

The photolysis of α -hydroperoxycarbonyls

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In this work, we theoretically elucidated the mechanism and predicted the major products of the photolysis of α -hydroperoxycarbonyls, known to be products of the atmospheric oxidation of biogenic volatile organic compounds (BVOC) and components of secondary organic aerosol (SOA) in rural and remote areas. Using 2-hydroperoxypropanal $OCHCH(OOH)CH_3$ as a model compound, we show that a major and likely dominant photolysis mechanism is a fast 1,5 H-shift in the initially excited singlet S1 state followed by spontaneous elimination of singlet oxygen to yield an enol $HOCH=CHCH_3$, while intersystem crossing (ISC) to the triplet T1 state and C–C scission into $HCO + HOOC^\bullet HCH_3$ followed by expulsion of a hydroxyl radical from the unstable $HOOC^\bullet HCH_3$ is another product channel. The direct S1 reaction was found to occur at such a high rate that the quantum yield in atmospheric conditions is expected to be close to unity. In the atmosphere, the enol should generally react with OH radicals or tautomerize into the more stable carbonyl $O=CH-CH_2CH_3$. Vinylalcohol is shown to be a major end product of the photolysis of hydroperoxyacetaldehyde, an isoprene oxidation product. Taking into account also the important enhancement of the absorption cross sections over those of the constituent monofunctional compounds as observed for the analogous β -ketohydroperoxides (J. Photochem. Photobiol. A Chem., 2000, 134, 119–125) the atmospheric photolysis rate of α -hydroperoxycarbonyls was estimated to be in the range of $(1 \text{ to } 5) \times 10^{-4} \text{ s}^{-1}$, generally faster than the rate of their OH reactions.