



Experimental and kinetic modeling study on methylcyclohexane pyrolysis and combustion



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ABSTRACT

Methylcyclohexane is the simplest alkylated cyclohexane, and has been broadly used as the representative cycloalkane component in fuel surrogates. Understanding its combustion chemistry is crucial for developing kinetic models of larger cycloalkanes and practical fuels. In this work, the synchrotron vacuum ultraviolet photoionization mass spectrometry combined with molecular-beam sampling was used to investigate the species formed during the pyrolysis of methylcyclohexane and in premixed flame of methylcyclohexane. A number of pyrolysis and flame intermediates were identified and quantified, especially including radicals (e.g. CH_3 , C_3H_3 , C_3H_5 and C_5H_5) and cyclic C6- and C7-intermediates (benzene, 1,3-cyclohexadiene, cyclohexene, toluene, C_7H_{10} and C_7H_{12} , etc.). In particular, the observation of cyclic C6- and C7-intermediates provides important experimental evidence to clarify the special formation channels of toluene and benzene which were observed with high concentrations in both pyrolysis and flame of methylcyclohexane. Furthermore, the rate constants of H-abstraction of methylcyclohexane via H attack, and the isomerization and decomposition of the formed cyclic C_7H_{13} radicals were calculated in this work. A kinetic model of methylcyclohexane combustion with 249 species and 1570 reactions was developed including a new sub-mechanism of MCH. The rate of production and sensitivity analysis were carried out to elucidate methylcyclohexane consumption, and toluene and benzene formation under various pyrolytic and flame conditions. Furthermore, the present kinetic model was also validated by experimental data from literatures on speciation in premixed flames, ignition delays and laminar flame speeds.

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1. Introduction

Detailed kinetic modeling of practical fuels is helpful to increase the fuel efficiency and reduce harmful emissions in engines. However, such modeling is challenging since practical fuels are complex mixtures of hundreds of compounds. Instead, surrogate fuels with well-defined and reproducible composition including alkanes, cycloalkanes, and aromatic compounds, etc. were proposed to substitute practical fuels for the development of kinetic models.

Recently, cycloalkanes have received increasing attention because of their high concentrations in practical fuels, for example, they make up 20–40% of typical North American diesel fuel [1,2]. The cycloalkanes with C6 rings tend to dehydrogenate to form aromatics and consequently may increase soot formation [3–10]. Among them, methylcyclohexane (MCH) is the simplest alkylated cyclohexane, and it has been selected as the representative cyclo-

alkane compound in several proposed jet-fuel surrogates [11–17]. MCH was also proposed as an endothermic fuel to cool supersonic aircraft via dehydrogenation to form toluene and hydrogen under the presence of catalyst [18].

Previous studies on MCH include the kinetics of its thermal decomposition using the technique of very low pressure pyrolysis (VLPP) [19], pyrolysis and oxidation of MCH and MCH/toluene blends in a turbulent flow reactor [20], a non-premixed diffusion methane/air flame doped with MCH [21], low- and intermediate-temperature oxidation in motored engines [22], ignition delay time measurement in rapid compression machine (RCM) at various pressures [23,24], and in shock tube at different temperatures and pressures [25–29]. Also, OH concentration time-histories were measured behind reflected shock waves in a shock tube [30] and laminar flame speeds were obtained at the range from 1 to 10 atm [31,32]. Rate constants of the H-abstraction from MCH via OH radical were measured and calculated by Sivaramakrishnan and Michael at high temperature [33]. A recent work by Skeen et al. [8] studied the low pressure laminar premixed flames of MCH at various equivalence ratios exploring the chemistry of MCH

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decomposition and the formation of aromatic species (e.g. benzene and toluene). More recently, Bounaceur et al. [34] developed a kinetic model to describe the thermal cracking of MCH, which focused on identification of the main consumption and production pathways, in particular the aromatization pathways. Although some aspects of MCH combustion have been studied previously, more reliable data on its pyrolysis and flame are desired including detailed quantitative species concentrations.

In this work, MCH pyrolysis at various pressures (30, 150 and 760 Torr), and premixed flame with equivalence ratio of 1.75 at 30 Torr were investigated using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). The pyrolysis and flame species were identified and their mole fractions were measured. A kinetic model with 249 species and 1570 reactions was developed based on our cyclohexane pyrolysis model [9] by adding a new sub-mechanism of MCH. The model was validated by the experimental results in this work, and premixed flames [8], the ignition delay times [26] and laminar flame speeds [32] reported in the literature. The reaction flux of MCH in pyrolytic and flame conditions was discussed with special attention to the formation of toluene and benzene based on the kinetic simulation.

2. Experimental method

The experimental work was performed at National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The beamline has been described in detail elsewhere [35]. Only brief description of the pyrolysis and flame apparatus is given herein [9,36–38]. The pyrolysis apparatus included a high temperature furnace mounted in the pyrolysis chamber. The pressure of the pyrolysis chamber was controlled by a MKS throat valve at pressures of 30, 150 and 760 Torr. The MCH sample was purchased from the Aladdin Reagent (Shanghai) Co., Ltd with a purity of 99%, which was vaporized in an Ar stream before flowing into the alumina flow reactor (with inner diameter 6.8 mm, and surface to volume ratio $\sim 6.0 \text{ cm}^{-1}$). The total flow rate of the mixture was kept to be 1.0 standard liter per minute (SLM) at 273.15 K under the three pressures, thus the inlet mole fraction of MCH is 0.02. The heating region of the flow reactor is 150 mm. The temperature profiles of the flow reactor under different heating temperatures were measured by a S-type thermocouple with a Ar flow of 1.0 SLM. Figure 1 shows the five temperature profiles measured at 30 Torr with different heating powers. In a test experiment, almost invariable temperature profiles were observed at both low and atmospheric

