136 s per cycle. Each cycle includes three featured periods: (1) The first mild oxidation period τ_1 , the duration of which is about 74-78 s; (2) The multiple “weak flames” period τ_2 , which involves about 5-7 weak flames, and (3) The second mild oxidation period τ_3 . The time interval between the neighboring two weak flames in τ_2 is about 5-7 s. The weak flames here also initially appear at around 900 mm. Multiple small oscillations in temperature can be observed at 400 mm simultaneously, which should be due to the upstream propagation of the weak flame. After the multiple weak flames appear, no flaming is detected during the period of τ_3 , which takes about 40-50 s until a hot flame appears at around 900 mm. The hot flame consumes all fuel components by propagation throughout the reactor, and then proceeds to next cycle.

As the equivalence ratio increases higher than 1.80, the reaction system shows a behavior with chaotic weak flames, as shown in Fig. 4d. Weak flames were observed, however the hot flame was never attained at such higher equivalence ratio. Additionally, we failed to capture any apparent periodic behavior under this condition, but random appearances of weak flames were always experienced.

Table 1 summarizes the different flame responses against the equivalence ratio. It is indicated that the sequence of flame responses observed in the auto-ignition regime as the equivalence ratio decreases is:

$$[\text{Weak flames}] \rightarrow [\text{weak flame(s)} + \text{hot flame}] \rightarrow [\text{hot flame}].$$

3.2.2 Similarities of the observed phenomenon to FREI [19, 24-26]

Similar periodic ignition and extinction behaviors, termed flames with repetitive extinction and ignition (FREI), have been observed in a heated microchannel for variety of hydrocarbons mixture such as methane-air [24, 25], DME-air [19], and n-heptane-air [26]. The ignition of FREI occurs downstream due to the high wall temperature ($>1000\text{K}$) and the ignition front propagates upstream. The flame is finally quenched in the upstream due to the large heat loss to the low temperature wall. Following some time delays after quenching, re-ignition is experienced as the fresh mixture flows in. In the present study, the reactor temperature was always controlled at relatively low temperatures ($<500\text{ K}$), not like that in the series of previous FREI studies [19, 24-26]. This is the reason why we have extremely longer ignition delays (tens of seconds) compared with that in the study [19] (20-100Hz, i.e. 0.01-0.05 s delay, for DME/air mixture).

A recent paper by Nakamura et al. [27] investigated the detailed process of FREI for a methane/air mixture. It numerically reproduced the flame bifurcation due to the separation of the unburned mixture in high-temperature ignition phase. What's more important, this paper newly found that the intermediates such as CO, CH₃, OH, and H could cause bifurcations of heat release peak in the weak reaction phase (at the low-temperature side). It is interesting to see that, as stated above, the bifurcated flames have been observed in the present study (i.e. the hot flame occurs at around 900 mm and propagates upstream and downstream). However, due to the fact that different kinds of intermediate products should be produced during the ignition events in the present system, there is no guarantee that the scenario leading to the ignition here is consistent

with the FREI study [e.g. 27]. Moreover, the main objective in this study is to investigate the trigger of the two-stage ignition in the low-temperature, which occurs somewhere in the “long” mixing zone between the fuel and the products; it could generate key important intermediates there. In this way, the species analysis during the ignition event is very important. In the next, we will discuss the issues about the intermediates based on the gas analysis results obtained by GC.

3.3 Time-sequential gas analyses of flames

Time-sequential gas analyses were conducted under the condition with the typical two-stage ignition behavior shown in Fig. 4c. The reason to pick this condition is that, mild oxidation, weak flame and hot flame are all included in each cycle, which enable us to investigate the roles of the intermediates in the transition from mild oxidation to weak flame, and then hot flame. Four sampling moments (t_1 to t_4) in each cycle, as shown in Fig. 8, were set as follows:

t_1 : 50 s after the hot flame;

t_2 : 15 s after the first weak flame;

t_3 : 15 s after the last weak flame;

t_4 : 10 s after the hot flame.

For gas sampling, rapid extraction was accomplished within one second (< 1.0 s) to ensure that the sampling was made at the objective sampling moment. As long as the extraction time was controlled as less than one second, no apparent difference in gas analysis results was found with different extraction speeds. Considering the sampling volume (1.0 ml) is much smaller than the volume of the reactor tube (about 158 ml), the disturbance to the flow field is considered as negligible. The gas sampling was made at

400 mm and 900 mm. Thanks to the concrete periodic behavior, we were able to conduct several times of analyses at each sampling moment to ensure the reproducibility of the results. Fig. 9 shows the gas analysis results. The volumetric concentrations of all species are normalized without nitrogen.

