

A Theoretical Kinetic Study of the Reaction of Hydrogen Atoms with 1- and 2-Pentene

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Introduction

Based on previous studies of propene [1] and the butene isomers [2,3] (1- and 2- butene and *iso*-butene), it was found that the reaction kinetics of hydrogen atom addition to carbon-carbon double (C=C) bonds plays a significant role in controlling experimental high-temperature ignition delay times, species profiles measured as a function of temperature and/or time in jet-stirred and flow reactors and flame speeds.

Alkenes are key components of hydrocarbon fuels and are important intermediates in the oxidation of alkanes [4]. Therefore, understanding their combustion chemistry not only helps in our understanding of their reactivity, but also in our understanding of how alkanes react. Despite their importance, alkenes have not been as extensively studied as alkanes, in particular larger alkene species such as pentene, which is an important component of gasoline [5].

Alkyl radicals are important intermediates in alkane pyrolysis/oxidation and can undergo unimolecular decomposition reactions including isomerisation reactions. Fragmentation of the radical species by β -scission can also occur, which results in the formation of smaller alkyl radicals and alkene species. These unimolecular decomposition reactions compete with bimolecular oxidation steps. The unimolecular decomposition reactions are normally the main reactions to occur over many conditions of temperature and pressure. These chemically/thermally activated species are important intermediates in the combustion of hydrocarbon fuels. The fragmentation pattern of the parent radical determines both the way the species oxidises and also the formation of product species [6]. This study is focused on the decomposition and β -scission reactions of pentyl radicals.

This work is motivated by the limited theoretical studies available for 1- and 2-pentene + H atoms over a wide range of temperatures (500–2000 K) and pressures (0.001–100 atm). It aims to provide a comprehensive study of the chemistry of H atom addition and abstraction reaction channels for 1- and 2-pentene. The data obtained will then be compared to the 1-butene system in an effort to provide detailed kinetic information so that it can be applied to larger systems. Temperature- and pressure- dependent rate constants have been calculated using Rice-Ramsperger-Kassel-Marcus (RRKM) theory with energy-grain Master Equation (ME) analysis based on the potential energy surfaces obtained.

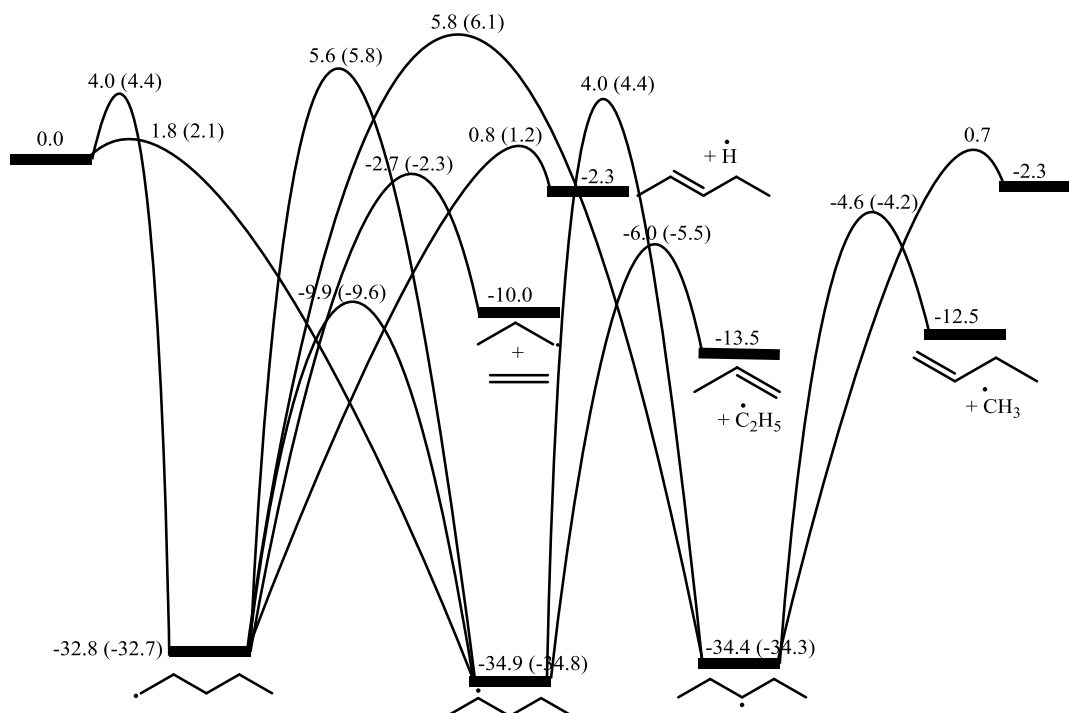


Fig 1 Complete potential energy surface for \dot{H} -atom addition to 1- and 2-Pentene. (in kcal mol⁻¹).

