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Rapid Hydrogen Shift Scrambling in Hydroperoxy Substituted Organic Peroxy Radicals

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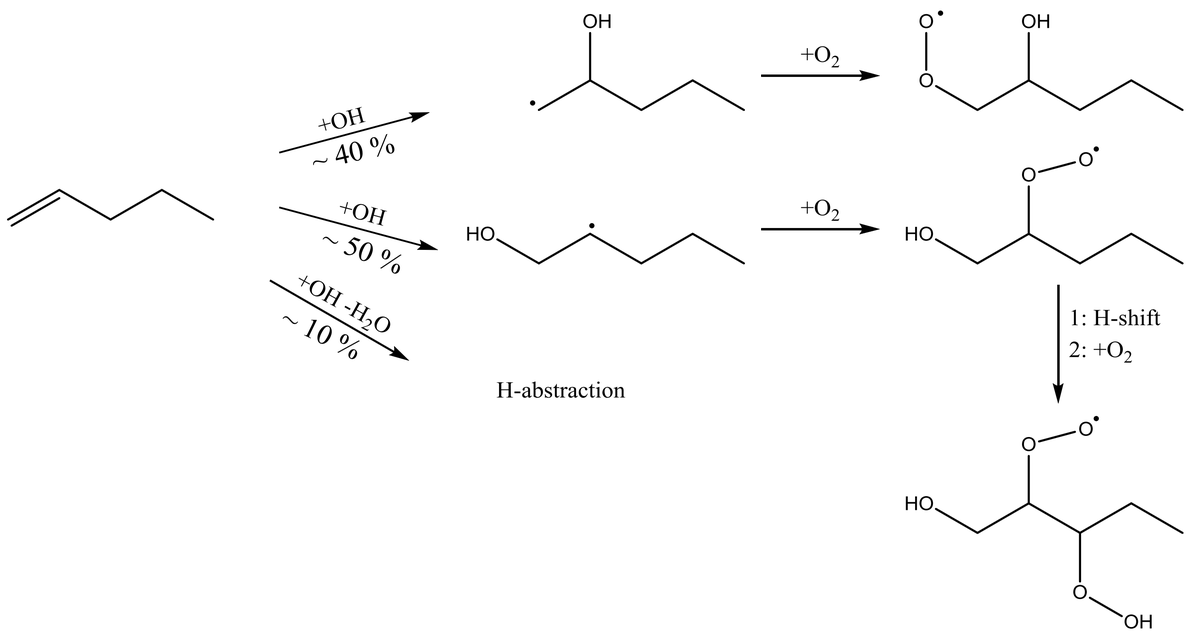
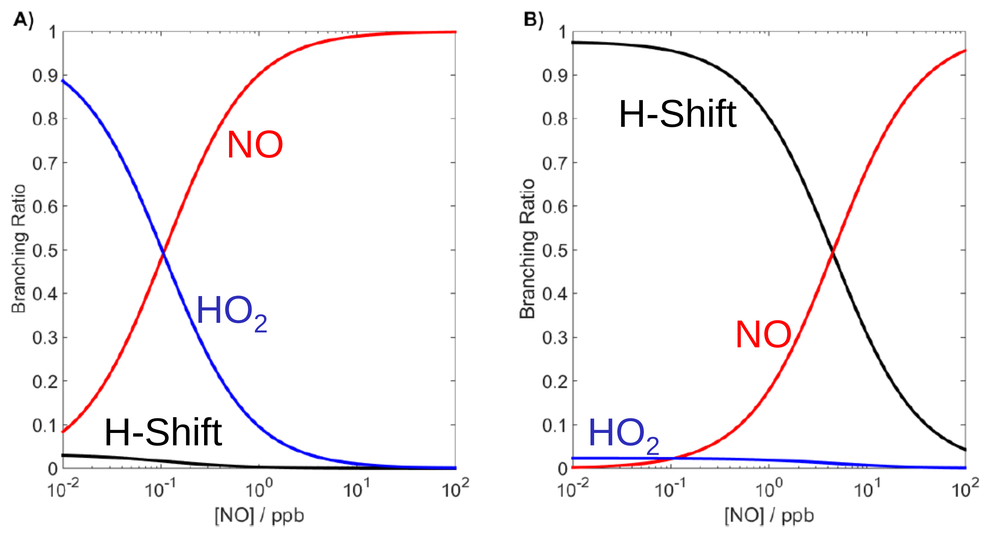
Introduction

The natural emissions of volatile organic compounds (VOC) contribute to the atmospheric production of oxidants and secondary organic aerosols. In the atmosphere, VOCs are oxidized to peroxy radicals, ROO, by the hydroxyl radical (OH) and O_2. The ROO radical can undergo isomerization reactions via intra-molecular hydrogen shift (H-shift) reactions, if theses are fast enough to compete with bimolecular reactions with NO and HO_2.



