



Hydroxyl radical regeneration in isoprene oxidation: upgraded mechanism LIM1

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The OH regeneration known to occur in isoprene oxidation at low/moderate NO is attributed in the Leuven Isoprene Mechanism to novel, theoretically characterized chemical pathways (LIM0: Peeters et al. 2009; Peeters and Muller 2010). Its key new features are (i) quasi-equilibration of the thermally labile beta-OH- and delta-OH-isoprenylperoxy isomers; (ii) 1,6-H shift isomerisation of the Z-delta-OH-peroxy isomers to yield hydroperoxy-methyl-butenals (HPALDs); (iii) fast photolysis of the HPALDs resulting overall in several OH radicals per HPALD. The OH-regeneration through photolabile HPALDs has recently found experimental support, but the peroxy isomerisation rate, HPALD yield and extent of OH recycling are still uncertain (Crouse et al. 2011; Wolfe et al. 2012).

In this work, the upgraded LIM1 mechanism is presented. Based on much higher levels of theory that fully account for dispersion effects, the crucial equilibrium ratio of the isomerising Z-delta-OH-peroxys over the majority beta-OH-isoprenylperoxys is reduced by a factor ≈ 5 and the isomerisation rate of the Z-delta-OH-peroxys by a factor ≈ 1.5 compared to LIM0.

The chemistry following the 1,6-H shift of the Z-delta-OH-peroxys is also much expanded and extended. Firstly, LIM1 introduces other pathways beside HPALD formation following the Z-delta-OH-peroxy isomerisation, but resulting likewise in OH recycling. This, together with the revised Z-delta-OH- equilibrium and isomerisation data above, affords a fair model-reproduction of the HPALD and other product yields observed by Crouse et al. (2011). Secondly, LIM1 proposes new fast reactions of HO₂ with the alpha-oxoketene products from the peroxy isomerisation routes; these reactions are shown to efficiently convert HO₂ into OH and are prime candidates for the unknown $X + HO_2 \rightarrow OH + \dots$ hydroxyl-recycling routes invoked in recent studies (Hofzumahaus et al. 2009; Whalley et al. 2011).

Modeling results using the IMAGES global CTM will be presented on the impact of the LIM1 chemistry on the HO_x levels. The LIM1-modeled increase of [OH] resulting from the peroxy isomerisation reaches a factor 1.5 to 3 in isoprene-rich areas. Specifically, model predictions are compared to the GABRIEL-observations for the Amazon basin where the chemistry is dominated by isoprene (Lelieveld et al. 2008): while the modeled HO₂* levels are only 15 - 30% below the observations, the predicted [OH] falls short of the LIF-measurements by a factor 1.5 - 2; a closer match for OH would require still higher bulk isomerisation rates of the isoprene-peroxys.