

EFFECT OF SOLVATION ON KINETIC ISOTOPE EFFECTS ON HYDROGEN ABSTRACTION FROM ETHANOL IN AQUEOUS SOLUTION

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Hydrogen abstraction from ethanol by atomic hydrogen is a well-known reaction which is one of the most important steps in ethanol decomposition.[1] Depending on the temperature this reaction can proceed via three different channels resulting in three different products. It has been shown that at room temperature this reaction goes through only one pathway, however, the reaction can proceed via two transition states (gauche (g) and trans (t)) which interconvert in each other by internal rotation.[2,3] Previous computational study on this reaction was focused on using the simplest presentation of solvent - continuum model of solvation and it was observed that the resulted hydrogen kinetic isotope effects (²H KIEs) deviate from the experimental data which may appear due to the lack of inclusion of specific interactions with the environment. Current research efforts focus on expanding the solvation model in order to test the effect of the explicit presence of water molecules on predicted isotope effects.

²H KIEs were calculated for four different substitution scenarios using two theoretical approaches; multi-path variational transition state theory (MP-VTST) [3,4] and a path integral formalism in a combination with free-energy perturbation and umbrella sampling (PI-FEP/UM).[5] The former method allowed for incorporating quantum effects such as tunneling and recrossing for multiple reaction paths with thermal rate constants determination which were further used for kinetic isotope effects calculation. The latter method enabled to treat the solvent purely explicitly by using a QM/MM protocol. It was observed that within the MP-VTST approach inclusion of a small number of water molecules did not always improve the predictions and the path integral model succeeded only when the QM region of the model was treated at a DFT level of theory. The influence of environment on the obtained isotopic fractionation as well as the contribution of various factors like conformation of the transition state and the position of water molecules directly interacting with the solute were analyzed and discussed.

References

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