



## Full Length Article

# Experimental and comparative modeling study of high temperature and very high pressure methylcyclohexane pyrolysis

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## ABSTRACT

Three sets totaling 118 individual methylcyclohexane shock tube pyrolysis experiments were completed at nominal pressures of 40, 100, and 200 bar to obtain species data and to determine whether the formation of alkylcyclopentanes, which have been found to be sooting and coking precursors in previous studies conducted in the supercritical phase, is possible at high pressures but dilute conditions. Some species profiles, namely ethane, propadiene, propyne, 1-butene, and toluene were affected by the experimental variation in pressure, but no alkylcyclopentanes were observed to form. An additional set comprised of 33 individual experiments was completed at 40 bar to match the concentration of the fuel present in the reflected shock reaction zone present in the 100 bar experiments. The species data obtained from the additional set of 40 bar experiments reproduced the 100 bar data nearly perfectly, emphasizing the dominance of the initial fuel concentration rather than pressure over the product distribution at the experimental conditions present in this study. The experimental data were also compared against simulations with a recently published methylcyclohexane mechanism and a generated mechanism with both mechanisms being able to predict the formation of major product species well. The generated mechanism is able to capture the current data better than the literature mechanism and is recommended for use at conditions similar to those in the present study, but requires larger computational effort and time and only contains pyrolysis reactions.

## 1. Introduction

Methylcyclohexane has long been of interest in combustion research because it is commonly used in surrogates, and is a constituent of real jet and propulsion fuels [1,2]. One of the more recent methylcyclohexane studies was conducted by Wang et al. using a flow reactor at pressures of 30, 150, and 760 torr [3]. The experimental data were then used for the development of a chemical kinetic mechanism that is an extension of their previous cyclohexane mechanism [4]. In the mechanism, Wang et al. included a reaction pathway resulting in the formation of methylenecyclopentane that proceeds through the ring opening of the cyclohexyl radical to form hex-5-en-1-yl which subsequently undergoes 5-exo-cyclization resulting in cyclopentylmethyl which after a 1,4 hydrogen shift forms methylcyclopentyl.

A similar pathway is suggested by Peukert et al. in their work pertaining to hydrogen abstraction of cyclohexane, but Peukert proposes that rather than forming methylenecyclopentane the methylcyclopentyl radical ultimately decomposes to propene and propadiene [5]. Peukert compared two available sets of reaction rate constants for the 5-exo-cyclization reaction of the hex-5-en-1-yl radical proposed by Granata

et al. [6] and Sirjean et al. [7] and found that the rates proposed by Granata would make the 5-exo-cyclization the dominant reaction involving hex-5-en-1-yl, and those by Sirjean would still result in the reaction being of importance. Peukert ultimately proposed reaction rate coefficients that fall between those of Granata and Sirjean.

The importance of the formation of methylenecyclopentane lays in that the reaction pathway is analogous to alkylcyclopentane reaction pathways, and alkylcyclopentanes have been found to be coking [8] and sooting [9] precursors. Alkylcyclopentanes have also been found to be the dominant products in methylcyclohexane pyrolysis under supercritical conditions [8,10,11]. Wang mentions that the analogous ring closure reactions are possible in methylcyclohexane dissociation from C<sub>7</sub>H<sub>13</sub> radicals, e.g. hept-6-en-1-yl radical, but that they are not included in the methylcyclohexane mechanism due to the negligible formation.

The supercritical experiments in which ring contraction was observed were conducted at high pressures up to 100 bar, but at lower temperatures, around or below 800 K, and had time scales of hours [8,10,11]. Other examples of high pressure methylcyclohexane experiments include the studies by Vanderover and Oehlschlaeger [12]

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encompassing pressures up to 69.5 atm, and two works by Vasu et al. [13,14], the first with pressures near 15 atm, and the second with pressures from 1 to 50 atm. All three of these studies were autoignition studies. MacDonald et al. [15] completed a methylcyclohexane pyrolysis shock tube study with pressures up to 23 atm, but only obtained species data for the fuel and ethylene.

Another notable and recent methylcyclohexane study is the modeling and experimental work by Pitz et al. [16]. The experiments were completed in a rapid compression machine producing ignition delay data in the 680–980 K temperature range at pressures of up to 20 bar. The oxidation chemical kinetic mechanism developed by Pitz was later further developed by extending it to higher temperatures and thoroughly and extensively validated against most of the notable existing methylcyclohexane experimental data by Narayanaswamy et al. [17], who validated the extended Pitz mechanism against the high pressure auto-ignition data of Pitz et al. (15 and 20 bar) [16], Vanderover and Oehlschlaeger (12 and 50 bar) [12], and both studies of Vasu et al. (20 and 45 bar) [13,14]. The limited species data of two autoignition studies was also used to validate the mechanism and included the OH and H<sub>2</sub>O profiles from the 2.1–2.2 bar shock tube work by Hong et al. [18] and the OH profiles from the 16 bar shock tube study by Vasu et al. [13]. All the detailed species validation was completed using lower pressure experimental results due to the lack of high pressure methylcyclohexane speciation data and were taken from the atmospheric pressure flow reactor study by Zeppieri et al. [19] and atmospheric pressure premixed flame data from the study by Wang et al. [3].