Computational Methods

All calculations have been carried out using Gaussian 09. The geometries of minima and transition state (TS) structures were optimised using a high level of theory UWB97XD [7], with Dunning's aug-cc-pvtz basis set [8]. Harmonic frequency analyses were then carried out using the same level of theory to ensure that the transition state corresponded to the reactant(s) and product(s) of interest. Intrinsic reaction coordinate (IRC) calculations were performed using the UWB97XD/6-31+G(d,p) level of theory. Low frequency torsional modes were treated as 1D hindered rotors and their potential were obtained using the M062X method [9], coupled with the 6-311++G(d,p) basis set. Single point energies were calculated at the ROCCSD(T)/aug-cc-pVTZ and ROMP2/aug-cc-pVXZ (where X = T and Q) levels of theory using the following formula:

$$E_{\text{CBS}} = E_{\text{ROCCSD(T)/aug-cc-pvtz}} + (E_{\text{ROMP2/aug-cc-pvqz}} - E_{\text{ROMP2/aug-cc-pvtz}})$$

The single point energy calculations were also performed using the unrestricted approach, CCSD(T)/aug-cc-pVTZ and MP2/aug-cc-pVXZ (where X = T and Q) levels of theory with basis set corrections using the formula $E_{\text{CBS}} = E_{\text{CCSD(T)/aug-cc-pVTZ}} + E_{\text{MP2/aug-cc-pVQZ}} - E_{\text{MP2/aug-cc-pVTZ}}$ and compared to the restricted open shell approach. Single point energy comparisons between these two methods are shown in Fig 1.

Temperature- and pressure-dependent rate constants were calculated using Rice Ramsperger-Kassel-Marcus (RRKM) theory with Master Equation (ME) analysis using the new master equation system solver, MESS.²² In the master equation, the variables E and J are the total vibrational-rotational energy and the total angular momentum quantum number respectively. In this work, conventional transition state theory was used to calculate rate constants for the abstraction reactions, and RRKM theory was used to calculate micro-canonical, J -resolved

dissociation processes and master-equation methods to determine phenomenological rate constants $k(T,p)$, for all of the non-abstraction reactions. Quantum mechanical tunnelling was accounted for by the inclusion of 1-D tunnelling through an asymmetric Eckart function. For the collisional transition properties, Lennard-Jones collision rates were used to approximate the energy transfer function via a single-exponential-down model. A $\langle \Delta E_d \rangle = 180 \times (T/300)^{0.95} \text{ cm}^{-1}$ model was used for C_5H_{12} as an analogy for the $\dot{\text{C}}_5\text{H}_{11}$ radical and the bath gas used was N_2 .

Conclusion

This work presents a comprehensive study of the chemistry of $\dot{\text{H}}$ -atom addition and abstraction with 1- and 2-pentene. The β -scission, isomerisation and $\dot{\text{H}}$ atom elimination reactions were investigated for both the $\dot{\text{H}}$ -atom addition and abstraction reaction channels. Pressure- and temperature-dependent rate constants for the addition of $\dot{\text{H}}$ atom with 1- and 2-pentene were also calculated using Rice Ramsperger-Kassel-Marcus (RRKM) theory with Master Equation (ME) analysis based on the potential energy surfaces obtained. Rate coefficients are provided and compared with literature values where possible. We find that the high-pressure limit rate coefficients presented in this work agree well with those from literature and relatively well with those from experimental data. Single point energies were calculated using two different approaches for the $\dot{\text{H}}$ -atom addition reaction channels, as stated above. It was found that the values obtained varied very slightly, with a difference of $0.47 \text{ kcal mol}^{-1}$ being the largest, making very little difference to the rate constants.

Pressure-dependent rate constants were also compared. It was found at 1 atm, and at a temperature range 750 – 2000 K that the formation of ethyl and propene from 1-pentene + $\dot{\text{H}}$ -atom was a dominant reaction channel. At 750 – 1200 K, the formation of ethylene + propyl from 1-pentyl radical was favoured. The formation of ethyl + propene from 2-pentyl radical, and 1-butene + methyl from 3-pentyl are dominant reaction channels at a temperature range ~500 – 1200K. For 2-pentene + $\dot{\text{H}}$ -atom, the formation of 3-pentyl radical is most favoured at 1 atm and over a wide temperature range. Pressures of 0.001, 0.01, 0.1, 10 and 100 atm were also compared.

Acknowledgements

We would like to acknowledge the support of Science Foundation Ireland in funding this project under project number-15/IA/3177, and also the Irish Centre for High-End Computing, ICHEC, under project numbers ngche037c and ngche042c for use of computational resources.

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