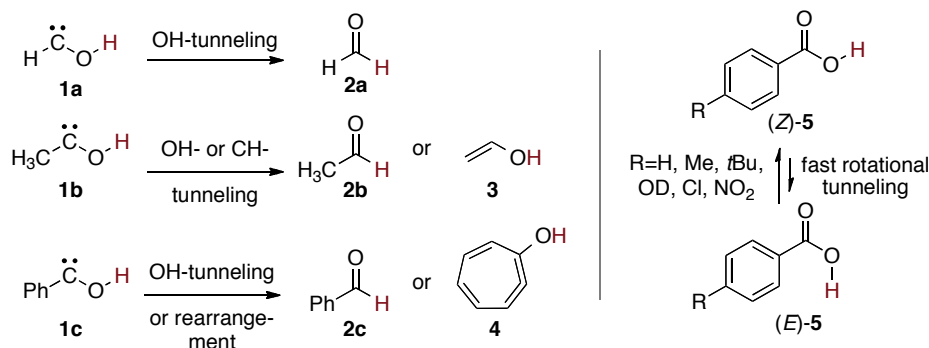
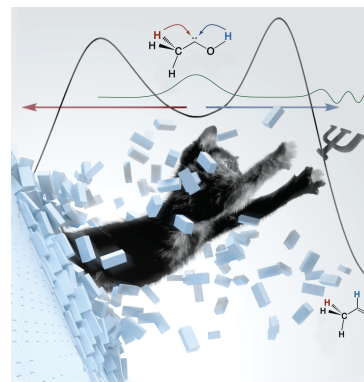


Tunneling Control of Chemical Reactions^[1]

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Chemical reactivity is traditionally understood^[2] in terms of kinetic versus thermodynamic control,^[3] wherein the driving force is the lowest activation barrier among the possible reaction paths or the lowest free energy of the final products, respectively. Here we expose quantum mechanical tunneling as a third driving force that can overwrite traditional kinetic control and govern reactivity based on nonclassical penetration of the potential energy barriers connecting the reactants and products. These findings are exemplified with the first experimental isolation and full spectroscopic and theoretical characterization of the elusive hydroxycarbenes ($R-C-OH$, **1**)^[4] that undergo facile [1,2]hydrogen tunneling to the corresponding aldehydes under barriers of nearly 30.0 kcal mol⁻¹ with half-lives of around 1–2 h even at experimental temperatures as low as 10 K, despite of the presence of paths with substantially lower barriers (e.g., CH-tunneling in **1b** to **3** or rearrangement of **1c** to **4**). We will demonstrate that this is a general phenomenon,^[5] as exemplified by other OH-tunneling examples such as the rotational isomerization of parent and substituted monomeric benzoic acid.^[6] Such tunneling processes do not merely represent corrections to the reaction rate, they *are* the reaction rate, i.e., the completely *control* the reaction outcome.^[1a]



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