

Ultrafast Irreversible Phototautomerization of *ortho*-Nitrobenzaldehyde through a Conical Intersection Triangle and Cascade

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Excited state hydrogen transfer (ESHT) plays an essential role in the functionality of chemical and biological systems. It is also one of the fastest chemical reactions, with time scales as short as 50 fs. In the title molecule, *ortho*-nitrobenzaldehyde (*o*-NBA) –one of the oldest photochemical compounds– the intramolecular ESHT is irreversible yielding a ketene/acid-nitro tautomer (**Ket**), which further reacts to yield *o*-nitroso benzoic acid. This transformation is at the basis of using *o*-NBA e.g., in pH jump experiments. Related nitroarenes also undergo irreversible phototautomerization and are used as photolabile protecting groups. This functionality is different from that found in other aromatic compounds, such as *o*-hydroxybenzaldehyde or *o*-hydroxyphenyltriazole, where ultrafast intramolecular ESHT is reversible, allowing their use as photoprotectors. Thus, the applications of ESHT depend very much on the reversible or irreversible character of the phototautomerization. In the present experimental and theoretical study, we establish for the first time the relaxation mechanism leading to the irreversible phototautomerization of *o*-NBA and clarify the difference with respect to the photostable compounds.

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