

An Ab Initio and Kinetic Study of the Reaction of $\dot{\text{H}}$ atoms with 1,3-Pentadiene

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Introduction

Diesel fuel contains both saturated and unsaturated hydrocarbons, with the unsaturated hydrocarbon portion being a much smaller fraction. Despite their relatively small amount (typically approximately 10% in gasoline), unsaturated hydrocarbons have a significant influence on the flame speed of fuels. Olefins and dienes can be formed through thermal or catalytic cracking of heavy petroleum fractions, and dienes can significantly contribute to the instability of the resulting fuels generated via petroleum cracking. [1] In order to study the stability of fuels, more studies of dienes need to be carried out. For C_5H_8 , there are 4 isomers, 1,2-, 1,3-, 1,4- and 2,3-pentadiene. This work mainly focuses on $\dot{\text{H}}$ -atom addition by $\dot{\text{H}}$ atoms with 1,3-pentadiene, and also includes 1,2-, 1,4- and 2,3-pentadiene as these species are also part of the $\dot{\text{C}}_5\text{H}_9$ potential energy surface (PES).

Based on our previous studies of the butene isomers (1-butene, 2-butene and isobutene), [2-4] the $\dot{\text{H}}$ -atom addition reaction was found to be significantly important for flame speed predictions. For instance, $\dot{\text{H}}$ -atom addition to the terminal carbon atom of 1-butene inhibits reactivity resulting in the consumption of $\dot{\text{H}}$ atoms and the production of relatively unreactive methyl radicals. However, $\dot{\text{H}}$ -atom addition to the non-terminal carbon atom of 1-butene promotes reactivity by ultimately generated two vinyl radicals and a $\dot{\text{H}}$ atom.

There is no direct study of the reaction of $\dot{\text{H}}$ atoms with 1,3-pentadiene, but some of the reactions on the associated $\dot{\text{C}}_5\text{H}_9$ PES have been reported in the literature. In the current work, we study the reactions on the $\dot{\text{C}}_5\text{H}_9$ PES including $\dot{\text{H}}$ -atom addition to the four distinct unsaturated carbon atoms on 1,3-pentadiene which form four $\dot{\text{C}}_5\text{H}_9$ isomers and the decomposition, isomerization, ring-formation reactions of these $\dot{\text{C}}_5\text{H}_9$ radicals. Due to the complication of the complete PES, a simplified PES is generated and the pressure-dependent rate constants are calculated using MESS [5] and compared with literature data. In addition, the H-atom abstraction reactions of 1,3-pentadiene by $\dot{\text{H}}$ atom forming $\dot{\text{C}}_5\text{H}_7$ radicals and H_2 are studied, the rate constants are also calculated.

Theoretical methods

The UWB97XD functional [6] with the aug-cc-pVTZ basis set [7] has been used in the geometry optimizations and vibrational frequency calculations for all of the species involved in these reactions. The WB97XD functional yields satisfactory accuracy for thermochemistry, kinetics, and non-covalent interactions. [6] The M062x/6-311++G(d,p) level of theory [8] has been used in the intrinsic reaction coordinate (IRC) calculations [9]. This method has also been used to scan the C–C bond of the reactants, transition states and the products to calculate the rotational potential energies of internal rotations. To obtain accurate well depths and barrier heights, spin-unrestricted open-shell single-point energies (SPE) for all the species are calculated using the CCSD(T) method [10] with the aug-cc-pVXZ basis set. The basis set correction is calculated by MP2/aug-cc-pVXZ level of theory (where $X = \text{T}, \text{Q}$). The expression is below:

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$$E_{\text{SPE}} = E_{\text{CCSD(T)/aug-cc-pVTZ}} + (E_{\text{MP2/aug-cc-pVQZ}} - E_{\text{MP2/aug-cc-pVTZ}}) \quad (1)$$

In this work, spin-restricted open-shell SPEs for the species on simplified $\dot{\text{C}}_5\text{H}_9$ PES are calculated using the same method with spin-unrestricted open-shell SPE calculations. The comparison of relative energies between spin-unrestricted and spin-restricted calculations are studied.

Pressure-dependent rate constants are calculated using the PAPR code, the central code is MESS which implements the one-dimensional Master Equation calculation for an arbitrary number of wells and products. [5] The single-exponential-down model $\langle \Delta E_d \rangle = 243(T/300)^{0.88} \text{ cm}^{-1}$ is used to predict the energy transfer function. The collision frequency is estimated using Lennard-Jones (L-J) parameters, ε is well depth (the maximum attractive energy) and σ is a characteristic distance (the distance at which the potential is zero). [11] In this work, the L-J parameters for C_5H_{12} calculated by Jasper and Miller are used for all $\dot{\text{C}}_5\text{H}_9$ radicals, $\sigma = 4.2 \text{ \AA}$, $\varepsilon = 192.0 \text{ cm}^{-1}$ for all $\dot{\text{C}}_5\text{H}_9$ radicals and $\sigma = 3.7 \text{ \AA}$, $\varepsilon = 67.9 \text{ cm}^{-1}$ for N_2 bath gas.

