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Full Length Article

Molecular dynamics simulation of the high-temperature pyrolysis of methylcyclohexane

Yalan Liu[a,b,1], Junxia Ding[a,1], Ke-Li Han[a,*]

[a] State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China
[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

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ABSTRACT

To better understand the initiation and intermediate reaction mechanisms associated with the high-temperature pyrolysis of methylcyclohexane (MCH), the dissociation of MCH is investigated using reactive molecular dynamics (RMD) and density functional theory (DFT) calculations. It is observed that the pyrolysis of MCH is initiated by four types of reaction channels. The initiation of the decomposition is mainly through the C—C bond homolysis of the six-membered ring, leading to ring opening and the formation of C_7H_{14} diradicals. Subsequently, the biradicals undergo successive decomposition by the β-scission of the C—C bonds to form ethylene. Furthermore, to provide a detailed description of the pyrolysis behavior of MCH, the distributions of key products, intermediate reactions and corresponding kinetic behavior are systematically analyzed at the atomic level. The apparent activation energy extracted from the RMD simulations is 263.60 kJ/mol at temperatures from 2300 K to 3100 K, which is reasonably consistent with the experimental results.

1. Introduction

Combustion is ubiquitous during our daily lives and plays a critical role in energy production. Therefore, great effort has been directed to elucidate the reaction mechanisms and kinetic behavior of pyrolysis and combustion processes. Since practical fuels involve various types of components, it is a great challenge to perform the relevant studies. An alternative solution is to use model fuels (i.e., alkanes, cycloalkanes, and aromatic compounds) to represent practical fuels. Compared to the comprehensive studies on alkanes and aromatic compounds, only a few studies regarding the thermal dissociation of cycloalkanes have been considered, even though they are an important chemical class in surrogate fuels. Recently, cycloalkanes have received increasing attention due to their high concentrations in practical fuels including diesel fuels [1], oil sand deposits and crude source [2]. Among the cycloalkanes, methylcyclohexane (MCH) is the simplest alkylated cyclohexane and has been chosen as the model compound for surrogate fuels by many studies [1,3–5]. In addition to being a conventional endothermic hydrogen fuel, it can also provide a heat sink up to 2.19 MJ/kg through dehydrogenation reactions, thereby meeting the requirement to cool jet engines [6].

During the past decades, limited studies focusing on the pyrolysis and combustion of MCH have been reported. Experimentally, Bajus et al. [7] studied the thermal decomposition of MCH in the presence of steam at elevated temperatures from 973.15 to 1063.15 K, resulting in the activation energy of 201.30 kJ/mol and frequency factor of $0.53 \times 10^{11}\ s^{-1}$. Zeppieri et al. [8] investigated the pyrolysis of pure MCH at high temperatures ranging from 1050 to 1200 K. Major species such as ethane, 1,3-butadiene, methane, and propene were observed during the pyrolysis process. Lai and Song [9] studied the decomposition of MCH in or near the supercritical phase at 723.15 K at a relatively high pressure (≥ 2 MPa). These researchers noted that the dominant reaction for MCH pyrolysis was isomerization to form alkylcyclopentanes via ring contraction. Kralikova et al. [10] investigated the kinetics of MCH pyrolysis at 0.1 MPa within the temperatures range of 700–820 K. They reported that the decomposition of MCH proceeded as a first order reaction with the activation energy of 251.20 kJ/mol and frequency factor of $6.31 \times 10^{15}\ s^{-1}$. Theoretically, the kinetic models of MCH and the decomposition rate of elementary reactions were reported by several groups [5,11–13]. Experiments and kinetic models usually provide necessary information with regard to reactions. However, pyrolysis reactions progress extremely fast, especially at high temperatures, and produce a large amount of intermediates and reactive radicals that correlate with thermodynamic conditions such as temperature and pressure [14]. It is an arduous task to disentangle the various fundamental steps from the final products obtained

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[*] Corresponding author.
E-mail address: klhan@dicp.ac.cn (K.-L. Han).
[1] These authors contributed equally.

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experimentally. In this sense, the current experiments and kinetic models are not enough to reveal the reaction mechanisms of MCH pyrolysis.

Reactive force field [15,16] (ReaxFF) is a promising way to study the complex chemical reactions. This approach is based on the general bond order and bond distance relationship, the connectivity of which is determined by bond orders calculated from bond distances. Thus this approach allows an accurate description of bond breaking and bond formation during the reaction process. In addition, the parameters used in ReaxFF are derived from quantum mechanical (QM) calculations and experiments. Using ReaxFF, a complicated system can be computed at a relatively high accuracy within a short simulation time. In recent years, ReaxFF has been used to investigate chemical reactive processes over a wide range of systems, including energetic composite materials [17], coals [18], high-energy materials [16], Si (1 0 0) surface oxidation [19], nanocavity formation [20], cystine adsorption [21] and hydrocarbons [22]. These successful applications demonstrate that ReaxFF is an accurate and computationally feasible approach to simulate complicated chemical reactions.

In this article, we describe a computational method together with the simulation details for the pyrolysis of MCH from the beginning. Subsequently, the results of the multimolecule NVT-MD gaseous phase simulations of the thermolysis of MCH are presented. We mainly focus on the analysis of the main hydrocarbon species formed, the initiation mechanisms, the intermediate reaction process, and the correlated kinetic behavior of MCH pyrolysis. The reactive molecular dynamics (RMD) simulation results not only identified the critical initiation and intermediate mechanisms of MCH pyrolysis, but also they will provide significant theoretical guide for the computational fluid dynamics (CFD) simulations. It is hoped that the analysis presented here will establish a more complete atomic understanding of the thermal decomposition of MCH.

