

## Accretion product formation from RO<sub>2</sub> radical self- and cross-reactions

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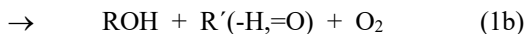
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### Abstract

Hydrocarbons are emitted into Earth's atmosphere in very large quantities by human and biogenic activities. Their atmospheric oxidation processes almost exclusively form RO<sub>2</sub> radicals as reactive intermediates whose atmospheric fate is not fully discovered yet. Here we show that gas-phase reactions of two RO<sub>2</sub> radicals produce accretion products, RO<sub>2</sub> + R'O<sub>2</sub> → ROOR' + O<sub>2</sub>, composed of the carbon backbone of both reactants. This pathway, not considered yet in the modelling of atmospheric processes, can be important 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.

### Introduction

It is generally accepted that the main products of the self- and cross-reaction of RO<sub>2</sub> radicals are either the corresponding oxyl radicals (RO), pathway (1a), or an alcohol (ROH) in conjunction with a carbonyl (R'(-H,=O)), pathway (1b).



As a result of earlier studies, the formation of dialkyl peroxides has been discussed additionally, pathway (1c). Stated peroxide yields from the self-reaction of the simplest RO<sub>2</sub> radicals, RO<sub>2</sub> = R'O<sub>2</sub> = CH<sub>3</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> or CH<sub>3</sub>C(O)O<sub>2</sub>, were reported to be small.<sup>[1-3]</sup>



The relevance of pathway (1c) has not been investigated yet for RO<sub>2</sub> radicals other than for the small model RO<sub>2</sub> radicals and is currently not considered in atmospheric modelling. However, recent experimental findings, especially from gas-phase ozonolysis of cyclohexene and terpenes, point to accretion product formation that could be at least partly explained by a process according to pathway (1c).

## Experimental Methods

The experiments have been performed in a free-jet flow system at  $T = 297 \pm 1$  K and a pressure of 1 bar purified air that allows investigations for nearly wall-free conditions.<sup>[4]</sup> The reaction time was 7.9 s. Ozone premixed with air (5 L min<sup>-1</sup> STP) is injected through the inner tube into the main gas stream (95 L min<sup>-1</sup> STP), which contains the second reactant (alkene) and other diluted in air. Ozone was produced by passing 1 - 2 L min<sup>-1</sup> (STP) air through an ozone generator (UVP OG-2) and blended with additional air to a total flow of 5 L min<sup>-1</sup> (STP) taken as the feed for the inner tube. The outer gas stream, 95 L min<sup>-1</sup> (STP), contained the other reactants premixed in a flask from a gas-metering unit. Ozone concentrations were measured at the outflow of the reactor by a gas monitor (Thermo Environmental Instruments 49C). A proton transfer reaction - mass spectrometer (PTR-MS; HS PTR-QMS 500, Ionicon) served as an on-line monitor for organic compounds. In the case of isopropyl nitrite photolysis for OH radical generation the flow system was surrounded by 8 NARVA 36W Blacklight Blue lamps, emitting in the range 350 - 400 nm for homogeneous illumination of the whole reaction zone. Product analysis has been conducted using the NH<sub>4</sub><sup>+</sup>-CI3-TOF (chemical ionization-time-of-flight) mass spectrometer based on the proton transfer (PTR3-TOF) mass spectrometer from the University of Innsbruck as well as a CI-APi-TOF (chemical ionization - atmospheric pressure interface - time-of-flight) mass spectrometer (Airmodus, Tofwerk) running either in the CH<sub>3</sub>COO<sup>-</sup> mode or the C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup> mode.