Results and discussion

• Potential Energy Surface

The $\dot{\text{C}}_5\text{H}_9$ PES is complicated and includes isomerization, decomposition and ring-formation reaction channels. There are 42 stationary points and 61 transition states included in the complete PES. Based on the energy barriers of the complete PES, a simplified PES has been generated including 8 wells, 8 products and 24 transition states. There are 6 wells not included in the simplified PES and these 6 wells can be divided into 2 types. Based on the types and energy barriers of the formation reaction for these wells, four tests are operated to analyse the effects of the neglected channels upon the rate constant calculation. Through the tests, the simplified PES of $\dot{\text{H}}$ -atom addition reaction of 1,3-pentadiene is proved to be reasonable and shown in

Fig..

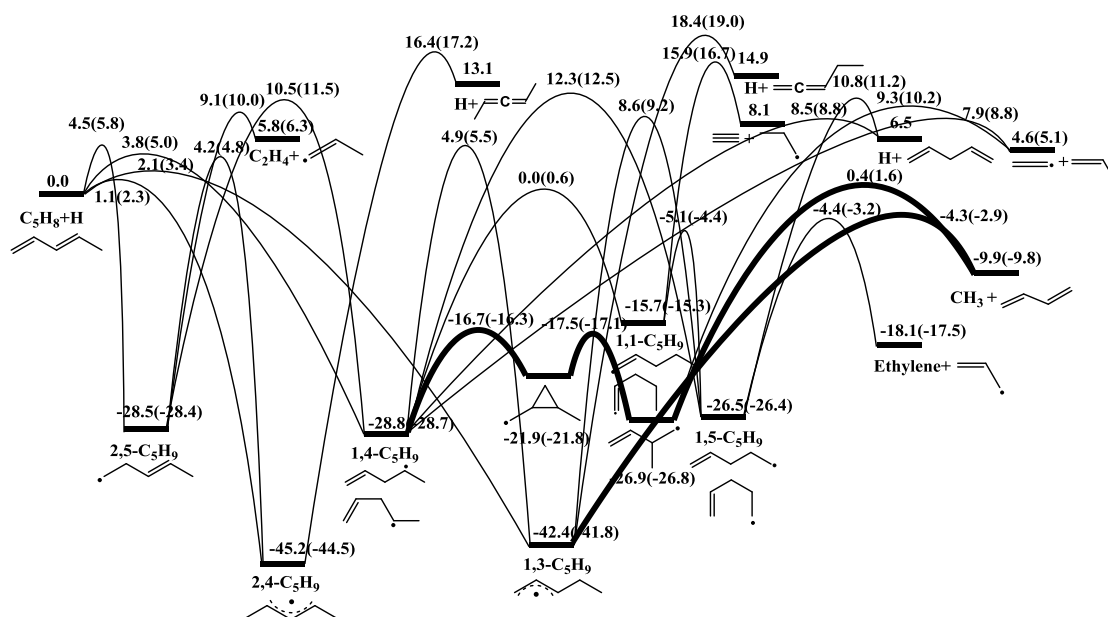


Fig.1. Simplified PES for $\dot{\text{H}}$ -atom addition reaction of 1,3-pentadiene

The spin-restricted and unrestricted open-shell SPEs are both shown in simplified PES, the spin-unrestricted open-shell SPEs are within the bracket. The largest difference between spin-restricted and unrestricted open-shell SPEs is 1.5 kcal mol⁻¹.

- Pressure-dependent kinetics for $\dot{\text{H}}$ -atom addition reaction of 1,3-pentadiene

The rate constants of the species involved in the simplified PES are calculated by MESS at the temperature range from 300 K to 2000 K. Some of the radicals become unstable at high temperature and the rate constants are missing, so the rate constants for unstable radicals are not available for the whole temperature range.

