## Accretion product formation from self- and cross-reactions of RO<sub>2</sub> radicals in the atmosphere

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The global emission rate of non-methane hydrocarbons from vegetation and human activities into the atmosphere is estimated to be about  $1.3 \times 10^9$  metric tons of carbon per year. Their gas-phase degradation process is mainly initiated by the reaction with hydroxyl (OH) or nitrate (NO<sub>3</sub>) radicals, chlorine atoms or ozone (O<sub>3</sub>). After initial attack of the oxidant, RO<sub>2</sub> radicals are almost exclusively formed as intermediates, which rapidly react further with NO, HO<sub>2</sub> or other RO<sub>2</sub> radicals or via RO<sub>2</sub> radical self-reaction. Here we show that self- and cross-reactions of two RO<sub>2</sub> radicals produce accretion products composed of the carbon backbone of both reactants.<sup>1</sup>

$$RO_2 + R'O_2 \rightarrow ROOR' + O_2$$
 (1)

RO<sub>2</sub> radicals bearing functional groups show fast accretion product formation rates competing with those of the corresponding reactions with NO and HO<sub>2</sub>. This pathway, not considered yet in the modelling of atmospheric processes, can be important, or even dominant for the fate of RO<sub>2</sub> radicals in all areas of the atmosphere. Moreover, the formed accretion products can be featured by remarkably low vapour pressure characterizing them as effective source for secondary organic aerosol.

<sup>&</sup>lt;sup>1</sup> Berndt et al., Angew. Chem. Int. Ed. Engl. (2018) doi:10.1002/anie.201710989.