## Direct observation of first oxidation products from the OH + isoprene reaction for pristine environmental conditions

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Isoprene,  $C_5H_8$ , inserts about half of the non-methane carbon flux of biogenic origin into the atmosphere. Its degradation is mainly initiated by the reaction with OH radicals. The formation of reactive intermediates and corresponding closed-shell products from the OH + isoprene reaction for low NO/HO<sub>2</sub> conditions is experimentally shown. Detailed product analysis has been achieved by mass spectrometric techniques using 6 different ionization schemes. Quantum chemical calculations support the usefulness of applied ionization schemes. Observed RO<sub>2</sub> radicals are the isomeric HO-C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> radicals and their isomerization products HO-C<sub>5</sub>H<sub>8</sub>(O<sub>2</sub>)O<sub>2</sub> and HO-C<sub>5</sub>H<sub>8</sub>(O<sub>2</sub>)<sub>2</sub>O<sub>2</sub> in traces. Main closed-shell products from unimolecular RO<sub>2</sub> reactions are hydroperoxy aldehydes, "HPALDs", and smaller yield products with the composition C<sub>5</sub>H<sub>8</sub>O<sub>4</sub> and C<sub>4</sub>H<sub>8</sub>O<sub>5</sub>.