

## Alpha-oxoketenes from HPALDs efficiently convert HO<sub>2</sub> into OH radicals in isoprene oxidation

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4-Hydroperoxy-2/3-methyl-but-2-enals (HPALDs) have been predicted to be produced by 1,6-H shift isomerisation of Z- $\delta$ -hydroxy-isoprenylperoxy radicals in the atmospheric oxidation of isoprene by OH at low NO.<sup>1,2</sup> They have recently been observed and recognized as important intermediates in isoprene oxidation,<sup>3</sup> although the peroxy isomerisation rate and HPALD yield as well as the contribution to OH recycling still remain very uncertain.<sup>3,4,5</sup> The HPALD formation and subsequent photochemistry involving very fast photolysis processes have been proposed to result overall in 2 HO<sub>2</sub> and up to 3 OH radicals, with  $\alpha$ -oxoketenes as main products.<sup>2</sup> On the other hand, recent modeling studies suggest that the very high OH observed in isoprene-rich areas could be explained (partly) by unknown compounds reacting fast with HO<sub>2</sub> and converting it into OH.<sup>6,7</sup> However, at present no VOCs or OVOCs are known to react fast with HO<sub>2</sub>. In this work, the reactions of HO<sub>2</sub> with the  $\alpha$ -oxo-ketenes from the HPALDs have been investigated theoretically. The potential energy surfaces, established using suitable DFT/ab initio methods, reveal that HO<sub>2</sub> adds to the  $\alpha$ -oxo-ketenes in a three-step process over submerged transition states, forming a peroxy radical. The theoretically estimated rate constants are sufficiently high that reaction with HO<sub>2</sub> should be the predominant removal route of the oxo-ketenes in the conditions of interest. The straightforward subsequent chemistry of the peroxy product is expected to result partly in the removal of a second HO<sub>2</sub>, and to yield overall 1 to 2 OH radicals, with methylglyoxal, CO<sub>2</sub>, CO, and acetylperoxy radical as main co-products. Modeling results, using the IMAGES CTM, are presented on the impact of these reactions on OH recycling and HO<sub>2</sub> levels in isoprene-rich areas for various scenarios regarding the isoprene-peroxy isomerisation rates and the yields of the HPALDs and their  $\alpha$ -oxoketene products.

### References

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