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Theoretical studies of the isomerisation of peroxy radicals by H-migration

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The isomerisation of alkylperoxy radicals, ROO, by H-migration, yielding an alkyl radical with a hydroperoxide functionality, QOOH, has only recently received significant attention at temperatures relevant to the atmospheric, following their perceived role in OH regeneration in the oxidation of VOCs in lower-NO_x conditions. The H-migration reactions in alkylperoxy radicals derived from alkanes typically have high barriers to reaction, making these isomerisations too slow to compete against the traditional bimolecular reactions of RO_2 with HO_2, RO_2 and NO. More substituted alkylperoxy radicals, however, often have access to H-migration channels with lower energy barriers, increasing the rate of isomerisation and hence the competitiveness against traditional sinks. In the Leuven isoprene oxidation mechanism (LIM), the H-migration in the unsaturated delta-hydroxy-isoprene-peroxy radicals in low-NO_x conditions was predicted to yield unsaturated hydroperoxide-substituted aldehydes, HPALDs. Photolysis of these compounds was then proposed as a source of OH, regenerating the OH originally consumed. Furthermore, similar chemistry was identified in subsequent oxidation steps, providing further sources of OH in the isoprene oxidation; model studies incorporating this novel chemistry showed a good agreement with field observations in the Amazon and the Pearl river delta.

H-migration in alkylperoxy radicals under atmospheric conditions has now been identified in the literature for many other intermediates, formed in the oxidation of isoprene, monoterpenes, acids, and alcohols. Direct experimental data on this reaction class remains scarce, currently leaving theoretical methodologies as the main source of information. As such, the reliability of these calculations is crucial in a correct assessment of the impact of OH regeneration from these compounds. In this work, we present a critical assessment of the uncertainties in the theoretical calculations, and their comparison against experimental data. This assessment serves as a basis for the development of a Structure-Activity Relationship (SAR) for H-migration in alkylperoxy radicals for atmospherically relevant compounds.