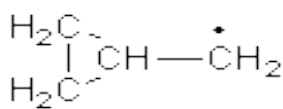


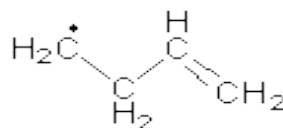
HEAVY ATOM TUNNELING

Wes Borden has been exploring reactions where tunneling is operational. These studies have been inspired by Bill Doering's¹ statement regarding tunneling in 1,5-sigmatropic shifts: "The tunneling effect is likely, in the opinion of some, to remain relegated to the virtual world of calculations". Borden's first two papers dealt with the kinetic isotope effects for the [1,5]-H shift in 1,3-cyclopentadiene and 5-methyl-1,3-cyclopentadiene.^{2,3}

His latest article examines carbon tunneling,⁴ which, due to the much heavier mass of the carbon nucleus relative to a proton, is likely to play a minimal role at best. Borden looked at the ring opening of cyclopropylcarbinyl radical **1** to 3-butene-1-yl radical **2**, passing through transition state **TS1-2**. The B3LYP/6-31G(d) optimized structures are shown in Figure 1.



1



2

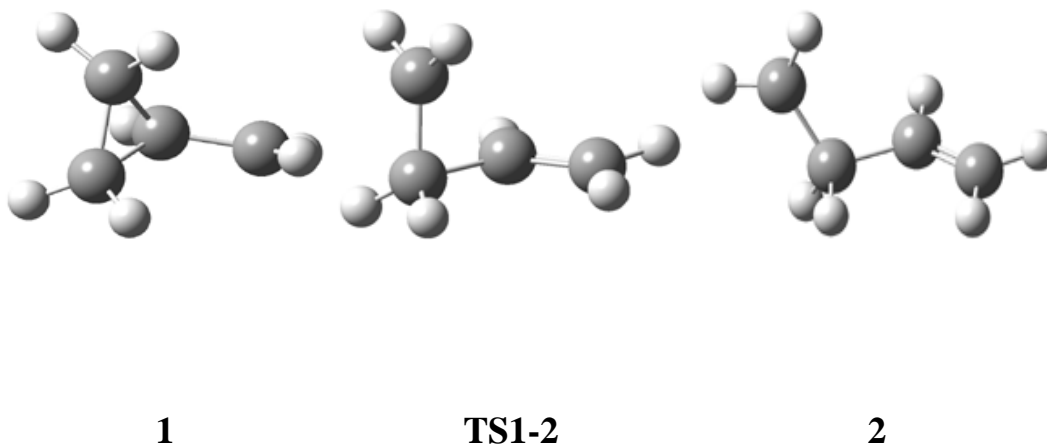


Figure 1. B3LYP/6-31G(d) optimized geometries of **1**, **2**, and **TS1-2**.⁴

The predicted rate of the reaction at 298 K using canonical variational transition state theory is increased by about 50% when small-curvature tunneling is included. This predicted rate is a bit smaller than the experimental value. Experiments also shows a linear Arrhenius plot, and Borden's calculations agree until one reaches very low temperatures. Below 150 K the Arrhenius curve begins to deviate from linearity, and below 20 K the curve is flat – the rate is no longer temperature dependent! Thus, at cryogenic temperatures, the tunneling rate far exceeds traditional crossing of the variational barrier. Borden hopes that experimentalists will reinvestigate this problem (and hopefully confirm his predictions).

Source: <http://comporgchem.com/blog/?p=72>