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Title:	On Substituent Effects in Hydrogen Tunneling Reactions of Hydroxycarbenes: A Computational and Phenomenological Approach
Authors:	Paliwal, Prerna (/jspui/browse?type=author&value=Paliwal%2C+Prerna)
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Abstract: There have been recent reports [D. Ley, D. Gerbig and P. R. Schreiner *Org. Biomol. Chem.* 10, 3781 (2012)] on experimental observations of hydrogen tunneling in 1,2- hydrogen rearrangement reactions involving hydroxycarbenes. In this thesis work, a model to understand the effect of substituents on these hydrogen tunneling rates has been examined. The model consists of a double-well tunneling system coupled to an anharmonic oscillator through a time dependent periodic coupling term. Here, the tunneling time has been calculated using an approach based on avoided crossings in a Floquet quasi-energy spectrum. The tunneling rates as a function of coupling strength and coupling frequency are calculated. At low values of coupling frequency (0.003-0.01 atomic units), there is an exponential decrease in the tunneling time as the coupling strength increases from 0.0001 to 0.01 atomic units. When the coupling frequency increases to 0.1, the phenomenon of tunneling is relatively suppressed. To understand the electronic effects on experimental hydrogen tunneling rates [P. R. Schreiner et al., *Nature* 453, 906 (2008); D. Gerbig et al., *J. Am. Chem. Soc.* 132, 7273 (2010); P. R. Schreiner et al., *Science* 332, 1300 (2011); D. Ley et al., *J. Am. Chem. Soc.* 133, 13614 (2011)], electronic structure calculations were performed using a density functional theory (DFT) based method B3LYP at 6-311++g(2d,2p) basis set. The transmission probabilities for various substituents have been calculated using the WKB approximation. A further analysis was done using localised molecular orbital energy decomposition analysis (LMOEDA) to semi-quantitatively understand the coupling between the substituent and tunneling mode of the molecule. It can be concluded that along the intrinsic reaction path, the interaction energy is maximum for activating substituents such as -OH or -NH₂, followed by cyclopropyl and least in the case of methyl substituted hydroxycarbene. Hence, strong interactions between the the substituent and the tunneling mode of the molecule suppress the tunneling phenomenon.


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