There are 8 products formed through the $\dot{\text{H}}$ -atom addition reaction of 1,3-pentadiene, the pressure-dependant rate constants from $\dot{\text{H}}$ +1,3-pentadiene to the products at different pressures 0.01 atm, 1 atm, 100 atm and over temperature range from 300 K to 2000 K are calculated. The results show that $\dot{\text{C}}\text{H}_3 + 1,3\text{-butadiene}$ is the most dominant product over the whole temperature range. This is also proved by the product branching ratios at 1 atm shown in Fig 2, the branching ratio of $\dot{\text{C}}\text{H}_3 + 1,3\text{-butadiene}$ is almost 1.0 at 300 K and larger than 0.8 from 300 K to 1000 K, then decrease to 0.56 at 2000 K. The branching ratios of Ethylene + 1,3- $\dot{\text{C}}\text{H}_5$, Vinyl + propene, $\dot{\text{H}} + 1,4\text{-pentadiene}$ increase to 0.17, 0.11 and 0.10 separately at 2000 K. However, the sum branching ratio of Ethylene + allyl, $\dot{\text{H}} + 2,3\text{-pentadiene}$, Acetylene + propyl and $\dot{\text{H}} + 1,2\text{-pentadiene}$ is 0.05 at 2000 K. Therefore, $\dot{\text{C}}\text{H}_3 + 1,3\text{-butadiene}$, Ethylene + 1,3- $\dot{\text{C}}\text{H}_5$, Vinyl + propene, $\dot{\text{H}} + 1,4\text{-pentadiene}$ are important products for $\dot{\text{H}}$ -atom addition reaction of 1,3-pentadiene and the other 4 products are unimportant products.

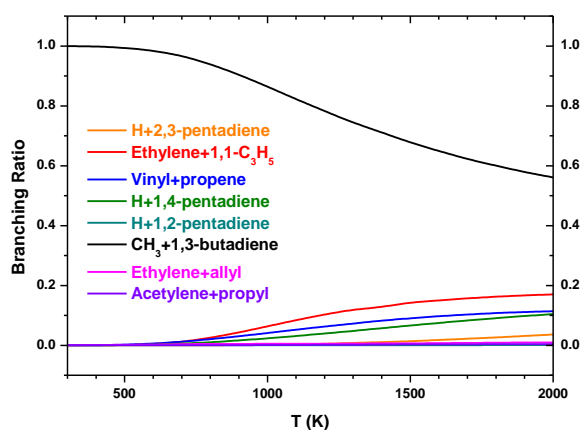


Fig.2. Product branching ratios of $\dot{\text{H}}$ -atom addition reaction to 1,3-pentadiene at 1 atm.

Conclusions

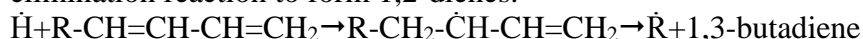
The H-atom addition and H-atom abstraction reactions of 1,3-pentadiene have been studied theoretically. The geometry optimizations and vibrational frequency calculations for all of the species are calculated at the UWB97XD/aug-cc-pVTZ level of theory, and the single point energy is calculated using the CCSD(T)/aug-cc-pVTZ level of theory with basis set corrections from MP2/aug-cc-pVXZ (where X = T and Q). Based on the energy barrier analysis, a simplified $\dot{\text{C}}_5\text{H}_9$ PES is generated and used to calculate pressure-dependent rate constants and branching fractions for the major channels using RRKM/ME calculations in MESS.

Based on the rate constants and branching ratio, the important products for $\dot{\text{H}}$ -atom addition reaction of 1,3-pentadiene is $\dot{\text{C}}\text{H}_3 + 1,3\text{-butadiene}$, Ethylene+1,3- $\dot{\text{C}}\text{H}_5$, Vinyl+propene and

$\dot{H}+1,4$ -pentadiene, the unimportant products are Ethylene+allyl, $\dot{H}+2,3$ -pentadiene, Acetylene+propyl, $\dot{H}+1,2$ -pentadiene.

There are 14 \dot{C}_5H_9 isomers involved in this work, $1,4-\dot{C}_5H_9$ radical and $1,3-\dot{C}_5H_9$ radical are the most important isomer because they contribute to the formation of methyl+1,3-butadiene. The most favoured channel to form methyl+1,3-butadiene is through $1,4-\dot{C}_5H_9 \rightarrow 2\text{-methyl-cyclopropylmethyl} \rightarrow 3\text{-methyl-1-buten-4-yl} \rightarrow \text{methyl+1,3-butadiene}$. The direct β -scission reaction $1,3-\dot{C}_5H_9$ radical also has significant effect on the formation of methyl+1,3-butadiene at high temperature.

Based on the kinetics calculations of \dot{H} atom addition to 1,3-pentadiene, a general rule for H atom addition to 1,3-dienes is proposed. When an alkyl group R is connected to C-C double bond and an \dot{H} atom is addition to the carbon atom which is attached to R, an allyl radical is formed. Then the β -scission reaction to form R+1,3-butadiene is much faster than \dot{H} -elimination reaction to form 1,2-dienes.



The pressure-dependent rate constants and high-pressure limit rate constants of $\dot{H}+1,3$ -pentadiene are compared with literature data and show reasonable agreement with the literature data. The results are also compared with propene and 1,3-butadiene to test the consistency of the rate constants, the comparison results shows good agreement and suggest that the rate constants for $\dot{H}+1,3$ -pentadiene can be used to predict the rate constants for larger 1,3-dienes.

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