



Full Length Article

Experimental and kinetic modeling study of the pyrolysis and oxidation of 1,5-hexadiene: The reactivity of allylic radicals and their role in the formation of aromatics



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HIGHLIGHTS

- New experimental datasets for 1,5-hexadiene pyrolysis and oxidation at 500–1100 K.
- Detailed kinetic model predicts experimental mole fractions including aromatics well.
- Different pathways for the formation of cyclopentadiene and aromatics are discussed.
- Identification of sensitive reactions for fuel conversion and aromatics formation.

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ABSTRACT

Resonantly stabilized radicals play an important role in the formation of aromatics. In this work, the pyrolysis ($\phi = \infty$) and oxidation ($\phi = 1$ and 2) of 1,5-hexadiene, diluted in He, has been studied experimentally in a jet-stirred reactor at atmospheric pressure. The temperature was varied between 500 and 1100 K and the residence time was fixed at 2 s. Gas chromatography was used to determine the reactor effluent composition. The dedicated analysis section allowed the identification and quantification of many hydrocarbon and oxygenated product species up to naphthalene. The pyrolysis of 1,5-hexadiene results in the formation of small alkenes and cyclic hydrocarbons, with a particularly high selectivity towards 1,3-cyclopentadiene and benzene. In the presence of molecular oxygen, various oxygenated intermediates, including acrolein, prop-2-en-1-ol and but-3-enyl-oxirane, were detected in the outlet gases, besides the pyrolysis products. A detailed kinetic model was developed, mainly with an automatic network generation tool, to simulate and interpret the performed experiments. The kinetic model includes molecular weight growth chemistry to predict mole fractions of the main aromatic species. Model calculated and experimental mole fraction profiles are in relatively good agreement. At low-temperature pyrolysis conditions, 1,5-hexadiene is in quasi-equilibrium with allyl radicals. Hydrogen abstraction from 1,5-hexadiene by allyl radicals has the strongest effect on conversion. The resulting hexa-2,5-dien-1-yl radical can react by intramolecular radical addition and eventually form 1,3-cyclopentadiene and benzene. Recombination of cyclopentadienyl with alkyl radicals followed by hydrogen abstraction and ring enlargement is an important formation path to aromatics. At oxidizing conditions, the pyrolysis reaction pathways are in competition with reactions involving hydroxyl and hydroperoxy radicals, as well as molecular oxygen. Above 900 K, 1,5-hexadiene is mainly consumed by C–C scission. The conversion and product distribution in 1,5-hexadiene oxidation are found to be sensitive to the branching ration of the reactions of allyl with hydroperoxy radicals. Formation of hydroxyl and allyloxy radicals increases the reactivity while the propene and molecular oxygen channel decreases the number of radicals in the system.

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1. Introduction

The pyrolysis and oxidation of hydrocarbon and oxygenated molecules often lead to the formation of polycyclic aromatic hydrocarbons (PAH) which are considered the main precursors for deposits or soot particles [1]. Resonantly stabilized radicals, such as propargyl, allyl and cyclopentadienyl, have been identified as important intermediates for PAH formation [2–5]. They have prolonged lifetimes compared to non-resonantly stabilized radicals and therefore accumulate at fuel-rich oxidation or pyrolysis conditions. Recombination with other radicals in the reactive system is an important consumption route leading to molecular weight growth [6]. In this respect, the self-recombination of propargyl radicals to benzene has been investigated thoroughly [5,7,8]. Other recombination channel routes that eventually lead to benzene include allyl plus propargyl, allyl plus allyl and cyclopentadienyl plus methyl radicals and addition of vinyl to 1,3-butadiene [2,6,9,10]. The relative importance of each benzene formation path depends on the operating conditions and the molecular structure of the feed molecule. For example, a significant proportion of benzene is formed in 1-alkene flames by the recombination of allyl with propargyl radicals via fulvene [2,11–13]. The recombination of allyl radicals has been identified as a significant reaction path during the pyrolysis (<1200 K) of molecules with a high selectivity towards allyl radicals [6,14,15].

The self-recombination of allyl radicals results in the formation of 1,5-hexadiene, which upon hydrogen abstraction from the allylic carbon atoms forms hexa-2,5-dien-1-yl radicals. Cyclization of hexa-2,5-dien-1-yl radicals produces C5 and C6 ring species [16,17]. Note that hexa-2,5-dien-1-yl radicals are also formed by vinyl addition to 1,3-butadiene [13].

