An Extended Conical Intersection Seam Associated with a Manifold of Decay Paths: Excited-State Intramolecular Proton Transfer in O-Hydroxybenzaldehyde

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O-Hydroxybenzaldehyde (OHBA) is a prototypical photoprotector exhibiting excited-state intramolecular proton transfer (ES-IPT). Here we report how its photostability depends on an extended conical intersection seam associated with a manifold of decay paths. Thus, the photoreactivity of OHBA derives from a flat excited-state potential energy surface with barriers of only tenths of electronvolts between the reactant and several conical intersection structures that lead to different products (Scheme 1): two isomers of a hydrogen-bonded intersection (HBI1−2) that lead back to the enol reactant or to the tautomerized keto form in its Z conformation; an intersection (ZEI) that mediates the Z−E isomerization of the keto tautomer; and a twisted-pyramidalized one (TP1) that leads to an oxetene adduct. The intersection structures are connected to each other, forming a continuous seam, and the competition between the products depends on where the seam is accessed after the initial excitation. The overall picture must be also valid for the methyl salicylate (MS) and salicylic acid (SA) analogues of OHBA since it reflects the characteristics reported previously for MS and SA.

Femtosecond resolved photoelectron spectroscopy experiments on OHBA find that the proton transfer and internal conversion are decoupled and occur with different time scales. While the proton on OHBA find that the proton transfer and internal conversion are constants of several picoseconds. Experiments on an OHBA rate is temperature and excitation wavelength dependent, with time transfer is complete in approximately 50 fs, the internal conversion barrierless planar proton transfer coordinate on the1

The competition between the different decay paths is shown in Figure 1, which is a sketch of the surface region formed by the S1 ketoniminata and the seam, based on the calculated paths and the mapping of the seam. The coordinate that leads from the minima to the seam is a rotation around the C2−C7 bond. This bond is a double bond in the keto tautomer and, rotation leads to ethylenic type intersections. The second relevant coordinate connects the 1ππ* and 1nπ* excited-state regions. It is a skeletal rearrangement composed mainly of the C1−O1 bond length coordinate.

The favored decay path from K−1ππ* is provided by two conical intersections, HBI1 and HBI2. At these structures, the torsional angle around the C2−C7 bond (O1−C2−C7−C1) is 45−55°. The two isomers have the same electronic structure and differ in the pyramidalization at C7 (O2−C7−H2−C5 values reported in Figure

Scheme 1
proceeds without a barrier to the enol. HBI1 and HBI2 can be reached from K_{1}^{\pi\pi*} with small barriers (<0.1 eV), in agreement with the short-lived fluorescence of this minimum.

Decay at the ZEI and TPI regions requires a higher degree of C_{2}C_{7} rotation, up to approximately 90°, and breaking of the hydrogen bond. Similar structures have been reported for MS,5 SA,3 and malonaldehyde (MA).14 ZEI is separated from K_{1}^{\pi\pi*} by a barrier of less than 0.1 eV.5 Decay at this region may be photoreactive, as both E and Z isomers of the keto tautomer can be formed and the barrier for thermal E→Z isomerization is high (1.84 eV). The alternative decay through TPI involves two activated steps, from K_{1}^{\pi\pi*} to K_{1}^{\pi\eta*} and from K_{1}^{\pi\eta*} to TPI, with barriers of 0.4 and 0.3 eV, respectively. Decay at TPI can lead to the Z keto tautomer or to the oxetene product. In the latter case, the reaction would lead to degradation.

The seam segments between HBI1, ZEI, and TPI have been mapped with conical intersection optimizations constraining the O_{2}C_{7}C_{2}C_{1} (HBI1–ZEI segment) and O_{2}C_{7}H_{2}C_{2} (HBI1–TPI segment) coordinates (see SI). A total of 11 intersection structures have been located, including unconstrained and constrained minima and the minimum energy path intersections (points of intersection found along the K_{1}^{\pi\pi*}→ZEI and K_{1}^{\pi\eta*}→TPI minimum energy paths) (see also Figures S118–S120 in SI). To show the connectivity, Figure 1 includes a projection of these structures on the C1–O2 and C2–C7–C1–O2 coordinates. Moving along the seam from ZEI to HBI and TPI, Si becomes more \eta* in character because of configuration mixing with the close-lying S_{2} state (see Figure S121 in SI). The S_{0}→S_{2} minimal energy separation is 1.2 eV at HBI2. This suggests that, similar to MA,14 there is a close-lying three-state intersection. The analysis of this intersection and a better mapping of the seam with intrinsic reaction coordinate calculations in the intersection space15 will be the subject of future work.

Overall, the HBI and ZEI regions of the seam are separated from the K_{1}^{\pi\pi*} minimum by barriers of less than 0.1 eV. The calculated values are 0.04, 0.05, and 0.07 eV for the barriers to HBI1, HBI2, and ZEI, respectively, and are within the accuracy of our CASPT2//CASSCF approach. There is also good agreement with the barriers of 0.14 and 0.2 eV1 fitted to experimental data. The slightly higher experimental barrier could reflect the slowing down of the process by intramolecular vibrational redistribution (IVR) from the skeletal in-plane modes activated during the hydrogen transfer to the out-of-plane twisting modes. Our results also suggest the E keto isomer as a possible photoproduction, although the higher degree of twisting required for the isomerization may disfavor the process, as it requires a larger amount of IVR. The formation of oxetene is less probable because of the higher barrier.

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Supporting Information Available: Computational details, Cartesian coordinates, and complete refs 9 and 10.

References

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