

DYNAMICAL EFFECTS ARISING FROM SHALLOW INTERMEDIATES

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We have used quasiclassical trajectories (QCT) to analyze the timing of bond formation and breaking in multistep reactions in the gas phase, such as Zimmerman's di- π -methane rearrangement of dibenzobarrelene in the triplet state^[1] and cycloaddition of tetrazines with alkenes followed by nitrogen extrusion.^[2] This type of molecular dynamics have allowed us to quantify the time gap for the formation of two consecutive bonds, and the lifetimes of the intermediates involved in the global transformations. Besides quantifying the duration of the reactive events, we have found cases in which dynamical effects oppose the intrinsic quantum mechanical preferences for competitive pathways –such as in extrusion of N₂ from the cycloadducts of tetrazine and cyclopropane^[1]–, or involve bypassing unstable intermediates – such as biradical rearrangements in the triplet state (Figure 1).^[2] Both reactions share the common characteristic of featuring shallow intermediates on their potential energy surfaces. As a consequence of these dynamical effects, classical Transition State and RRKM theories are not able to reproduce the intermediate lifetimes and products distribution predicted by quasiclassical trajectories. Through these examples, we show the importance of molecular dynamics for the accurate description of multistep reactions in the gas phase, and show how some potential energy surface topologies can lead to dynamical effects for which classical theories are no longer valid, a phenomenon that is becoming increasingly frequent in common organic transformations.

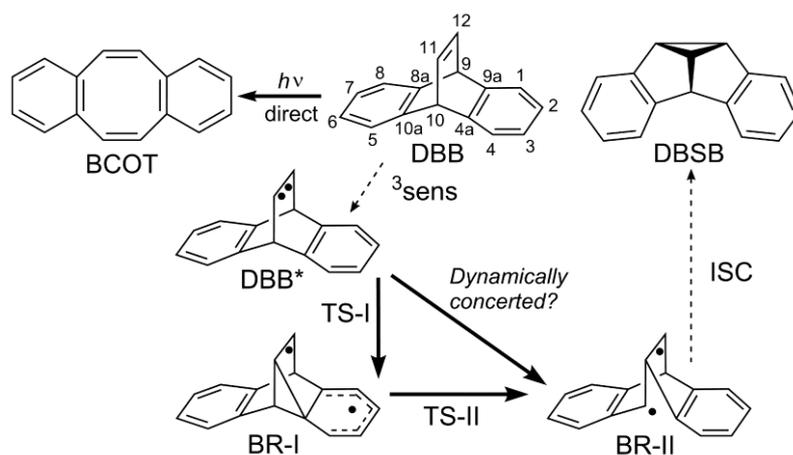


Figure 1. Mechanism for the Zimmerman di- π -methane rearrangement of dibenzobarrelene.

1) G. Jiménez-Osés, P. Liu, R. A. Matute, K. N. Houk, *Angew. Chem., Int. Ed.* **2014**, 53, 8664.

2) L. Törk, G. Jiménez-Osés, C. Doubleday, F. Liu, K. N. Houk, *J. Am. Chem. Soc.* **2015**, 137, 4749.