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# Light- and Heavy-Atom Tunneling in Rearrangement Reactions of Cyclopropylcarbenes

**Dennis Gerbig, David Ley, and Peter R. Schreiner***

*Justus-Liebig University, Heinrich-Buff-Ring 58, 35392 Giessen, Germany*

*prs@org.chemie.uni-giessen.de*

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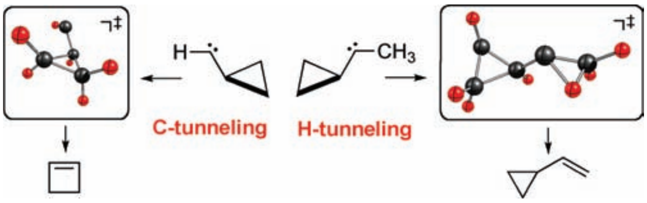
## ABSTRACT

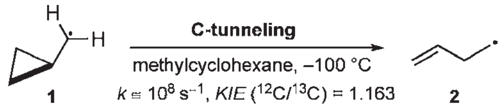


**We investigated both light- and heavy-atom tunneling in the rearrangements of a series of cyclopropylcarbenes using canonical variational transition state theory with multidimensional tunneling corrections (CVT/MT) and the Wentzel–Kramers–Brillouin (WKB) formalism. Halogeno- and hydroxy-substituted cyclopropylcarbenes were found not to undergo carbon tunneling owing to wide reaction barriers. However, while carbon tunneling plays a major role in the ring expansion of parent cyclopropylcarbene yielding cyclobutene, cyclopropylmethylcarbene is prone to undergo hydrogen tunneling to give cyclopropylmethylene.**

The unique reactivity of organic compounds incorporating the cyclopropyl moiety has long since attracted the interest of synthetic and physical organic chemists alike. The interplay between ring strain and its exceptional electronic stabilization earns the cyclopropyl group a distinctive place among its higher-membered cyclic homologues.[1]

Very recently, Borden and co-workers suggested heavy-atom tunneling in this reaction on the basis of canonical variational transition state (CVT) computations including small-curvature tunneling (SCT) corrections.[2,3] Tunneling drives such reactions forward even under cryogenic conditions at temperatures well below 20 K. Due to the large mass of carbon, examples of heavy-atom tunneling are rare.[4–7] The authors recently provided compelling experimental evidence for their hypothesis by studying the $^{12}C/^{13}C$ kinetic isotope effect (KIE) for the ring-opening reaction (Scheme 1).[8] The experimental observation of heavy-atom tunneling in **1** as well as our findings on [1,2]H-tunneling in cyclopropylhydroxycarbene[9] motivated us to take cyclopropylcarbenes as model compounds for studying the implications of tunneling contributions to hydrocarbon rearrangements. We employed approaches based on a canonical variational transition state theory with multidimensional tunneling corrections[10,11] (CVT/MT) as well as the Wentzel–Kramers–Brillouin (WKB)

**Scheme 1.** Experimental Evidence for Carbon Tunneling in the Ring-Opening of the Cyclopropylmethyl Radical (**1**) to the But-1-en-4-yl Radical (**2**) at Low Temperatures



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methodology[9,12−14] to probe temperature-dependent tunneling contributions in the characteristic reaction pathways of these carbenes, such as ring expansion by insertion into a carbon−carbon single bond and [1,2]H-shifts (Scheme 2). The contribution of heavy-atom tunneling in ring expansion was studied for unsubstituted cyclopropyl- (**3**),[15−20] cyclopropylmethyl- (**4**),[21,22] cyclopropylhalogeno- (Cl, **5**; F, **6**),[23−29] and cyclopropylhydroxycarbene (**7**).[9] For **3**, the significance of [1,2]H-tunneling, yielding vinylcyclopropane (**13**), was evaluated as well.