As stated previously, it took about 21 s and 48 s for the fresh mixture gas to reach at 400 mm and 900 mm, respectively. Therefore, gas composition at t_1 for the location of 400 mm should be mostly replaced by the fresh DME/air mixture except certain quantity of H_2 (it might be due to the relatively higher diffusion coefficient of H_2). Interestingly, at the 900 mm point, the relatively large amount of CO , CO_2 and H_2O exist; they might be the products of upstream propagated hot flame in the previous cycle. More importantly, it should be noted that $HCHO$ and $HCOOH$ also exist there; probably these would be originally formed by the mild oxidation of DME/air mixture, not the low-temperature ignition.

Point t_2 is during the multiple weak flames period τ_2 (Fig. 4c). It is understood that, the weak flame can only partially consume the DME/air mixture, thus DME and O_2 always exist at this time. Compared with t_1 , the volumetric concentration of CH_4 and C_2H_2 at 900 mm is higher, which indicates that CH_4 and C_2H_2 might be the products due to the weak flames.

Point t_3 is after the last weak flame of period τ_2 , i.e. during the second mild oxidation period τ_3 . Thanks to the previous oxidation periods τ_1 and τ_2 , a plenty of intermediates accumulate in the system. Therefore, the intermediates including $HCHO$, $HCOOH$ and CH_3OCHO reach their maximum concentrations at 900 mm. No $HCOOH$ and CH_3OCHO are detected at 400 mm, which might be due to the insufficient time to

produce and accumulate there. The disappearances of CH_4 and C_2H_2 at this time imply that both of them result from flames (weak or hot) but not the mild oxidation.

As mentioned previously, the second mild oxidation period τ_3 is ended by a hot flame, which occurs at around 900 mm and then refreshes the reactor by flame propagation. As shown at t_4 , DME and other intermediate species (HCHO , HCOOH and CH_3OCHO) are completely consumed and converted into CO , CO_2 , H_2O , H_2 , CH_4 , and C_2H_2 . The propagation of the hot flame makes it almost uniform throughout the reactor, showing that the composition at 400 mm is almost same as that at 900 mm.

3.4 Potential auto-ignition mechanism at low-temperature

According to the existing model proposed by Curran et al. [11], the mechanism of DME oxidation at low-temperature is dominated by the competition between the chain-propagation and chain-branching reaction steps. The chain-branching steps should be responsible for the low-temperature auto-ignition (explosion). As stated above, chain-branching in the DME oxidation system depends on the availability of the $\text{CH}_2\text{OCH}_2\text{OOH}$ radical. This chain-branching precursor is expected to be relatively stable and has a long lifetime below 600 K [8, 11, 15]. During the experimental work by Liu et al. [22], the reactions responsible for the low-temperature ignition were first detected at about 533 K with residence time of 3.9 s. It is suggested that the longer exposure time in our study may give a fairly long enough time for the $\text{CH}_2\text{OCH}_2\text{OOH}$ radical accumulating and reacting with O_2 , and then undergo the decomposition reactions to release more than one reactive radical (mainly OH radicals) to realize a chain-branching. However, once the temperature gets higher than 600 K, the β -scission of the precursor $\text{CH}_2\text{OCH}_2\text{OOH}$ radical is imposed to be dominant in the

process of DME oxidation [11]. Therefore, the chain-branching reactions can be suppressed by the β -scission of the precursor ($\text{CH}_2\text{OCH}_2\text{OOH}$) on account of the sudden heat release of the weak flame. Thus, the weak flame represents the “self-inhibited behavior” that prohibits consuming the reactants completely.

The decomposition reaction of one $\text{CH}_2\text{OCH}_2\text{OOH}$ radical into two HCHOs and one OH has been proposed as the main chain-propagation pathway, which occurs in the temperature range of 600-725 K [8, 11]. However, we have detected non-negligible amount of HCHO, HCOOH, and CH_3OCHO in the mild oxidation period (see Fig. 9b), suggesting that there should be other chain-propagation pathways under 500 K. The model of Curran et al. [11] invokes the species hydroperoxymethyl formate (HPMF, $\text{HO}_2\text{CH}_2\text{OCHO}$) to be responsible for the second OH radical release of chain-branching pathway. However, Liu et al. failed to detect HPMF and indicated that HPMF is less thermally stable than assumed or there are other reactions of HPMF [22]. Moreover, Anderson and Carter showed that the fate of HPMF is potentially very complicated and proposed several possible decomposition paths of HPMF [14]. Once the HPMF follows the decomposition reactions that release no OH radical, it turns to be a new chain-propagation pathway. The ambiguity of reactions related to HPMF also can be one of the important reasons that cause the strong temperature dependency of the auto-ignition regime as shown in Fig. 3.

