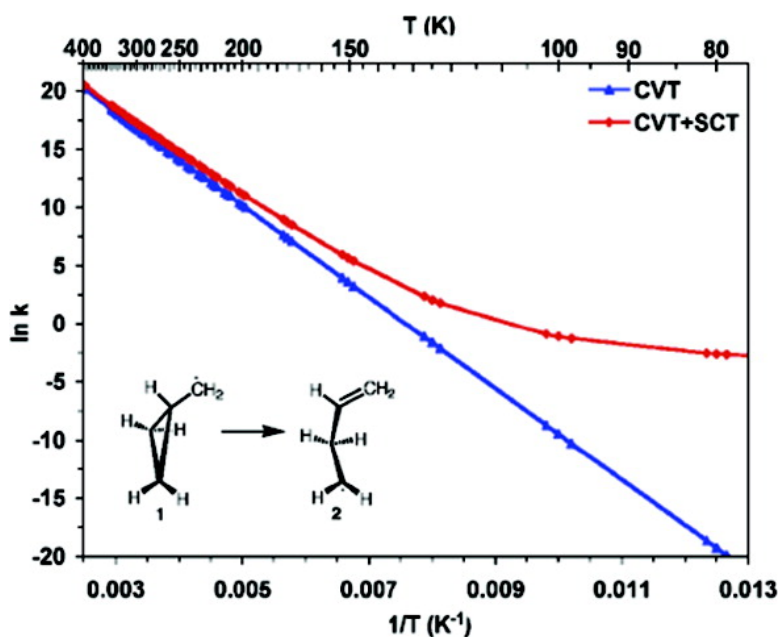


Calculations Predict Rapid Tunneling by Carbon from the Vibrational Ground State in the Ring Opening of Cyclopropylcarbinyl Radical at Cryogenic Temperatures

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Calculations Predict Rapid Tunneling by Carbon from the Vibrational Ground State in the Ring Opening of Cyclopropylcarbinyl Radical at Cryogenic Temperatures

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Experiments and calculations have found that quantum mechanical tunneling by hydrogen plays an important role in many types of reactions.¹ These include sigmatropic rearrangements of hydrocarbons,^{2,3} oxidative addition and reductive elimination reactions of organometallic compounds,⁴ and many enzyme-catalyzed transformations.⁵

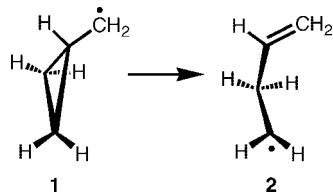
The 12 times larger mass of carbon, compared to hydrogen, is expected to make tunneling by carbon much less ubiquitous than tunneling by hydrogen.^{1a} Reactions in which carbon tunneling is known to play an important role are, in fact, comparatively rare.^{1b} Examples of such reactions, shown in Scheme 1, include π bond shifting in 1,3-cyclobutadiene (eq 1)⁶ and the ring expansion reactions of 1-methylcyclobutylfluorocarbene (eq 2)⁷ and noradamantylchlorocarbene (eq 3).⁸

In this Communication, we report the results of calculations that predict tunneling by carbon should result in the rapid occurrence of a very different type of reaction—the ring opening of cyclopropylcarbinyl radical (**1**) to 3-buten-1-yl radical (**2**)—at cryogenic temperatures. This prediction should be readily amenable to an experimental test.

The ring opening of **1** to **2** has been studied extensively, because the rapid rate of this reaction has made it useful as a “radical clock” for timing the rates of other free radical reactions.⁹ At 298 K, the rate constant for ring opening of **1** has been measured, albeit indirectly, to be $k = 1.0 \times 10^8 \text{ s}^{-1}$.¹⁰ The rate constants for this reaction have also been obtained at temperatures as low as 128 K¹¹ and as high as 395 K.¹²

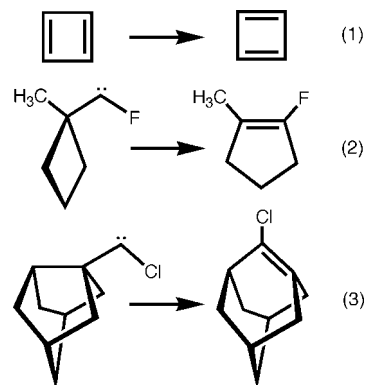
An Arrhenius plot over this very wide temperature range is reasonably linear and gives $E_a = 7.05 \text{ kcal/mol}$ and $\log A = 13.15 \text{ s}^{-1}$.¹⁰ The linear Arrhenius plot and the high A factor both suggest that, over most of this temperature range, the rearrangement of **1** to **2** proceeds largely by passage over the reaction barrier, rather than by tunneling through it.

Nevertheless, our calculations predict a very different pathway for ring opening of **1** to **2** at cryogenic temperatures. At temperatures up to 20 K, the reaction is predicted to occur exclusively by temperature-independent tunneling (i.e., $E_a = 0.0 \text{ kcal/mol}$) from the lowest vibrational level of **1**, with $k = A = 2.22 \times 10^{-2} \text{ s}^{-1}$.



