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New insights on Photo-Fries rearrangement: a model for photodegradation of carbamate pesticides

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Photo-Fries rearrangement (PFR) is a photochemical conversion of aryl esters to *ortho*- and *para*-hydroxyphenones.[1] This reaction is a key step in the synthesis of a large number of compounds and plays an important role in the design of functional polymers and in the photodegradation of drugs and an important class of carbamate pesticides. Although there are a large number of experimental studies about the mechanism of PFR, the last theoretical work is from 1992 and some points of PFR reaction are still under debate. Given the knowledge gap between theory and the most recent experimental works,[2] our aim has been to provide a comprehensive picture of PFR, based on high-level multiconfigurational theoretical methods.

In this work, we present a three-state model for the Photo-Fries rearrangement (PFR) based on CASSCF(14,12)/CASPT2(14,12) calculations.[3] It provides a comprehensive mechanistic picture of all steps of the reaction, from the photoabsorption to the final tautomerization, as shown in Figure 1.

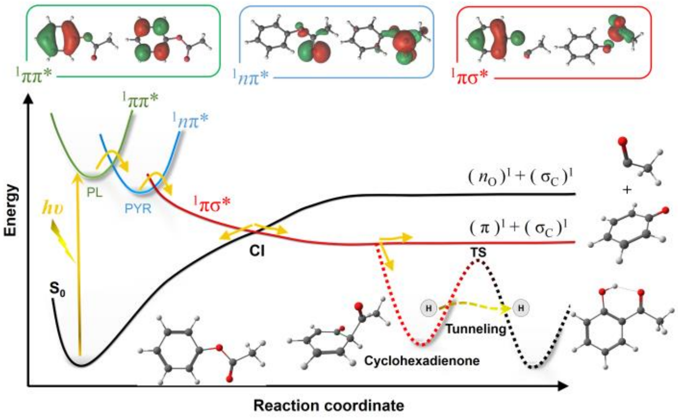

Figure 1: Schematic overview of the three-state model for Photo-Fries rearrangement applied to phenyl acetate.

The three states participating in the PFR are an aromatic $^1\pi\pi^*$, which absorbs the radiation; a pre-dissociative $^1n\pi^*$, which transfers the energy to the dissociative region; and a $^1\pi\sigma^*$, along which dissociation occurs. The transfer from $^1\pi\pi^*$ to $^1n\pi^*$ involves pyramidalization of the carbonyl carbon, while transfer from $^1n\pi^*$ to $^1\pi\sigma^*$ takes place through CO stretching. Different products are available after a conical intersection with the ground state. Among them, a recombined radical intermediate, which can yield *ortho*-PFR products after an intramolecular 1,3-Hydrogen tunneling. The three-state model is developed for phenyl acetate, the basic prototype for PFR, and it reconciles theory with a series of observations from time-resolved spectroscopy. It also delivers a rational way to optimize PFR yields since diverse substituents can change the energetic order of the $^1\pi\pi^*$ and $^1n\pi^*$ states, preventing or enhancing PFR.

Calculations for the S_1 minima show that changing the methyl by an amino group inverts the energetic order of the planar ($^1\pi\pi^*$) and pyramidal ($^1n\pi^*$) minima (Figure 2). While with the methyl group, the $^1n\pi^*$ state is more stable by 0.1 eV, with the amino group, the $^1\pi\pi^*$ becomes the most stable by 0.2 eV in **b** and by 0.4 eV in **c** and **d.** We can rationalize this effect based on the resonance structures that characterize the amino substituted molecules, stabilizing the lone pairs and increasing the energies of the $^1n\pi^*$ state.

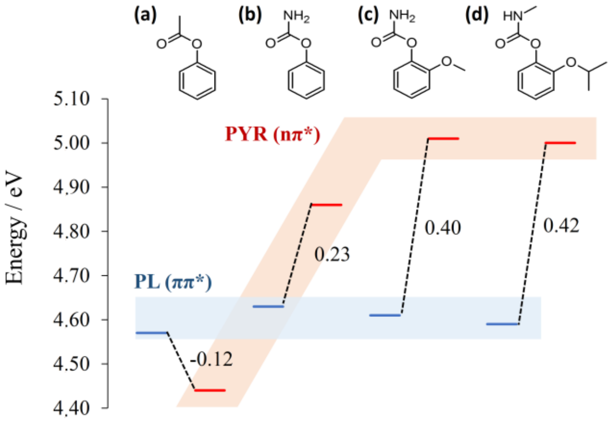

Figure 2: Energies of the planar ($^1\pi\pi^*$) and pyramidal ($^1n\pi^*$) S_1 minima of (a) phenyl acetate, (b) phenyl carbamate, (c) ortho-methoxyphenyl carbamate, and (d) 2-isopropoxyphenyl N-methylcarbamate (Propoxur) in the gas phase.

Key-words: Photo-Fries Rearrangement, Multiconfigurational, Photochemistry.
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