



HO_x radical regeneration in isoprene oxidation via peroxy radical isomerisations: secondary OH formation following hydroperoxy-methyl-butenal photolysis

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To explain the unexpectedly high OH and HO₂ radical concentrations recently observed over several isoprene-rich areas, we proposed and theoretically quantified a novel isoprene oxidation mechanism for low NO_x conditions.¹⁻³ The major features in the Leuven Isoprene Mechanism (LIM) are (a) fast interconversion of the thermally labile β -OH-peroxy, *Z*- δ -OH-peroxy and *E*- δ -OH-peroxy isomers of the allyl-stabilized hydroxy-isoprene adducts; (b) fast, allyl-assisted 1,6-H-shift isomerisations of the *Z*- δ -OH-peroxys carrying most of the peroxy reaction flux and yielding HO₂ + 4-hydroperoxy-2/3-methyl-but-2-enals (HPALDs); and (c) rapid photolysis of the labile HPALDs to regenerate OH. Evidence for our new mechanism could be construed from recent literature,² including the observation of HPALDs in a photoreactor study at levels consistent with LIM-based expectations.⁴ Also, modelling studies have demonstrated the major potential impact of the new chemistry on the OH-level in isoprene-rich areas and have shown that LIM can closely reproduce the unusually high observed [OH] and [HO₂] in specific areas.^{5,6}

In the present theoretical study, employing high levels of both *ab initio* and statistical rate theories, we address the detailed follow-up chemistry of the OCH-C(CH₃)=CH-CH₂O[•] and OCH-CH=C(CH₃)-CH₂O[•] radicals co-produced with OH from HPALD photolysis. We find that – different from the traditional-reactions scheme adopted by Archibald et al.⁵ – the acyl radicals that result from the prompt 1,5-H shift of the formyl-H to the oxy-O[•], follow competing pathways governed by unimolecular peroxy radical reactions far faster than the traditional atmospheric reactions with NO_x and HO₂, and yielding in part multi-chromophore hydroperoxide intermediates as fast photolytic OH-sources. Of prime importance for the issues at hand, it could be concluded that the co-product radicals of HPALD-photolysis yield quasi-directly 1 to 2 additional OH radicals, bringing the total to 2 to 3 hydroxyl radicals regenerated per HPALD photolyzed, in line with our earlier suggestions^{2,6} and underscoring the potentially dominant role of HPALD formation.

References

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