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Experimental and kinetic modeling investigation on decalin pyrolysis at low to atmospheric pressures

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ABSTRACT

The pyrolysis of decalin was studied in a flow reactor using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) at the pressures of 4, 20, and 101 kPa and the temperatures from 920 to 1500 K. Dozens of pyrolysis species were identified and their mole fraction profiles were measured as a function of temperature, particularly several free radicals and aromatic species. Besides, a detailed kinetic model consisting of 484 species and 1774 reactions was proposed and used to simulate the present experimental data. The rate of production analysis and sensitivity analysis was performed in order to provide deep insight into the pyrolysis kinetics of decalin. The decomposition of decalin is initiated by the C–C bond dissociation reactions of both decalin and its C₁₀H₁₈ isomers, while the H-atom abstraction reactions consume most of decalin. Monocyclic aromatic hydrocarbons (MAHs) are mainly produced in the fuel decomposition process instead of the mass growth process from small molecules, indicating that the two fused six-membered ring structure offers a solid infrastructure to form MAHs. Polycyclic aromatic hydrocarbons (PAHs) are mainly produced in the mass growth process from PAH precursors such as benzyl radical (A1CH₂), phenyl radical (A1-), and 1,3-cyclopentadienyl radical (CYC₅H₅). The relatively high degree of saturation of decalin facilitates ring-opening pathways in its decomposition. This enhances the formation of MAHs but limits the formation of PAHs, leading to the lower sooting tendency of decalin than tetralin. Furthermore, the model was also validated on the shock tube pyrolysis data of decalin in the literature.

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1. Introduction

Cycloalkanes are important components in commercial transportation fuels. For example, their volume fractions can reach one-third in diesel oil [1] and 20% in kerosene [2]. Cycloalkanes can be divided into two groups, i.e. monocyclic alkanes and polycyclic alkanes. The combustion of monocyclic alkanes has attracted great concerns of the combustion community [3–15]. However less attention has been paid on the combustion of polycyclic alkanes, even though these components have comparable volume fractions to monocyclic alkanes in diesel oil and kerosene [12]. Decalin is a representative polycyclic alkane composed of two fused six-membered rings. It is not only an important component in diesel oil and kerosene, but also a component existing widely in products of oil shale, oil sand, and direct coal liquefaction [16]. Consequently it is selected as a representative naphthenic component in the de-

velopment of surrogate fuels and their kinetic models [12,17–19]. It is also used as a fuel component for liquid fuel based ramjet propulsion system due to its high energy density [20]. Additionally, decalin is also an effective endothermic fuel for engine cooling [21]. The wide use of decalin leads to an urgent need of investigations on both its pyrolysis and oxidation.

There are several previous experimental work on the pyrolysis of decalin. Bredael and Rietvelde [22] investigated the pyrolysis of decalin in a quartz flow reactor at 0.5 atm and temperatures of 973–1223 K. The similar pressure and temperature range were later used by Hillebrand et al. [23] to investigate the pyrolysis of decalin in a stainless steel flow reactor. Taylor and Rubey [24] investigated the thermal decomposition of decalin in a quartz flow reactor at atmospheric pressure. Ondruschka et al. [25,26] investigated the pyrolysis of decalin in a tubular quartz reactor at temperatures of 770–1020 K using both gas chromatography (GC) and mass spectrometer. Zeppieri et al. [27] studied the pyrolysis of decalin in an atmospheric flow reactor using GC. Yu and Eser [28] studied the pyrolysis of decalin in a Pyrex glass tube reactor under near-critical and supercritical conditions. Zamostny et al. [29]

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studied the pyrolysis of decalin in a micro-pyrolysis reactor at the pressure of 400 kPa and the temperature of 1083 K using GC. It is recognized that previous studies relied on GC diagnosis which can only detect stable species. Information on reactive intermediates is desired for the purpose of understanding decalin pyrolysis and validating its kinetic models.

Due to the large molecular weight and complex molecular structure, there are only few of theoretical and kinetic modeling studies of decalin. Chae and Violi [30] calculated the formation pathways of monocyclic aromatic hydrocarbons (MAHs) from the thermal decomposition of decalin. Ranzi and co-workers [31,32] proposed a lumped kinetic model of decalin and validated it against ignition delay time and the jet stirred reactor (JSR) oxidation data. Up to now, no detailed kinetic model of decalin has been proposed.

