Studies of Excited State Potential Energy Surfaces:

Can the Hammond Postulate be Applied to Photochemical Reactions?

Freya M. Harvey

The Hammond postulate is a guiding principle in ground-state chemistry for locating and estimating the structure of transition states along a reaction coordinate. It is based on the concept of a potential energy surface, which itself arises from the Born-Oppenheimer approximation.

For photochemical reactions, the Born-Oppenheimer approximation can break down at excited state transition states (ESTS) and at conical intersections (CI). The concept of a single potential energy surface governing the structure at these points is not valid. For this reason, the Hammond postulate has not yet been extended to the excited state.

In previous work on the photolysis of o-nitrobenzyl derivatives, our group observed that the Bell-Evans-Polanyi principle was followed, and the position of the conical intersection varied with the substituents. Thus, we became interested in whether the Hammond postulate could be extended to the excited state.

We imagined the following series of γ-deuterated substrates, with a deuterium atom *anti* to a bulky OTBS group. These molecules can undergo a Norrish-Yang Type II photoreaction. The ratio of the resulting H:D-styrene gives us information about the geometry of the ESTS on the triplet energy surface. Varying the electron density on the aromatic rings on either side of the molecule varies the position of the ESTS and the CI along the photochemical reaction coordinate.

R = H, OMe, CF_3
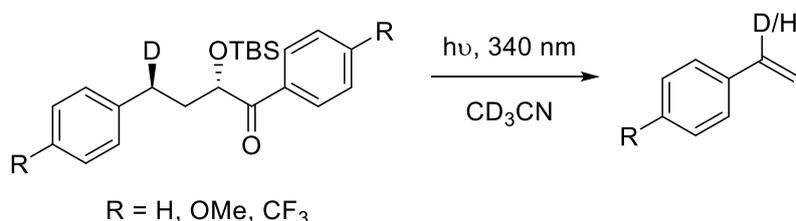
We synthesized and photolyzed the above substrates, and we observed a trend in the H:D-styrene ratios, going towards a more reactant-like ESTS structure with growing electron density in the aromatic rings. This indicates that the Hammond postulate is applicable to the excited state for this family of molecules. We have also synthesized and photolyzed the series of *syn* isomers, and we have measured the kinetic isotope effects.

A pathway towards a second series of β-deuterated substrates to study the conical intersection was also investigated.

Jury:
Prof. Dr. Christian Bochet (thesis supervisor)
Prof. Dr. Oliver Wenger (external co-examiner)
Prof. Dr. Andreas Kilbinger (internal co-examiner)
Prof. Dr. Fabio Zobi (president of the jury)