



## HO<sub>x</sub> 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 HO<sub>2</sub> radical concentrations recently observed over several isoprene-rich areas, we proposed and theoretically quantified a novel isoprene oxidation mechanism for low NO<sub>x</sub> conditions.<sup>1-3</sup> 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 HO<sub>2</sub> + 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,<sup>2</sup> including the observation of HPALDs in a photoreactor study at levels consistent with LIM-based expectations.<sup>4</sup> 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 [HO<sub>2</sub>] in specific areas.<sup>5,6</sup>

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(CH<sub>3</sub>)=CH-CH<sub>2</sub>O• and OCH-CH=C(CH<sub>3</sub>)-CH<sub>2</sub>O• radicals co-produced with OH from HPALD photolysis. We find that – different from the traditional-reactions scheme adopted by Archibald et al.<sup>5</sup> – 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<sub>x</sub> and HO<sub>2</sub>, 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<sup>2,6</sup> and underscoring the potentially dominant role of HPALD formation.

### References

1. J. Peeters, T. L. Nguyen, L. Vereecken, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5935
2. J. Peeters, J.-F. Müller, *Phys. Chem. Chem. Phys.*, 2010, **12**, 14227
3. T. L. Nguyen, L. Vereecken, J. Peeters, *Chem. Phys. Chem.*, 2010, **11**, 3996
4. F. Paulot, J. D. Crouse, H. G. Kjaergaard, A. Kurten, J. M. St. Clair, J. H. Seinfeld, P. O. Wennberg, *Science*, 2009, **325**, 730
5. A. T. Archibald, M. C. Cooke, S. R. Utembe, D. E. Shallcross, R. G. Derwent, M. E. Jenkin, *Atmos. Chem. Phys.*, 2010, **10**, 8097
6. T. Stavrakou, J. Peeters, J.-F. Müller, *Atmos. Chem. Phys.*, 2010, **10**, 9863