2. Computational methods

In this work, we performed RMD simulations employing the ReaxFF method to investigate the pyrolysis mechanisms of MCH. The ReaxFF parameters reported by van Duin and Chenoweth [22] were used here without modifications. These parameters have been widely used in the study of hydrocarbon systems. Page [23] and Lümmen [24] used these parameters to study the partial oxidation and thermal decomposition of methane at low and high temperatures, respectively. Liu et al. [25] investigated the mechanism and kinetics for the initial steps of the pyrolysis and combustion of 1,6-dicyclopropane-2,4-hexyne with the ReaxFF method. Chenoweth et al. [26] applied ReaxFF to study the initial mechanism and kinetics of the pyrolysis and combustion of *exo*-tricyclo[5.2.1.0$^{2.6}$]decane (JP-10). Wang et al. [27] reported a chemical kinetics modeling of the pyrolysis and combustion of n-dodecane. Dong et al. [28] simulated the pyrolysis and combustion of benzene at ultrahigh temperature. Ding et al. [29] used ReaxFF to describe the detailed reaction mechanism of n-heptane pyrolysis at high temperature. Chen et al. [30] applied ReaxFF to study the pyrolysis of hexadecane at high temperature and pressure. These successful applications demonstrate that the ReaxFF parameters are feasible to study the pyrolysis of hydrocarbon fuels.

The RMD simulations were performed with a constant number of atoms (N); in a constant volume (V) at a specified temperature (T), otherwise known as the NVT ensemble. The temperature was controlled using the Nosé-Hoover thermostat method [31]. Sixteen MCH molecules were evenly placed in a cubic periodic unit cell measuring 25.00 Å × 25.00 Å × 25.00 Å using the Packmol program [32]. The initial density of the system was 0.17 g/cm^3, and the approximate pressure ranged from 14.20 to 42.50 MPa in the temperature range from1000 K to 3500 K according to the van der Waals equation of state of the chosen temperature and density. The system was initially equilibrated at 1000 K for 10 ps with a time step of 0.1 fs, which is expected to be efficient in the present work [33]. This step has been widely employed in several systems [22,34,25,27,35] and has been proved to be appropriate. After equilibrium, 10 random configurations were generated for the system by performing 10 ps NVT/MD simulation under equilibrium conditions and saving the atomic positions and atomic velocities every 1.0 ps. For each of these 10 configurations, the system was heated to a target temperature of 3500 K within 500 ps, and then another 500 ps simulation was continued at 3500 K to obtain the detailed reaction mechanism. The bond order cutoff for molecule recognition was set at 0.3. This bond-order cutoff is used only for analysis purposes and does not affect the simulation results [34].

To further validate the accuracy of the reactive force field, the main initial reactions observed during the multimolecular dynamic simulations were calculated by the QM method with the Gaussian 09 program package [36]. The geometrical structure of the reactants and products were performed using the B3LYP functional [37,38]; together with the 6-311G + +(d,p) basis set. A spin-unrestricted set was employed for the open-shell species. The reaction potential energy surface (PES) was also scanned to search the transition state. Harmonic vibrational frequency calculations were performed in order to confirm the optimized structure is the minimum on the potential energy surface. The energies discussed below are the relative electronic energies at 0 K.

3. Results and discussion

3.1. Annealing simulations results

For an overview of the pyrolysis of MCH, a series of 10 annealing simulations were performed in the temperature range from 1000 to 3500 K. According to previously published work, 10 times of multimolecular simulations are adequate [39]. The major fragment distributions and temperature profiles during the simulation process are shown in Fig. 1. The results indicate that pre-equilibrated MCH molecules just begin to decompose at 230 ps at a temperature of approximately 2200 K, and that the dissociation of all MCH molecules is accomplished at 430 ps. According to the dissociation rate of MCH, the pyrolysis process could be divided into two stages. The first stage is from 230 ps to 330 ps. For temperatures ranging from 2200 to 2600 K, the decomposition rate of MCH is relatively slow; only 31.25% of fuel molecules are consumed during this period. At temperatures ranging of 2600–3000 K, the consumption rate of MCH increased, and approximately 68.75% of the fuel molecules are depleted during the second stage (330–430 ps). After 430 ps, all MCH molecules are dissociated. The intermediates formed during the decomposition of MCH continue

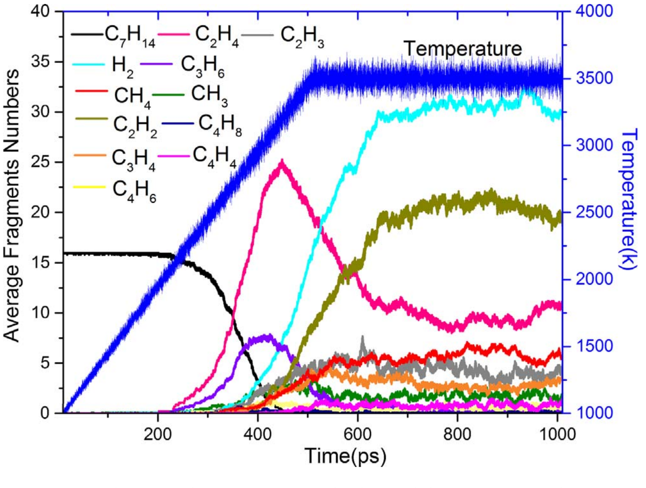

Fig. 1. Time evolution of the main compounds observed during RMD simulation of sixteen MCH molecules at a density of 0.17 g/cm^3. The blue line denotes the temperature profile during simulations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)