**Scheme 2.** Ring Insertion Reactions of Cyclopropylcarbenes **3**−**7** and [1,2]H-Migration of **4** To Give **13**

**3** **8** R = H
**4** **9** R = Me
**5** **10** R = Cl
**6** **11** R = F
**7** **12** R = OH

**4** **13**

For the evaluation of CVT/MT rate constants, zero-curvature (CVT/ZCT) and small-curvature (CVT/SCT) approximations as implemented in the POLYRATE software[30−32] package were employed. The GAUSSRATE interface to Gaussian09[33] was used to set up the direct dynamics computations. Tunneling rate constants were evaluated in the temperature range from 0 to 300 K with the B3PW91 density functional[34−36] in combination with the cc-pVTZ correlation-consistent triple-$\zeta$ basis set.[37] Due to the low temperatures, computations were carried out with the quantized-reactant-state-tunneling (QRST) option enabled: Instead of assuming continuous tunneling energies, tunneling rates were only evaluated at the energies corresponding to the eigenstates of the reaction coordinate mode of the reactant. The intrinsic reaction path (IRP)[38] was established with the implemented Page−McIver algorithm.[39,40] For the WKB methodology (which is also a zero-curvature type approximation), the IRP was generated at the B3PW91/cc-pVTZ level utilizing the Hessian-based predictor corrector algorithm[41] (as implemented in Gaussian09) and corrected for zero-point vibrational energies (ZPVE) along the path, which were obtained by the evaluation of the respective projected frequencies. All points on the path were then augmented with coupled cluster single-point energies using the CCSD(T) approach,[42−45] employing the cc-pVTZ (frozen core) and cc-pCVTZ (with core correlation)[46] basis sets. For the evaluation of coupled cluster energies, the ORCA program package[47] was used throughout. The attempt energy of barrier penetration was set equal to the zero-point energy of the frequency corresponding to the reaction coordinate $\xi$.[38] Tunneling from higher vibrational modes due to thermal activation was accounted for by utilizing a standard Boltzmann approach for weighing the tunneling probabilities of each vibrational level according to their respective occupation numbers. Computing one-dimensional barrier action integrals along the IRP gave tunneling probabilities that allowed the calculation of tunneling rate constants by using the WKB relation. The overall rate constants (henceforth identified as CVT/WKB) were then calculated as the sum of the WKB tunneling rates and the CVT thermal reaction rates at the B3PW91/cc-pVTZ level. This approach was found to give the best agreement of

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CVT/WKB and CVT/MT results among all tested combinations of other popular density functionals and basis sets.[48,49]

Halogeno- and hydroxy-substituted cyclopropylcarbenes do not undergo tunneling at any temperature mainly due to high (and wide)[4] reaction barriers and are thus limited to over-the-barrier reaction dynamics (see Supporting Information). These findings are in accordance with earlier studies on cyclopropylfluoro- and cyclopropylchlorocarbenes.[50] However, the enthalpic barriers for the ring insertions of **3** and the [1,2]H-shift in **4** are only 2.4 kcal mol$^{-1}$ [AE-CCSD(T)/cc-pCVTZ//B3PW91/cc-pVTZ] and 11.1 kcal mol$^{-1}$ [CCSD(T)/cc-pVTZ//B3PW91/cc-pVTZ], respectively, and exhibit a rather narrow profile. Hence, the ring expansion of **3** and the [1,2]H-migration in **4** were found to include significant tunneling contributions to the respective rate constants. We computed the KIE for tunneling as $k(^{12}\mathrm{C})/k(^{13}\mathrm{C})$ for ring expansion in **3** with $^{13}$C at the carbene center and as $k(\mathrm{H})/k(\mathrm{D})$ for [1,2]H-migration in **4** by exchanging the CH$_3$ for a CD$_3$ group. Arrhenius plots for the computed rearrangement kinetics of **3** and **4** are depicted in Figures 1−4.

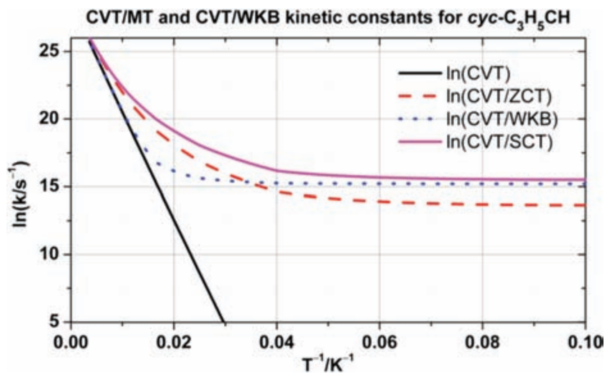

**Figure 1.** Arrhenius plot of heavy-atom tunneling rate constants in the ring expansion of **3**.

Due to the low barrier of ring expansion in **3**, the respective tunneling rates are generally predicted to be very large (Figure 1). The high level CVT/WKB rates coincide very well with the CVT/SCT results in the low temperature limit, whereas the CVT/ZCT computation gives, as expected, lower rates. At very low temperatures, the reaction rates are essentially constant and are dominated by tunneling. At high temperatures, the reaction rates approach a classical linear temperature dependence.

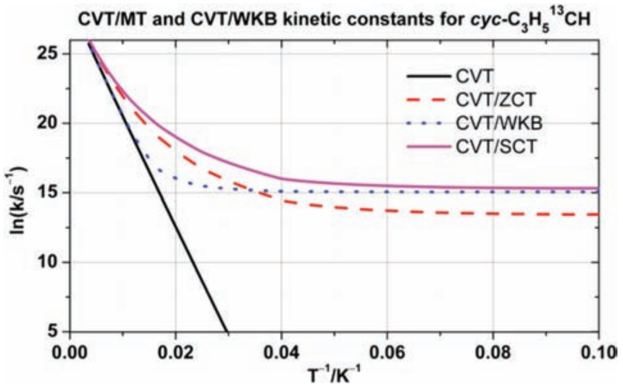

**Figure 2.** Arrhenius plot of heavy-atom tunneling rate constants in the ring expansion of **3** with $^{13}$C as the central carbon atom.