Conclusion

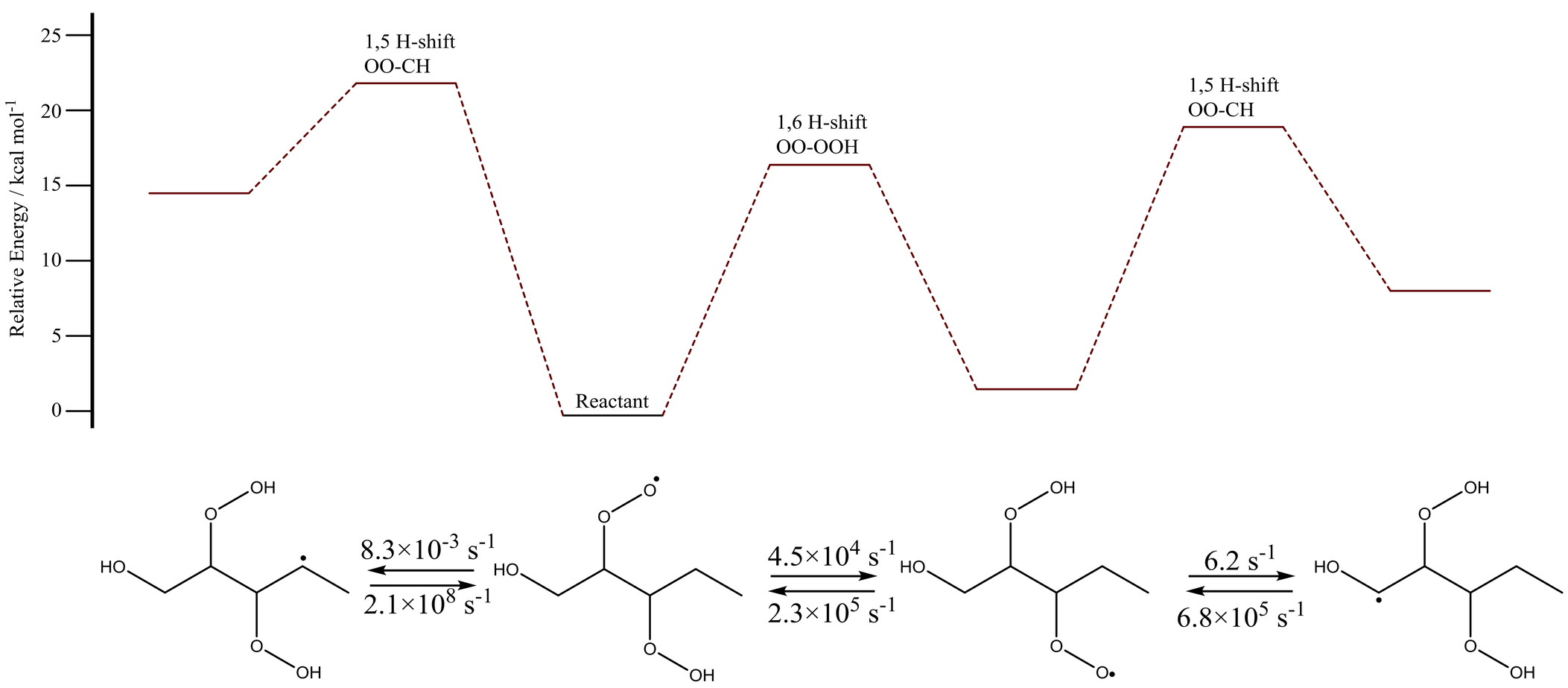
The branching ratio is defined as the percentage of product formed from a specific pathway, with respect to the total amount of product formed. As shown below, inclusion of this new very fast H-shift reaction greatly changes the branching ratio. These hydroperoxy peroxy radicals occur in many autoxidation reactions of VOCs and it is imperative that they be considered in VOC oxidation reactions.



The branching ratios without (left) and with (right) the very fast H-shift between the OO and OOH groups.

Results

Using *ab initio* based Transtition State Theory, we discovered a type of very fast H-shift reactions. In hydroperoxy peroxy radicals both the forward and reverse rate constants were found to be greater than 10^4 s^{-1} for the H-shift between the OO and OOH groups. This H-shift leads to the formation of two distinct peroxy radicals with different possible subsequent reactions.



References

S. Jørgensen, H.C. Knap, R.V. Otkjær, A. Jensen, M. L. H. Kjeldsen, P. O Wennberg and H. G. Kjaergaard, submitted to *J. Phys. Chem. A* (2015)