

Deep Hydrogen Tunneling in Hydroxycarbenes and Carboxylic Acids

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Joint theoretical and experimental work[1-3] has achieved the first isolation and characterization of three hydroxycarbenes ($R-C-OH$; $R = H, CH_3, C_6H_5$) that exhibit remarkable tunneling phenomena. High-level electronic structure computations were critical in unraveling the unexpected behavior of these species. Critical features of the $R-C-OH$ potential energy surfaces were pinpointed by focal point analyses (FPA) based on large correlation-consistent basis sets and coupled cluster theory extended through the CCSD(T) and CCSDT(Q) levels. Complete quartic force fields were evaluated and employed in VPT2 and variational computations to obtain highly accurate vibrational energy levels that precisely match the experimental bands observed in the matrix isolation experiments. 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. In solid argon at 11 K, all three hydroxycarbenes exhibit facile H-tunneling ($t_{1/2} \approx 1-3$ h) through prodigious energy barriers of about 30 kcal mol^{-1} , a striking phenomenon validated by our high-accuracy CCSD(T) computations of tunneling rates. In the case of methylhydroxycarbene, a novel type of mechanism is witnessed – *tunneling control* that yields a product at complete variance to classical kinetic control of the chemical reaction.

Our theoretical investigations have also demonstrated that tunneling is an effective low-temperature mechanism for conformational isomerizations of carboxylic acids. Our CCSD(T)/cc-pVTZ computations show that the *E* form of benzoic acid lies $6.2 \text{ kcal mol}^{-1}$ above the *Z* conformer with a sizable intervening barrier of $5.1 \text{ kcal mol}^{-1}$. Nevertheless, at 0 K tunneling engenders an $E \rightarrow Z$ decay of C_6H_5COOH with $t_{1/2} < 10^{-4}$ s, explaining why the *E* conformer has eluded experimental isolation. For the $E \rightarrow Z$ conformational change in C_6H_5COOD , our computations reveal that deuterium tunneling is operative with a half-life of 4 minutes, in nice accord with matrix isolation observations.[4] Among other examples, we have discovered that oxalic acid ($HOOC-COOH$) exhibits a “domino tunneling” phenomenon, in which the **tTt** conformer decays to **cTt** and subsequently to the lowest **cTc** form by hydrogen tunneling through barriers near 12 kcal mol^{-1} with $t_{1/2}$ values of 50–175 h.

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References

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