



## **HOx regeneration in isoprene oxidation: evidence for new unimolecular peroxy radical reactions with strong implications for tropospheric chemistry**

Jozef Peeters (1), Thanh Lam Nguyen (2), Luc Vereecken (1), and Jean-Francois Muller (3)

(1) K. Universiteit Leuven, Department of Chemistry, Leuven, Belgium (jozef.peeters@chem.kuleuven.be, Fax: 32-16 327379), (2) University of Michigan, Ann Harbor, United States, (3) Belgian Institute for Space Aeronomy, Brussels, Belgium (jfm@aeronomie.be, Fax: 32 2 374 8423)

HOx re-generation in the oxidation of isoprene, with its global emissions of about 500 Tg/yr, has a large impact on the global oxidizing capacity of the atmosphere. Recently, we proposed and theoretically quantified new pathways for the OH-initiated oxidation of isoprene that might explain the much higher than observed OH concentrations in isoprene-rich environments (Peeters et al., *Phys.Chem.Chem.Phys.*, 11, 5935, 2009). The new reaction mechanisms put forward and characterized using high-level theoretical methods include (i) the very fast interconversion (by O<sub>2</sub> elimination and addition) of the various conformers/isomers of the major isoprene peroxy radicals, (ii) the 1,5-H shift of the major  $\beta$ -OH-peroxys generating OH with coproducts MACR or MACR, and most importantly, (iii) the 1,6-H shift of specific conformers (Z- $\delta$ -OH-peroxys) followed by reaction with O<sub>2</sub> generating HO<sub>2</sub> and very photolabile hydroperoxy aldehydes (denoted HPALDs), and (iv) fast photolysis (with quantum yield approaching unity) as the main sink of the HPALDs, generating OH and a radical which will give rise to additional OH formation.

In this communication we present evidence, from recent experimental observations, for the newly proposed chemistry. The yields of the main first-generation products (HOx, HPALD, MVK, MACR, but also the hydroxy-aldehydes HALD) will be examined as a function of NO. The implications regarding the role of isoprene in the atmosphere will be also briefly discussed. A global modelling study aiming at quantifying the impact of the new chemistry will be presented in a companion paper in this session.