

Tunneling Control of Chemical Reactions

Wesley D. Allen

*Center for Computational Chemistry and Department of Chemistry,
University of Georgia, Athens, Georgia 30602 USA*

The conceptual foundations of chemical kinetics were laid by the development of transition state theory (TST), a powerful model that describes a chemical reaction as the passage of a system through an activated complex (saddle point) and over the top of a barrier on a molecular potential energy surface. The practical application of such theories of physical chemistry to competing organic reactions led to the classic principles of kinetic versus thermodynamic control of chemical transformations. The advent of multistep organic syntheses of complex molecules helped establish these principles as effective means of predicting chemical selectivity. As originally constructed and usually employed, kinetic control refers to a reaction system regulated by the relative heights of competing transition states, the process with the lower activation barrier being preferred. In reactions under thermodynamic control, the possible products are formed in proportion to the equilibrium constants for their interconversion, the species with the lower (free) energy being favored. The rate of a reaction can be significantly affected by quantum mechanical tunneling, a classically forbidden process whereby the system yields products by apparently passing under an energy barrier rather than over the top. Here we present new experiments and theoretical analyses to demonstrate that tunneling can not only be a primary mechanism of a single chemical reaction but can change the very outcome in the midst of various reaction possibilities. In other words, tunneling can redirect the kinetics of a system to give products entirely different from those arising under traditional kinetic or thermodynamic control.

Our joint theoretical and experimental work^{1,2} on novel hydroxycarbenes ($R-C-OH$; $R = H, CH_3, C_6H_5$) has achieved the first isolation and characterization of these species. Critical features of the relevant potential energy surfaces were pinpointed by focal point analyses (FPA) based on large correlation-consistent basis sets and coupled cluster theory extended through CCSD(T) and in cases CCSDT(Q). Complete quartic force fields were determined and employed in VPT2 and variational computations to obtain highly accurate vibrational energy levels that precisely matched the experimental bands. Our latest multireference coupled-cluster (Mk-MRCC) capabilities were used to study the open-shell singlet S_1 states of these hydroxycarbenes and establish their UV/Vis spectra. All three hydroxycarbenes exhibit rapid H-tunneling ($t_{1/2} \approx 1-3$ h) at 11 K through prodigious energy barriers of about 30 kcal mol⁻¹, a remarkable phenomenon confirmed by our high-accuracy CCSD(T) computations of barrier penetration integrals. In the case of methylhydroxycarbene, a surprising *tunneling control* mechanism yields a product at complete variance to kinetic control of the chemical reaction.

(1) Peter R. Schreiner, Hans Peter Reisenauer, Frank C. Pickard, Andrew C. Simmonett, Wesley D. Allen, Edit Mátyus, and Attila G. Császár, *Nature* **453**, 906-909 (2008). See commentaries and news articles on this work in *Nature* (Vol. 453, p. 862), *Chemistry World* (July 2008, p. 23), and *Angewandte Chemie* (Vol. 47, p. 2).

(2) Dennis Gerbig, Hans Peter Reisenauer, Chia-Hua Wu, David Ley, Wesley D. Allen, and Peter R. Schreiner, *J. Am. Chem. Soc.* **132**, 7273-7275 (2010), communication.