This paper reports a new experimental study of decalin pyrolysis. The experimental work was performed in a flow reactor at pressures of 4, 20, and 101 kPa and temperatures of 920–1500 K. Synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) was used for comprehensive detection of pyrolysis species, such as free radicals, isomers, MAHs and polycyclic aromatic hydrocarbons (PAHs). This paper also reports the first attempt to develop a detailed kinetic model of decalin pyrolysis. The present model was validated on the new experimental data. Rate of production (ROP) analysis and sensitivity analysis were also performed to provide insights into the decomposition of decalin and formation of pyrolysis products.

2. Experimental method

The experiments were performed at National Synchrotron Radiation Laboratory (NSRL), Hefei, China. Detailed descriptions of the two beamlines and pyrolysis apparatus used in this paper have been reported elsewhere [33–35]. Thus only a brief description is given here. The experimental apparatus consists of a pyrolysis chamber with an electrically heated furnace, a differentially pumped molecular-beam sampling system, and a photoionization chamber equipped with a home-made reflection time-of-flight mass spectrometer (RTOF-MS). During the experiment, the gas mixture of Ar and decalin (1% in mole) with a total flow rate of 1000 standard cubic centimeters per minute (SCCM) was fed into an α -alumina flow reactor with 7.0 mm inner diameter and 150 mm heating length. The pyrolysis products are sampled by a quartz nozzle located at 10 mm downstream from the reactor outlet. The sampled products form a molecular beam and enter the ionization region after passing through a nickel skimmer. After ionized by the synchrotron VUV light, these products are detected by

the RTOF-MS. The chamber pressure in each experiment was maintained at 4, 20, and 101 kPa, respectively.

Detailed methods of temperature measurements and pressure calculations along the centerline of flow reactor have been described elsewhere [36,37]. The temperature distributions along the centerline of the flowtube were measured by a thermocouple. Each temperature profile is named after its maximum value (T_{max}) which is also used as the experimental temperature in the following discussion. The uncertainties of temperature measurement are estimated to be within ± 30 K with repetitious measurements and measurements of other types of thermocouples. Detailed descriptions of the methods of species identification and mole fraction evaluation have also been described elsewhere [36,37]. The uncertainties of evaluated mole fractions are estimated to be within $\pm 10\%$ for decalin and argon, within $\pm 25\%$ for pyrolysis products with known photoionization cross sections (PICSSs), and a factor of 2 for those with estimated PICSSs. The PICSSs of pyrolysis species are available in the online database [38].

3. Kinetic modeling

The present model consists of 484 species and 1774 reactions. A detailed sub-mechanism of decalin was developed, and the rate constants were mainly referred to analogous reactions of cyclohexane and alkylcyclohexanes [3,9,13,39,40], such as the C–C bond dissociation reactions and the H-atom abstraction reactions of decalin, the β -C–C scission reactions of three decalyl radicals, etc. In addition, rate constants of the reactions of six $C_{10}H_{18}$ products were referred to analogous reactions of alkenes from our previous *n*-decane model [41]. The sub-mechanism of MAHs and PAHs was taken from our recently reported toluene model [42,43]. The sub-mechanism of C_4 – C_0 species was taken from our previous *n*-decane model [41]. Thermodynamic data were mainly taken from the thermodynamic database reported by Goos et al. [44] and above models [3,9,13,39–43]. For some key species in the sub-mechanism of decalin without available thermodynamic data, the THERGAS software [45] which uses the group additivity methods proposed by Benson [46] was used to calculate their thermodynamic properties. The reaction mechanism and thermodynamic data are available in the *Supplementary Materials*. The sub-mechanism of decalin will be introduced in detail in the following sections. Table 1 lists the structures of some initial decomposition products of decalin and their and nomenclatures in the present model, while a more detailed list of all species discussed in this paper is presented in Table S1 of the *Supplementary Materials*. The numbers around decalin in Table 1 denote different carbon positions.

Table 1
Molecular structures and nomenclatures of some initial decomposition products of decalin.

DECALIN	RDECALIN-1	RDECALIN-2	RDECALIN-3
CYC ₁₀ H ₁₈	PC ₄ H ₉ -CYC ₆ H ₉	PC ₄ H ₇ -CYC ₆ H ₁₁	CH ₂ -C ₃ H ₇ -CYC ₆ H ₉
CH ₃ -C ₃ H ₅ -CYC ₆ H ₁₀	C ₂ H ₃ C ₂ H ₅ CYC ₆ H ₁₀	CH ₂ -NC ₃ H ₆ -CYC ₆ H ₉	PC ₄ H ₈ -CYC ₆ H ₉
C ₂ H ₃ C ₂ H ₄ CYC ₆ H ₁₀	PC ₄ H ₈ -3-CYC ₆ H ₉	PC ₄ H ₇ -CYC ₆ H ₁₀ -2	CH ₂ -C ₃ H ₅ -CYC ₆ H ₁₀

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