According to the gas analysis results, CH_4 is found to be one of the key products of the low-temperature ignition, which is consistent with the experimental and numerical results of Oshibe et al. [19]. Moreover, the results indicate C_2H_2 to be another product formed through the explosive reactions. Traditionally, the transition from steady state to explosive kinetics often results in cool flame. Again, the cool flame does not reach

the adiabatic flame temperature, and, therefore, the fuel is not fully consumed. Thus, it is considered that the weak flame captured in present study might correspond to the transition state between mild oxidation and low-temperature explosion (hot flame in this study). According to the models established by Dagaut et al. [8] and Curran et al. [11], one DME molecule needs one oxygen molecule to complete the chain-propagation pathway:

However, it needs two oxygen molecules to complete the chain-branching pathway:

Thus the optimum equivalence ratio to complete the chain-branching pathway should be smaller than that of the chain-propagation pathway. Therefore, as the equivalence ratio decreases, it is transited from the weak flame to the hot flame, as shown in Fig. 4 and Table 1.

4. Conclusions

Two kinds of flames (weak and hot) in DME/air mixture were captured when the temperature and equivalence ratio were finely controlled in certain narrow range under atmospheric pressure. During the specific narrow ignition regime, the weak flame is transited to the hot flame with the decreasing of equivalence ratio from 3.20 to 1.38. It is concluded that the enhancement on chain-branching reactions by relatively sufficient oxygen should be responsible for this transition. Two-stage ignition, which includes both weak flame and hot flame, appears as a transition state between the weak flame and the hot flame. Time-sequential gas analyses were conducted along a typical

periodic two-stage ignition behavior. The results indicate that CH_4 and C_2H_2 act as two kinds of species formed due to the low-temperature auto-ignition. On the other hand, the intermediates HCHO , HCOOH , and CH_3OCHO , formed due to the mild oxidation, are completely consumed by the hot flame. The observed auto-ignition behaviors should be induced by the well-known chain-branching precursor $\text{CH}_2\text{OCH}_2\text{OOH}$ radical, which may accumulate in a relatively longer exposure time. Experimental confirmations of related intermediates are expected in the future study for promoting the established models.

Acknowledgements

This work was supported by Hokkaido Gas Company Research Fund (2006 and 2008), Suzuki Foundation (2007-2008), Iwatani-Naoji Foundation's Research Grant (2009-2010), JFE 21st Century Foundation (2009-2010), Hokkaido University Clark Foundation (2011), and JSPS-CAS Bilateral Joint Project (2012-2013). Stimulative preliminary tests performed by former colleagues (Mr. Tsukanaka and Mr. Sagawa) are inevitable to complete this work. Fruitful discussions with Prof. Zhao and Jiang at CAS were very helpful. Authors would like to express our sincere thanks to their continuous supports and helps provided to us.

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Table 1

Flame responses against various DME/air mixture equivalence ratios. Temperature was controlled at 488K. (○: existence, ×: nonexistence)

equivalence ratio		<1.38	1.38~1.58	1.58~1.80	1.80~3.20	>3.20
flame response	hot flame	×	○	○	×	×
	weak flame	×	×	○	○	×

List of Figures

Figure 1 Overall reaction scheme for dimethyl ether oxidation proposed by Curran et al. [11].

Figure 2 Schematic of experimental setup.

Figure 3 Low-temperature auto-ignition regime of DME-air mixture.

Figure 4 Temperature histories of various auto-ignition behaviors. The temperature of mixture was controlled at 488K. Equivalence ratios were: (a) 1.47; (b) 1.65; (c) 1.73; (d) 2.87. The blue dashed line represents the temperature history at 400 mm from inlet, while the red solid line represents that at 900 mm from inlet.

Figure 5 Direct photographs of the hot flame propagation. Red cycles indicate the locations where the flames were observed.

Figure 6 Flame images taken by a digital video camera at 900 mm from inlet.

(a-1) direct image of weak flame;

(a-2) gray scale image of weak flame;

(b-1) direct image of hot flame;

(b-2) gray scale image of hot flame.

Figure 7 Schematic illustration of a periodic two-stage ignition behavior.

Figure 8 Gas sampling moments set in each cycle. The blue dashed line represents the temperature history at 400 mm, while the red solid line represents that at 900 mm.

t_1 : 50 s after the hot flame;

t_2 : 15 s after the first weak flame;

t_3 : 15 s after the last weak flame;

t_4 : 10 s after the hot flame.

Figure 9 Species volumetric concentrations normalized without N_2 towards the typical two-stage ignition behavior shown in Fig. 4c.

(a) gas compositions at 400 mm; (b) gas compositions at 900 mm.