The reactions of allyl radicals obtained via 1,5-hexadiene formed via 1,5-hexadiene decomposition have been studied before. In 1960, Ruzicka et al. [18] pyrolysed 1,5-hexadiene in a quartz vessel at 9.3 kPa between 733 K and 794 K at various reaction times. A mechanism was proposed based on hydrogen abstraction reactions by allyl radicals and addition of allyl radicals to double bonds. Golden et al. [19] reported in 1969 the direct measurement of the equilibrium coefficient at 913 K and 1063 K for the reaction between two allyl radicals and 1,5-hexadiene. Homer et al. [20] did experiments with very low helium carrier gas pressures (1.3–6.7 kPa) between 977 K and 1070 K in a flow type reactor coupled to a mass spectrometer, to investigate the scission reaction without the interference of secondary reactions. Pyrolysis experiments in a stirred-flow type reactor with toluene carrier flow between 850 K and 950 K at low pressures (1.6–2.3 kPa) were conducted by Akers et al. in 1967 [21]. Three competing pathways for the consumption of allyl radicals were proposed, i.e. recombination back to 1,5-hexadiene, hydrogen abstraction reaction from toluene and recombination with a benzyl radical. In 1973, Nohara et al. [22] performed experiments in a flow-type apparatus between 773 K and 893 K with nitrogen dilution at atmospheric pressure. A new reaction scheme was proposed with elementary reactions that focus on the formation of C5 products. McDonald et al. [23] studied the cyclic products formed from 1,5-hexadiene by continuous wave CO₂ laser-induced experiments at low pressures. More recently, in 2005, Isemer et al. [24] determined rate expressions for the self-reaction of allyl radicals and the reactions between allyl radicals and acetylene, hydrogen gas and methane in shock tube experiments for temperatures between 1000 K and 1400 K. Additional measurements of the allyl radical recombination rate coefficient using the pulsed-laser photolysis/cavity ring-down spectroscopy technique have been reported by Matsugi et al. [25], new shock tube results have been published by Fridlyand et al. [26] and theoretical calculations for this reaction are done by Georgievskii et al. [27]

Further insight in the oxidation chemistry of hexadiene isomers is provided by McEnally et al. [28] who studied non-premixed 2D methane flames doped with hexadiene isomers. The focus of this research was on the role of hexadienes in high temperature soot formation. In 2010, a detailed kinetic model was developed by Sharma et al. [17] to study the chemistry of 1,3-hexadiene and 1,4-hexadiene in these flames. They concluded that recombination of methyl and propargyl radicals with cyclopentadienyl are important formation pathways for benzene and styrene respectively.

The reactivity of allyl radicals is also of importance during the oxidation and pyrolysis of propene. The oxidation of propene has been thoroughly studied experimentally and the results have been used by Burke et al. [29,30] to develop a well-validated oxidation model. Wang et al. [6] have developed a fundamentally-based kinetic model to characterize the molecular weight growth during propene pyrolysis.

The current work addresses the lack of comprehensive experimental data sets for 1,5-hexadiene pyrolysis and oxidation conditions in a jet-stirred reactor at low to intermediate temperatures. This is motivated by the interest to understand the role that 1,5-hexadiene and allylic radicals play in the formation of aromatics within the primary decomposition chemistry. Therefore In this work, hydrocarbon and oxygenated product species up to naphthalene have been identified and quantified. In order to interpret the data, a detailed kinetic model has been developed using an automatic network generation tool. This model was augmented with kinetic data from several recent literature-reported theoretical calculations. The model is able to predict the trend of the main product species, including aromatics, well. The reaction pathways responsible for the formation of the main product species, 1,3-cyclopentadiene and aromatics have been identified by rate of production and sensitivity analyses.

2. Experimental methods

The applied experimental setup is an isothermal quartz jet-stirred reactor with a dedicated feed section and analysis section for outlet gases. The main features of the apparatus are discussed below, details can be found elsewhere [31,32].

Helium and oxygen were provided by Messer (purities of 99.99% and 99.999% respectively) while 1,5-hexadiene was provided by Sigma-Aldrich (purity of 98%). The helium and oxygen flow rates to the reactor are controlled with two gas-mass-flow controllers (Bronkhorst). The 1,5-hexadiene flow rate is regulated using a liquid-Coriolis-flow controller (Bronkhorst). The liquid is mixed with helium and passes through an evaporator (kept at 450 K). Afterwards, in oxidation experiments, oxygen is added to the gaseous flow.

The gaseous mixture flows through an annular preheating zone, where it is heated to the reactor temperature, and enters the jet-stirred reactor through four nozzles. The nozzles and reactor are designed to avoid thermal and concentration gradients. Thermo-coax resistance wires provide heating for the annular preheating zone and the reactor. A type K thermocouple measures the temperature in the center of the reactor (measured temperature gradients <5 K). The pressure is set with a needle valve downstream of the reactor.

The exit of the reactor is connected to several gas chromatographs through heated transfer lines, kept at 473 K, to avoid condensation. The reactor effluent composition is quantified using three gas chromatographs. Response factors were determined by injecting known amounts of pure substances or using the effective carbon number method. The first gas chromatograph is equipped with a thermal conductivity detector and uses a Carbosphere packed column for separation. The second gas chromatograph

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