

## OH Addition Reactions to 1-pentene and 1-hexene: A Multi-Path Variational Transition State Study.

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Keywords: 1-pentene + OH Reaction, 1-hexene + OH Reaction, Variational Transition State Theory

### INTRODUCTION

Hydroxyl radical addition reactions to alkenes is described by a mechanism taking into account the reversible formation of a  $\pi$ -type prebarrier complex ( $\pi$ -PC), followed by the addition steps, which can lead to different products, considering the addition of the OH radical to each carbon atom at the double bond. Moreover, the  $\pi$ -prebarrier complex may also show distinguishable conformations, which refer to the upward or downward OH attack to the double bond.<sup>1</sup> The reactant itself may also show several conformers and the single mechanism described above may be attributed to each single conformer. The collection of the distinct mechanisms composes the so-called multi-path case.<sup>2</sup>

The central question is how important are the distinct mechanisms for the less abundant conformers to the description of the global kinetics? In this work, this question is first explored by examining two cases, the 1-pentene + OH and 1-hexene + OH reactions, aiming the prediction of accurate rate coefficients.

### METHODS

The chemical reactions were studied at the DFT level, adopting the BHandHLYP functional and the aug-cc-pVDZ (ACCD) basis set. Theoretical calculations include geometry optimizations and vibrational frequencies and reaction paths calculations. Canonical variational rate coefficients were calculated in the range from 200 – 500 K.

### RESULTS AND DISCUSSION

Molecular properties were predicted for each conformer of 1-pentene and 1-hexene and relative abundances, at 298 K, were calculated on the basis of the Boltzmann distribution.

For the most stable conformers,  $\pi$ -PC and saddle points (SP) were located at the

BHandHLYP/ACCD level. For instance, along the 1-hexene + OH reaction path, the prebarrier complexes lie 3.25 and 1.95 kcal mol<sup>-1</sup>, below isolated reactant, for the upward and downward OH additions, respectively. Saddle points for OH addition to the central and terminal carbon atoms show relative energies 0.18 and 0.38 kcal mol<sup>-1</sup>, respectively (upward OH addition) and 0.05 and 0.76 kcal mol<sup>-1</sup>, respectively (downward OH addition). Similar values were obtained for 1-pentene + OH energy profile.

BHandHLYP/ACCD rate coefficients for both reactions have been calculated at 200 – 500 K, neglecting the contribution of the less stable conformers of the alkenes. Room temperature rate coefficients for 1-pentene + OH and 1-hexene + OH reactions are predicted as  $1.25 \times 10^{-12}$  and  $9.04 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. These values are underestimated by 20 and 40 times, comparing to the experimental values.<sup>3,4</sup>

### CONCLUSIONS

The results obtained so far indicate that the BHandHLYP/ACCD level reasonably predicts the room temperature rate coefficients and a satisfactory picture of the reaction mechanism and energy profile has been achieved at this level of theory. Nevertheless, the contribution of other conformers may be important in order to achieve a better agreement with the experimental value, and such evaluation represents a work in progress.

### ACKNOWLEDGMENTS

The authors thank CNPq.

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