

QM REFLECTION OFF A BARRIER

Organic chemists are beginning to recognize that tunneling may be more pervasive than previously thought. This blog has noted a number of interesting occurrences of tunneling, and here's one more, by Karmakar and Datta.¹

The barrier for the intramolecular earrangement (Reaction 1) taking the carbene **1** into **2** is estimated to be $44.1 \text{ kcal mol}^{-1}$ at M06-2X/6-31+G(d,p), prohibitively large. However, the intermolecular rearrangement (Reaction 2) has a much smaller barrier of $11.4 \text{ kcal mol}^{-1}$. The structures of the transition states for these two reactions are shown in Figure 1.

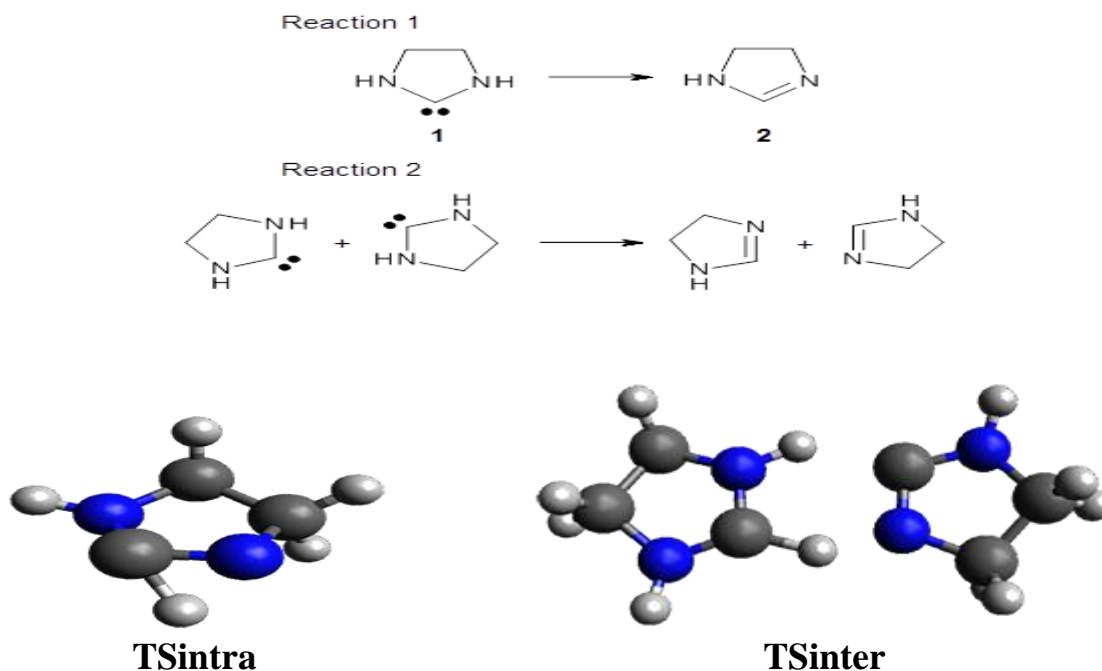


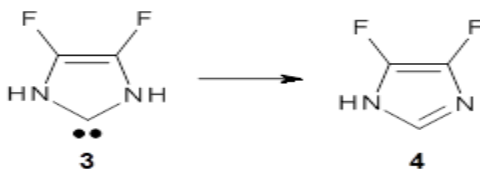
Figure 1. M06-2X/6-31+G(d,p) optimized transition states for Reactions 1 and 2.

Given that the barrier width is likely to be very small for the intramolecular route, perhaps tunneling may play a role. The rate predicted with canonical variational transition-state theory (CVT) and small curvature tunneling (SCT) at 298K is negligible. However, for the intermolecular process, the rate at 298K including tunneling is $3.56 \times 10^4 \text{ s}^{-1}$, more than 10 times greater than predicted with CVT alone, and tunneling makes a dramatically larger difference at lower temperatures.

The intermolecular barrier for the rearrangement of **3** into **4** is very small, only $1.6 \text{ kcal mol}^{-1}$.

This manifests in a very interesting rate prediction: the reaction is actually predicted to be *slower* at temperatures above 150K when tunneling is included than when tunneling is omitted. This is a result of quantum mechanical reflection *off of the barrier*, and this becomes noticeable with the very small barrier.

In addition, the kinetic isotope effects are smaller than expected when D is substituted in for H. These predictions await experimental confirmation.



Source: <http://comporgchem.com/blog/?p=3313>