

HYDROGEN ATOM ABSTRACTION FROM ETHANOL BY ATOMIC HYDROGEN 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 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] Recent computational research over this reaction is based on continuum model of solvation. In this work we expand solvation model to test the effect of specific explicit solvation on predicted kinetic isotope effects (KIEs).

Different models of aqueous solution including continuum and explicit solvation have been applied. Pure quantum mechanical calculations were used for smaller models whereas hybrid QMMM calculations were used for larger models. Kinetic isotope effects (KIEs) have been calculated for all hydrogen atoms using various theoretical approaches such as multipath variational transition state theory (MP-VTST) and path integrals methods.[3,4,5] These methods allow incorporating quantum effects such as tunneling and recrossing for multiple reaction paths with thermal rate constants determination which are further used for kinetic isotope effects calculation. The influence of environment on the obtained isotopic fractionation has been also analyzed and discussed.

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[1] Meana-Pañeda, R.; Fernández-Ramos, A. *J. Chem. Phys.* **2014**, *140*, 174303.

[2] Lossack, A. M.; Roduner, E.; Bartels, D. M. *J. Phys. Chem. A* **1998**, *102*, 7462.

[3] Simón-Carballido, L.; Alves, T.V.; Dybala-Defratyka, A.; Fernández-Ramos, A. *J. Phys. Chem. B* **2016**, *120*, 1911.

[4] Yu, T.; Zheng, J.; Truhlar, D.G. *J. Phys. Chem. A* **2012**, *116*, 297–308.

[5] Major, D. T.; Gao, J. *J. Chem. Theory Comput.* **2007**, *3*, 949-960