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# Investigation on primary decomposition of ethylcyclohexane at atmospheric pressure

Zhandong Wang<sup>a</sup>, Huiting Bian<sup>b</sup>, Yu Wang<sup>a</sup>, Lidong Zhang<sup>a,\*</sup>,  
Yuyang Li<sup>b</sup>, Feng Zhang<sup>a,\*</sup>, Fei Qi<sup>a</sup>

<sup>a</sup> National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, PR China

<sup>b</sup> State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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## Abstract

To get a better understanding of the combustion chemistry of cycloalkanes with long side chain, the pyrolysis of ethylcyclohexane (ECH) was studied in a flow reactor at atmospheric pressure. The pyrolysis species were analyzed by two methods, synchrotron vacuum ultraviolet photoionization mass spectrometry and gas chromatography. Dozens of species were identified and quantified, including lots of isomers. The emphasis of this study is to investigate the primary decomposition of ECH, including its initial decomposition, isomerization, and further reactions of the cyclic  $C_8H_{15}$  radicals formed from the H-abstraction of ECH. The observation of  $C_8H_{16}$  alkene indicates the existence of ring-opening isomerization reaction of ECH. The ring-opening isomerization reaction of cyclic  $C_8H_{15}$  radicals produces alkenyl radicals, whose further decomposition constitutes the various chain and branched intermediates in ECH pyrolysis. The formation of isoprene and vinylcyclopentane is discussed, which highlights isomerization reactions of radical addition on the double bond of alkenyl radicals, such as oct-6-en-1-yl and oct-5-en-1-yl radicals. The theoretical calculation on the reaction pathways of oct-5-en-1-yl radical also shows that its internal H-migration pathway via eight-membered ring might be competitive to the one via five-membered ring. On the other hand, the decomposition of cyclic  $C_8H_{15}$  radicals causes the formation of cyclic intermediates, i.e.  $C_8H_{14}$  alkenes, methylenecyclohexane and cyclohexene, which are potential aromatic precursors.

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## 1. Introduction

The rapid consumption of fossil fuels and the increasing pollutant emissions demand much more cleaning combustion with higher fuel utilizing efficiency. On the other hand, the research on synthetic gasoline, diesel and kerosene from gas to liquids (GtL), coal to liquids (CtL) and bio-mass

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\* Corresponding authors. Fax: +86 551 65141078.

E-mail addresses: [zld@ustc.edu.cn](mailto:zld@ustc.edu.cn) (L. Zhang), [feng2011@ustc.edu.cn](mailto:feng2011@ustc.edu.cn) (F. Zhang).

to liquids (BtL), etc. [1–3] are in progress to hold the sustainability of energy and guarantee the energy supply security. Therefore a better understanding of the combustion properties of the fossil and synthetic fuels is desired. Cycloalkanes are important components in transport fuels, which also have been included in several proposed surrogate fuels [1,2,4,5]. However, detailed investigation on cycloalkane fuels is insufficient. The cycloalkanes with six-membered ring tend to generate large amount of carcinogenic pollutants such as 1,3-butadiene, and precursors of polycyclic aromatic hydrocarbons (PAHs), such as benzene and toluene through dehydrogenation and/or dealkylation of the fuels [6,7]. The formation of isoprene in methylcyclohexane combustion [7,8] also needs consideration since isoprene may be a carcinogen in humans.