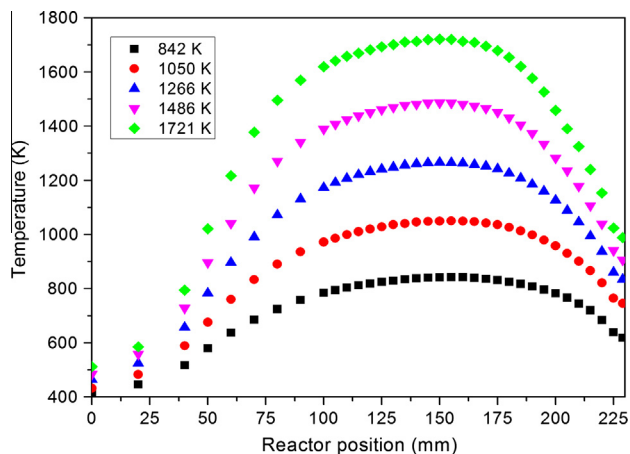


Fig. 1. The temperature profiles along the centerline of the flow tube were measured by moving a S-type thermocouple from the tube inlet to the sampling point of the quartz nozzle. Five temperature profiles with maximum values of 842, 1050, 1266, 1486 and 1721 K measured at 30 Torr are shown.

pressures, which can be explained by that the Nusselt number in a laminar flow tube is generally unrelated with pressure, especially in the pressure region of this work. Therefore the temperature profiles are also used to simulate experiments at 150 and 760 Torr. The temperature profile is named by its maximum temperature (T_{max}), which is used as the experimental temperature. The uncertainty of T_{max} is estimated to be within $\pm 30 \text{ K}$, while those at other positions are expected to be less. Since the initial total flow rate is kept constant, the residence times vary with temperature and pressure. The calculated residence times at 30, 150 and 760 Torr in the temperature range studied are $7.4\text{--}5.4 \times 10^{-3}$, $3.8\text{--}2.8 \times 10^{-2}$ and $2.2\text{--}1.6 \times 10^{-1} \text{ s}$, respectively. The method of mole fraction evaluation can be found in the literature [9].

The premixed flame of MCH with equivalence ratio of 1.75 was stabilized on a McKenna burner with a diameter of 60 mm under 30 Torr. The flow rates of Ar and O_2 were 1.066 and 0.914 SLM, respectively. The flow rate of liquid MCH sample was 0.868 ml/min (equal to 0.152 SLM in the gas phase). The inlet mass flow rate and cold-flow (300 K) velocity were $2.28 \times 10^{-3} \text{ g s}^{-1} \text{ cm}^{-2}$ and 35 cm s^{-1} , respectively. The methods used for species identification and mole fraction evaluation were reported previously [39,40]. The flame temperature profiles were measured by a Pt-6%Rh/Pt-30%Rh thermocouple with a diameter of 0.1 mm coated with $\text{Y}_2\text{O}_3\text{-BeO}$ anti-catalytic ceramic [41,42]. Radiation heat loss [43] and cooling effects of sampling nozzle [44] were calibrated. The uncertainty of the maximum flame temperature is estimated to be $\pm 100 \text{ K}$. We estimate the uncertainty of the flame temperature at other positions is less than that of the maximum flame temperature.

The photoionization cross sections (PICs) of most species in this work were measured in the literature [45–52] and are available in our online database [53]. For species with unknown values, the PICs were estimated from molecules with similar structures, for example, 2-methyl-1,3-butadiene refers to 3-methyl-1,2-butadiene [52], C_7H_8 (*o*-isotoluene and *p*-isotoluene) refers to toluene [48], cyclic C_7H_{10} refers to 1,3-cyclohexadiene [47], cyclic C_7H_{12} refers to cyclohexene [47], and 2-heptene refers to 2-hexene [52]. Besides, the PICs of cyclopentadienyl radical (C_5H_5), cyclopentadiene (C_5H_6) and fulvene were taken from the estimated values in the literature [54,55]. In the pyrolysis experiments, the uncertainties of the measured mole fractions are estimated to be $\pm 10\%$ for H_2 and CH_4 , $\pm 25\%$ for the products with known PICs and a factor of 2 for those with estimated PICs. The experimental uncertainties of the total C and H balances are around $\pm 10\%$ compared to inlet fluxes of C and H elements. In the premixed flame data, the uncertainties of evaluated mole fractions are about $\pm 10\%$ for major species, $\pm 25\%$ for intermediates with known PICs, and a factor of 2 for those with estimated PICs. It should be noted that it is possible that the errors for some species could be even larger.

3. Theoretical calculation

H attack reactions usually play significant roles in flames. These reaction pathways of MCH were computed by the CBS-QB3 method [56] in this work. This composite method starts from a B3LYP/6-311G(2d,d,p) geometry optimization and vibrational analysis, then the single point energy is corrected by a series of high accuracy methods including a complete basis set extrapolation [57]. The quantum chemistry calculations were performed using the Gaussian 09 program [58]. The calculated reaction pathways are shown in Fig. s1 in the supplementary material. Based on these reaction pathways, the temperature-dependent rate constants were computed by the transition state theory (TST). The vibrational mode corresponding to the internal rotation of the methyl group was treated as a hindered rotor with a symmetric hindrance potential

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