In the intermediate interval from about 20 to 50 K, the overall rates slowly increase despite negligible thermal contributions to the reaction. This behavior can be explained by invoking the concept of thermally activated tunneling,[5] in which tunneling may occur not only from the vibrational ground state but also from the next higher vibrationally excited states as well. As expected, rate constants with $^{13}$C at the carbene center are slightly lower (Figure 2).

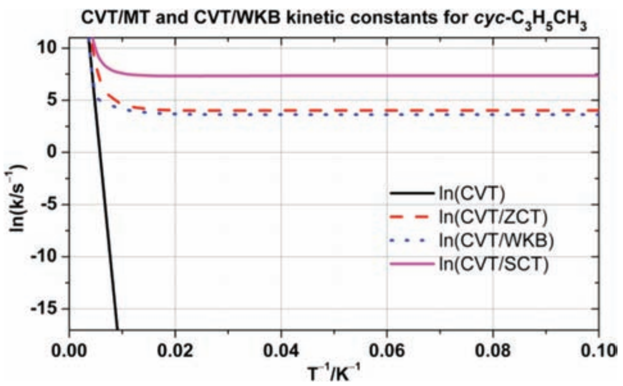

**Figure 3.** Arrhenius plot of light-atom tunneling rate constants in the [1,2]H-migration of **4**.

The KIE at 10 K was computed as 1.173 for CVT/WKB, 1.222 for CVT/ZCT, and 1.218 for CVT/SCT. The results are in accordance with heavy-atom tunneling and thus comparable to those of **1**. The KIE also shows the same dependence on temperature and decreases as tunneling becomes more thermally activated. The dependence of the CVT/WKB rates compared to CVT/ZCT and CVT/SCT rates on temperature is far less pronounced and shows a rather abrupt jump from tunneling to predominantly thermal reactivity, most probably due to the rather simple Boltzmann approach for including tunneling from higher vibrational states in the WKB approximation. [1,2]H-migration in **4** occurs much more slowly than ring insertion in **3**. In contrast to carbon tunneling, all computational methods predict the hydrogen migration reaction to be

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essentially independent of temperature over a large interval. Tunneling governs the reaction rate up to a temperature of about 100 K. The computed KIE is greater than $10^5$ for all methods employed and demonstrates that [1,2]D-tunneling is by several orders of magnitude slower. For higher temperatures, tunneling is rapidly surpassed by the thermal [1,2]H- and [1,2]D-shifts. In the case of light-atom tunneling, CVT/WKB rates coincide best with CVT/ZCT rates (Figures 3 and 4).

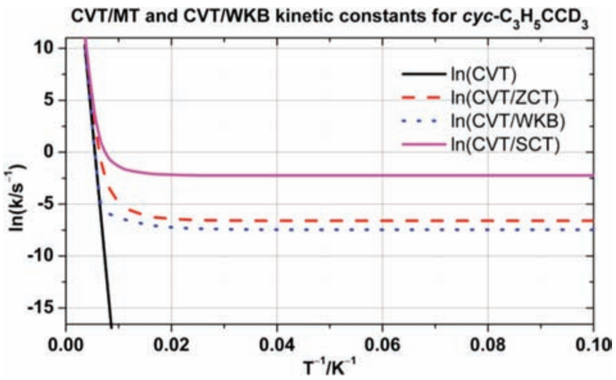
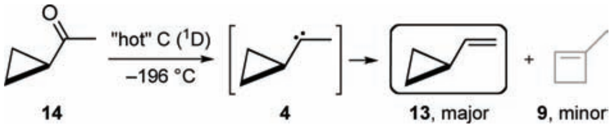


**Figure 4.** Arrhenius plot of light-atom tunneling rate constants in the [1,2]H-migration of **4** with a $CD_3$ group.

Tunneling of hydrogen may well explain the earlier findings of Shevlin et al.: Upon deoxygenation of cyclopropylmethylketone (**14**) at −196 °C with carbon atoms, which were generated in an electrical arc between graphite electrodes,[51] they found **13** to be more abundant than **9** (Scheme 3).

**Scheme 3.** Deoxygenation of Cyclopropylmethylketone (**14**) with Carbon Atoms Mainly Leads to Vinylcyclopropane (**13**)



In their report, they proposed [1,2]H-migration to be the dominant reaction of **4** at low temperatures, whereas ring insertion becomes more important only at higher temperatures when the latter reaction can proceed in the classical over-the-barrier fashion.

The latest theoretical and experimental examples of hydrogen and carbon tunneling, i.e., those dealing with light- and heavy-atom tunneling in well-known fluxional molecules,[7,52] suggest that tunneling is very likely to be the dominant mechanism for reactions occurring with considerable rates even at very low temperatures, especially in rearrangement reactions involving hydrogen or carbon migrations at short interatomic distances. Hence, tunneling in chemical reactions may very well be the rule rather than the exception.

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**Supporting Information Available.** Optimized geometries. Enthalpic barriers for ring insertions. Tabulated rate constants (CVT/MT and CVT/WKB) for C-tunneling in **3** and H-tunneling in **4**. GAUSSRATE input files. This material is available free of charge via the Internet at http://pubs.acs.org.

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