Another high pressure oxidation experimental and modeling study was recently completed by Weber et al. [20]. Weber obtained methylcyclohexane auto-ignition data at pressures of up to 50 bar and used the experimental data to validate the modeling efforts. The model was not validated against any speciation data. Yet another experimental and autoignition study, completed in a shock tube at lower pressures of up to 4 atm, was conducted by Orme et al. [21]. The authors did validate the developed methylcyclohexane mechanism against speciation data from another study using the venerable near-pyrolysis flow reactor data of Zeppieri et al. [19]. The mentioned methylcyclohexane studies are not all inclusive, and a far more thorough review is presented by Pitz and Mueller [1]; however, the works discussed illustrate that the high pressure oxidation methylcyclohexane experiments only offer auto-ignition data or very limited species data which was used to detect the ignition of the fuel mixture, and modeling efforts which wish to include validation of detailed species data are restricted to only atmospheric pressure data presented by a couple of studies.

Currently, the only high temperature gas phase methylcyclohexane pyrolysis experiments with substantial species data are those of Wang et al. [3] and Zeppieri et al. [19] and the experiments did not exceed pressures of 1 atm; however, the study by Wang did also include sub-atmospheric experiments at pressures of 30 and 150 torr. The methylcyclohexane experimental pyrolysis database is lacking gas phase high pressure and high temperature pyrolysis speciation data. Extending the current methylcyclohexane experimental database to high pressures and temperatures would allow for the validation of current, and creation of new, chemical kinetic mechanisms at conditions relevant to modern combustors, in addition to determining whether or not the formation of alkylcyclopentanes can be observed in gas phase at high pressures.

## 2. Experimental apparatus

The High Pressure Shock Tube (HPST) has been described in detail before and only a brief overview will be given [22]. The 120-in.-long, 1 in. bore driven section is separated from the 60-in.-long, 2 in. bore driver section by a scored 3003 aluminum diaphragm. Nominally, diaphragms of 25 thousandths of an inch overall thickness and 14 thousandths of an inch wall thickness (the thickness of the material left in the score), 32 thousandths of an inch overall thickness and 27

thousandths of an inch wall thickness, and 50 thousandths of an inch overall thickness and 43 thousandths of an inch wall thickness, were used to achieve nominal post shock pressures of 40, 100, and 200 bar, respectively. Depending on the performance of the diaphragms the wall thickness would be adjusted by half or one thousandth of an inch from the nominal wall thickness between batches of diaphragms to minimize the deviation in the post shock pressure.

The diaphragms utilized for 40 bar shocks also doubled as “cleaning” diaphragms, which were used to fire cleaning shocks. A cleaning shock was fired immediately after each shock which contained fuel. No gas samples were extracted from most of the cleaning shocks because the cleaning shocks were fired while the gas chromatography analysis was in progress for the previous shock to minimize the amount of time necessary for each individual experiment to be completed. A typical experimental run would be complete in approximately 70 min. In addition to the cleaning shocks, the end wall of the shock tube would be occasionally opened and the inside of the driven section of the shock tube would be dry swabbed to remove any residue build up. No solvents were used during the swabbing process to avoid contaminating future samples and to reduce the time necessary for the shock tube to be operational again.

Six PCB-113A series transducers are mounted in the wall of the driven section to measure the speed of the incident shock wave approaching the end wall with a seventh transducer in the end wall used to obtain the reflected shock pressure profiles. A chemical thermometer is used to calibrate the incident shock speeds to the temperature in the reflected shock reaction zone [23,24]. Two chemical thermometers were used for the presented studies. Cyclopropanecarbonitrile was used to calibrate over a temperature range of approximately 1000–1100 Kelvin (K) and 1,1,1-trifluoroethane over approximately 1300–1400 K. Shock speeds leading to temperatures between those of the two chemical thermometers were interpolated, and those falling outside were extrapolated. The reaction rate coefficients used for cyclopropanecarbonitrile were those determined by Lifshitz et al. [25] and coefficients for 1,1,1-trifluoroethane were given by Matsugi et al. [26].

The post shock samples are extracted and analyzed by means of online gas chromatography sampling as described by Comandini et al. [27]. The species were identified using gas calibration mixtures and a Hewlett-Packard (HP) 5973 Mass Selective Detector. Quantification was completed using two HP 6890 gas chromatographs equipped with flame ionization detectors coupled with the Supelco Petrocol (24160-U) and Agilent GS-GasPro (113-4362) capillary columns. 1,3-Cyclopentadiene, methylenecyclopentane, 1,3-cyclohexadiene, cyclohexene, and cyclohexane were calibrated by vaporizing a known amount of a liquid sample and have an estimated uncertainty of up to 10%. All the remaining species were calibrated using calibration mixtures provided by Air Liquide and have a specified uncertainty of 5% specified by the manufacturer. The average carbon balance for all the experimental sets exceeded 95% with the carbon balance for each individual experiment being available in the experimental data Excel file attached in [supplemental materials](#).

## 3. Effects of pressure on methylcyclohexane pyrolysis

Three sets of experiments at nominal pressures of 40, 100, and 200 bar (with the exact experimental conditions for each individual experiment available in the [supplemental material](#)) with a nominal reaction time of 2.2 milliseconds (ms) were carried out with methylcyclohexane as the fuel. The initial methylcyclohexane mole fractions at 187, 188, and 181 parts per million (ppm), respectively. The reported fuel mole fractions were quantified by GC analysis of the test gas fuel mixture after the mixture was allowed to homogenize for a minimum of 12 h after preparation. Fig. 1 contains the product species profiles of ethane, ethylene, propadiene, propyne, 1-butene, and toluene. The peak amounts of ethane, propadiene, and propyne were observed to increase

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