Two-stage ignition of DME/air mixture at low-temperature (<500 K) under atmospheric pressure
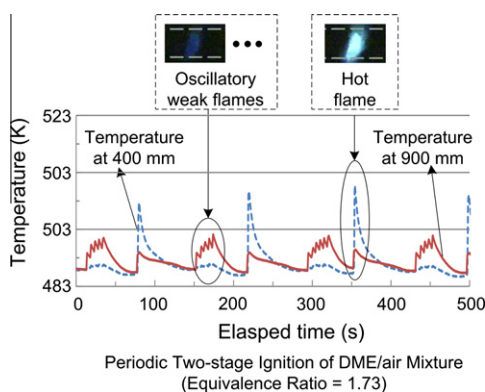
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HIGHLIGHTS

► 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

Periodic Two-stage Ignition of DME/air Mixture (Equivalence Ratio = 1.73)

ARTICLE INFO

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 CH_2OCH_2OOH 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.

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

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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 (CH_3OCH_2OO) 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 CH_3OCH_2OO 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 CH_3OCH_2OO radical after a barrier-less reaction with O_2, and then the CH_3OCH_2OO radical isomerize to form a hydroperoxy-methoxymethyl radical (CH_2OCH_2OOH). In the temperature range of 530–600 K, CH_2OCH_2OOH 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 CH_2OCH_2OOH radicals, where there is a negative temperature coefficient (NTC) zone; the DME consumption is suppressed by the chain-propagation pathway of decomposition of CH_2OCH_2OOH 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]
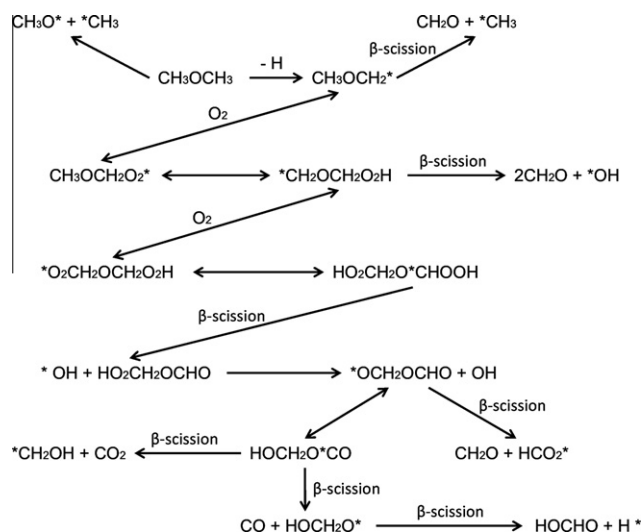

Fig. 1. Overall reaction scheme for dimethyl ether oxidation proposed by Curran et al. [11].

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 car-