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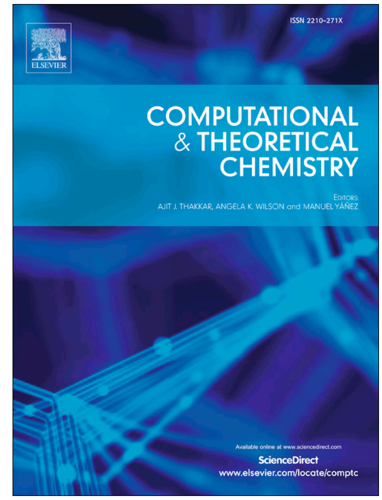

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Density Functional Theory Studies of the Uncatalysed Gas-Phase Oxidative Dehydrogenation Conversion of *n*-Hexane to Hexenes

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ABSTRACT

Density Functional Theory (DFT) modelling studies were conducted for the activation of *n*-hexane in the gas-phase under experimental conditions of 573, 673 and 773K.

The aim of the study was to establish the most favourable radical mechanism for the oxidative dehydrogenation (ODH) of *n*-hexane to 1- and 2-hexene. Modelling of the 3-hexene pathway was omitted due to absence of this product in laboratory experiments. Computations were performed using GAUSSIAN 09W and molecular structures were drawn using the GaussView 5.0 graphics interface. The B3LYP hybrid functional and the 6-311+g(d,p) basis set were utilized for all the atoms. The most kinetically and thermodynamically favourable pathways are proposed based on the determination of the relative total energies ($\Delta E^{\#}$, ΔE, $\Delta G^{\#}$ and ΔG) for the different reaction pathways. The initial C-H activation step is β-H abstraction from *n*-hexane (C_6H_{14}) by molecular oxygen (O_2) to form the alkoxy ($C_6H_{13}O\cdot$) and hydroxyl ($\cdot OH$) radicals. This is proposed as the rate-determining step (RDS) with the calculated $\Delta E^{\#}$ = +42.4 kcal/mol. Two propagation pathways that involve, separately, the $C_6H_{13}O\cdot$ and $\cdot OH$ radicals may lead to the formation of 2-hexene. In both the propagation pathways, the $C_6H_{13}O\cdot$ and $\cdot OH$ radicals activate further C_6H_{14} molecules to produce $C_6H_{13}OH$ and H_2O, respectively, and the alkyl radicals ($\cdot C_6H_{13}$). Thereafter, one pathway involves the interaction of the $\cdot C_6H_{13}$ radical with further molecular O_2, and leads to a second C-H activation step that yields 2-hexene and the peroxy radical ($\cdot OOH$). The other pathway is associated with hydrogen transfer from the $\cdot OOH$ radical to $C_6H_{13}OH$ that is produced earlier, leading to water and the alkyl peroxy radical ($C_6H_{13}OO\cdot$). The $C_6H_{13}OO\cdot$ radical undergoes intramolecular H-abstraction to yield 2-hexene and the $\cdot OOH$ radical, and the latter disproportionate through intermediate $\cdot OH$ radicals to produce O_2 and H_2O in the termination step.

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