

Hello, my name is Mariana Jimenez, and I am presenting a computational study of tunneling in the electrocyclic reactions of helical systems.

The reactions investigated are electrocyclic ring closures, which are the cyclization of a conjugated π -electron system by the conversion a π -bond to a σ -bond and the formation of a ring. Doubleday et al. computationally investigated the ring closure of hexatriene to cyclohexadiene and found that at 272 K there was a 35% tunneling probability in the reaction.

An area of interest in the investigation of other systems that may experience tunneling contributions in their electrocyclic reactions are helical systems. This is because the cyclizations of helical systems can't always be rationalized or explained by the Woodward-Hoffman rules. In the systems we investigated, the fjord, or terminal, carbons are closer in proximity to each other inferring a greater potential for tunneling due to a narrow barrier.

Solomek et al. investigated the ring-closure of dimethyl-cethrene and they found an 8.7 kcal/mol discrepancy in the measured energy barriers for cethrene. This discrepancy indicates that tunneling influences the course of the reaction. We used these results as a benchmark for our project. Calculations were run on model systems, C₁₄H₁₂ and C₁₆H₁₂ and [5]Helicene to gain a better understanding of their potential energy surfaces and predict the role of tunneling in their reactions.

The typical path for reactions to take is over the energy barrier, however we are interested in the tunneling path that goes through the barrier as seen in the following figure. Tunneling probability can be predicted for a parabolic barrier model using the following equation.

Calculations were run using Gaussian software and using the M06-2X/6-31G* and UM06-2X/6-31G* methods for geometry optimizations, vibrational frequencies, intrinsic reaction coordinates, and tunneling calculations. Most of these calculations were run unrestricted by mixing the HOMO and LUMO since the systems of interest possess singlet diradical character.

We compared our results of the preliminary calculations to hexatriene, which is the parent reaction. Through these calculations we were able to find the symmetries of each of the systems and use the results to calculate their relative energies. Using the IRC calculations we were also able to calculate the distances moved by the atoms which could contribute to their tunneling potential. A stable-ring opened structure couldn't be found for Model system B which suggests that the ring-opened minimum doesn't exist. By increasing the C-C distance starting from the ring closed form, the energy was observed to rise continuously without decreasing back down to a minimum.

An intrinsic reaction coordinate is a minimum reaction path between the transition state and relative minima of a reaction. We can see that there are dramatic differences in energetics between the systems which can be attributed to the changes in number of Clar sextets in each system. A Clar aromatic sextet is characterized by 6 π electrons localized in a single benzene ring. The energetic results for the cethrene reaction from Solomek et al can be seen in the purple lines.

We can see that the reaction is only slightly exothermic, since there is no change in the number of Clar sextets from the reactant to the product. The C₁₄H₁₂ and C₁₆H₁₂ electrocyclic ring closures goes from having no Clar sextets to two Clar sextets and the large exothermicity brings the transition state down so that its only slightly above the reactant. This causes the reaction to have almost no barrier and shows that this reaction probably isn't a good model for Cethrene. On the other hand, [5] Helicene goes from having 3 Clar sextets to 0, so this reaction is extremely endothermic. For this reason, it is not considered a good model for cethrene either.

The next step was to predict the tunneling potential using Bell's formula. At high enough temperatures, only the first is necessary to predict the % contribution of tunneling. If tunneling is not present, $k = 1$, and $k > 1$ if tunneling does contribute to the reaction. The prediction of the tunneling contributions were calculated for model system A, [5] Helicene, and the parent system, hexatriene, at 250, 272, and 300 K. We weren't able to calculate tunneling potential for model system B because no ring open formed could be identified. We can observe that tunneling potential actually decreases as the temperature of the reaction increases.

Through our investigations of model systems A, B, and [5]Helicene we found that neither of them are good models for cethrene due to the different energetics of their reactions. In the future we will focus on devising new model systems with structures that are similar to that of cethrene and running calculations on them to investigate the role of tunneling in their reactions. We also intend to perform full calculations on cethrene and its cyclization reaction.

Thank you for your time.

If someone asks me what singlet diradical character is what do I say?