Our calculations were performed using the B3LYP version of DFT, which is comprised of Becke's hybrid, three-parameter, functional¹³ and the correlation functional of Lee, Yang, and Parr.¹⁴

Scheme 1



The 6-31G(d) basis set¹⁵ was employed. Canonical variational transition state theory (CVT)¹⁶ was used to locate the transition state for the ring opening of **1** to **2**.^{17,18} Quantum effects on the reaction dynamics were computed, using the small-curvature tunneling (SCT) approximation.¹⁹ Direct dynamics calculations were carried out with GAUSSRATE²⁰ as the interface between Gaussian 03²¹ and POLYRATE.²²

At 298 K, $k(\text{CVT}) = 1.79 \times 10^7 \text{ s}^{-1}$ for ring opening of **1**; whereas inclusion of tunneling results in a ca. 50% higher rate constant of $k(\text{CVT} + \text{SCT}) = 2.82 \times 10^7 \text{ s}^{-1}$. Inclusion of tunneling brings the calculated rate constant into slightly better agreement with the experimental value of $k = 1.0 \times 10^8 \text{ s}^{-1}$ at this temperature.¹⁰

An Arrhenius plot of the CVT + SCT rate constants is shown in Figure 1. Over most of the ca. 270° temperature range in which the rate constants for ring opening of **1** were measured,^{10–12} the Arrhenius plot in Figure 1 appears linear, as was found to be the case for the Arrhenius plot of the experimental rate constants. However, the activation parameters derived from the CVT + SCT rate constants are actually temperature-dependent, decreasing from $E_a = 7.6 \text{ kcal/mol}$ and $\log A = 13.0 \text{ s}^{-1}$ at 400 K to $E_a = 6.0 \text{ kcal/mol}$ and $\log A = 11.2 \text{ s}^{-1}$ at 150 K. The CVT + SCT activation parameters are in reasonable agreement with the experimental values of $E_a = 7.05 \text{ kcal/mol}$ and $\log A = 13.15 \text{ s}^{-1}$, which fit most of the experimental data, especially at high temperatures,¹⁰ and with $E_a = 5.9 \pm 0.6 \text{ kcal/mol}$ and $\log A = 12.5 \pm 0.9 \text{ s}^{-1}$, which provide a better fit to the rate constants at low temperatures.¹¹

As shown in Figure 1, the curvature of the Arrhenius plot of the CVT + SCT rate constants starts to become very evident at temperatures below 150 K. At 100 K, $E_a = 2.0 \text{ kcal/mol}$ and $\log A = 3.9 \text{ s}^{-1}$. The slope of the Arrhenius plot continues to decrease until, at 30 K, $E_a = 0.005 \text{ kcal/mol}$ and $\log A = -1.65 \text{ s}^{-1}$. In going from 30 to 20 K the CVT + SCT rate constant decreases by only 2%, and below 20 K, it is unaffected by temperature. At these

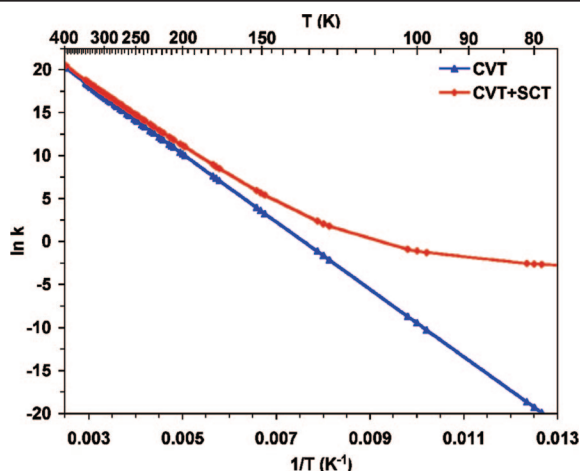


Figure 1. Arrhenius plots of the CVT and CVT + SCT rate constants for the ring opening of **1** to **2** from 80 to 400 K.

cryogenic temperatures, $k(\text{CVT} + \text{SCT}) = 2.22 \times 10^{-2} \text{ s}^{-1}$ is the rate constant calculated for tunneling through the reaction barrier, from the lowest vibrational level of **1**. Tunneling makes the CVT + SCT rate constant at 20 K 10^{70} larger than the CVT rate constant for passage over the top of the reaction barrier.

Why is ring opening of **1** to **2** calculated to be very fast at cryogenic temperatures, when the reaction occurs exclusively by carbon tunneling? The probability, P , of tunneling through a parabolic barrier is given approximately by^{1a}

$$P \approx \exp[-w\pi^2(2mE)^{1/2}/h] \quad (4)$$

where w is the width of the barrier, m is the reduced mass of the particle that tunnels, E is the energy below the top of the barrier at which tunneling occurs, and h is Planck's constant. Equation 4 shows that tunneling by a particle that is many times more massive than hydrogen can have a significant probability if the barrier through which tunneling occurs is low and, especially, if the barrier is narrow. In the case of the ring opening of **1** to **2**, the barrier height is only about 7 kcal/mol, and, more importantly, the barrier is quite thin. The biggest change in geometry is the lengthening of one C–C distance from 1.53 Å in **1** to 2.51 Å in **2**. Consequently, tunneling from the lowest vibrational level of **1** is rather efficient.

Below 20 K, the half-time for the ring opening of **1** is calculated to be only about 30 s and totally independent of temperature. A reaction that occurs so quickly at cryogenic temperatures and which is temperature-independent must involve tunneling from the lowest vibrational level of the reactant. Therefore, our calculations predict that experimental evidence for this type of tunneling in the ring opening of **1** to **2** at cryogenic temperatures will be found in the high rate of this reaction and in its temperature independence. We look forward to an experimental test of our computational predictions.

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Supporting Information Available: Optimized B3LYP/6-31G(d) geometries, energies, thermal corrections, and harmonic frequencies

for **1** and **2**, and the transition structure connecting them, CVT and CVT + SCT rate constants from 6 to 400 K, and the complete lists of authors for refs 21 and 22.

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