Our recent work has studied the pyrolysis and flame of cyclohexane and methylcyclohexane under a wide range of experimental conditions [6,7]. A detailed kinetic model of methylcyclohexane combustion was developed, which was validated by various experimental data including pyrolysis in a flow reactor, laminar premixed flames, ignition delay times and laminar flame speeds. As a further step of the systemic study on cycloalkane fuels, ethylcyclohexane (ECH) is chosen as a target in this work. Previous studies on ECH are scarce compared to cyclohexane and methylcyclohexane. The ignition delay times of ECH/air mixture were measured by Vanderover and Oehlschlaeger [9] with equivalence ratios of 0.25, 0.5 and 1.0 under pressures ranging from 10.8 to 52.8 atm. The laminar flame speeds of ECH combustion from 1 to 5 atm were measured by Ji et al. [10] and Wu et al. [11]. Besides the global parameters, Husson et al. [12] measured species concentration of ECH oxidation in a jet-stirred reactor at the low- and intermediate-temperature ranges. The kinetic model of ECH combustion was developed by Wang et al. [13], which was included in the *JetSurF 2.0*. More data such as the pyrolysis and flames of ECH are definitely required to get a more comprehensive validation of the kinetic models. Pyrolysis of ECH is a good circumstance to investigate the fuel decomposition mechanism, and also the formation of aromatics. On the other hand, cycloalkanes are a kind of endothermic hydrocarbons as coolant in hypersonic vehicles through thermal cracking or catalytic cracking, which requires a deep insight into their pyrolysis mechanism.

In this work, the pyrolysis of ECH under atmospheric pressure was conducted, and the mole fraction profiles of pyrolysis species with temperature were measured. The species featuring the pyrolysis chemistry of ECH such as the  $C_8H_{16}$  alkene, and several  $C_4$ – $C_7$  unsaturated species are presented. Their formation is elucidated with the help of theoretical calculation and kinetic

modeling. Furthermore, the formation of some cyclic  $C_6$ – $C_8$  alkenes is discussed, which are potential precursors for the formation of the first aromatic ring.

## 2. Experimental method

The experimental work was performed at National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The pyrolysis apparatus included a high temperature furnace mounted in the pyrolysis chamber. The ECH sample was evaporated and diluted with Ar, then flowed into the alumina flow reactor with an inner diameter of 6.8 mm in the furnace. The total flow rate of the mixture was kept at 1.0 standard liter per minute (SLM) at 273.15 K, and the mole fraction of ECH is 0.02. The heating length of the reactor is 150 mm. The temperature profiles of the flow reactor under different heating temperatures were measured by an S-type thermocouple, and are named by its maximum value ( $T_{max}$ ).  $T_{max}$  is used as the experimental temperature and the uncertainty is estimated to be within  $\pm 30$  K [6,7].

Two independent analytic methods were used for the identification and quantification of the pyrolysis species. In the first measurement, the pyrolysis apparatus was connected to the synchrotron VUV photoionization mass spectrometry (PIMS). Details about this method can be found in the literature [6,7,14]. 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 photoionization cross sections (PICSS) and a factor of 2 for those with estimated PICSS. In this work, the PICSS of the following species, i.e. 2-methyl-1,3-butadiene, 1,3-heptadiene, and  $C_8H_{14}$  isomers were estimated. The evaluation of 2-methyl-1,3-butadiene and 1,3-heptadiene was performed at 10.0 and 8.8 eV with the PICS of 21.47 and 6.94 Mb, respectively. For  $C_8H_{14}$  isomers, the quantification of 1-ethylcyclohexene and ethylidene-cyclohexane was carried out at 8.8 eV with the PICS of 6.29 Mb; and the quantification of 3-ethylcyclohexene and 4-ethylcyclohexene was carried out at 9.1 eV with the PICS of 4.5 Mb. The experimental uncertainties of the total C and H balances are around  $\pm 10\%$  compared to inlet fluxes of C and H elements.

Gas chromatography (GC) was used to analyze the pyrolysis products as well, which were sampled by a quartz tube, then flowed through a heated transfer line at 473 K to the six-way valve sampling of the gas chromatography. HP-PLOT Q (Agilent Technologies, 30 m  $\times$  320  $\mu m$   $\times$  20  $\mu m$ ) and GsBP-1ms (GS-Tek, 30 m  $\times$  250  $\mu m$   $\times$  0.25  $\mu m$ ) capillary columns with a flame ionization detector (FID) were used to quantify the  $C_1$ – $C_4$  hydrocarbons, and species with more than five carbon atoms, respectively. The calibration methods

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