## Results

First, product formation from the OH radical initiated oxidation of 1,3,5-trimethylbenzene has been investigated using ozonolysis of tetramethylethylene (TME) as OH radical source. 1,3,5-trimethylbenzene represents an example of aromatic compounds, which are important emissions in urban areas. Measured concentrations of the main RO<sub>2</sub> radicals, i.e. CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub> from TME ozonolysis and HO-C<sub>9</sub>H<sub>12</sub>(O<sub>2</sub>)<sub>x</sub>O<sub>2</sub> with  $x = 1 - 3$  from the aromatic, increased almost linearly with rising ozone and subsequently rising OH radical concentrations. Besides the RO<sub>2</sub> radicals, also the signals of the accretion products according to pathway (1c) from self- and cross-reactions of the RO<sub>2</sub> radicals in the system were detected. Strongest signals appeared for the products C<sub>12</sub>H<sub>18</sub>O<sub>6</sub>, C<sub>18</sub>H<sub>26</sub>O<sub>8</sub> and C<sub>6</sub>H<sub>10</sub>O<sub>4</sub> formed from the possible combinations of the two most abundant RO<sub>2</sub> radicals, i.e. from CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub> and HO-C<sub>9</sub>H<sub>12</sub>(O<sub>2</sub>)O<sub>2</sub>.

Additional experiments confirmed that unwanted processes did not influence the product formation during the ionization in the mass spectrometer.

The general validity of product formation via pathway (1c) is demonstrated from a measurement series using 1-butene, isoprene, n-hexane or methane instead of 1,3,5-trimethylbenzene in the experiments with OH radical formation from TME ozonolysis. In each case, the corresponding accretion products from the self- and cross-reactions of OH-reaction derived RO<sub>2</sub> radicals, i.e. HO-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, HO-C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, C<sub>6</sub>H<sub>13</sub>O<sub>2</sub> or CH<sub>3</sub>O<sub>2</sub>, respectively, and CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub> were identified. It is to be noted that also small signals appeared for CH<sub>3</sub>OOCH<sub>3</sub> from the CH<sub>3</sub>O<sub>2</sub> radical self-reaction in line with earlier observations.<sup>[1-3]</sup> Reliable data analysis in this case, however, was impossible.

Figure 1 shows the experimental findings from the OH + 1-butene reaction using TME ozonolysis for OH radical generation.

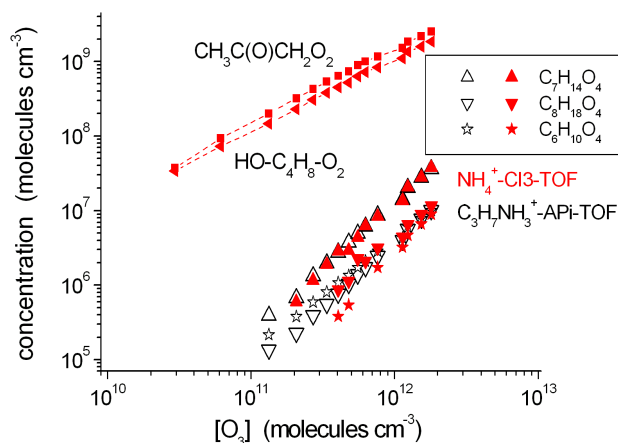


Figure 1: RO<sub>2</sub> radical and accretion product formation from the OH+1-butene reaction with OH radical formation via TME ozonolysis. Measurements have been performed by NH<sub>4</sub><sup>+</sup>-CI3-TOF (full symbols) and by C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub><sup>+</sup>-API-TOF (open symbols). Reactant concentrations: [1-butene] = 2.0 × 10<sup>12</sup> and [TME] = 2.0 × 10<sup>11</sup> molecules cm<sup>-3</sup>.

## Discussion

Accretion product formation according to pathway (1c) has been observed for all possible RO<sub>2</sub> radical self- and cross-reactions in the different reaction systems investigated. Therefore, a complex spectrum of accretion products can be expected in the atmosphere. Rate coefficients of accretion product formation from the self- and cross-reactions of RO<sub>2</sub> radicals, as measured in this work, span a range of more than three orders of magnitude. The different RO<sub>2</sub> reactivity in pathway (1c) is most likely connected to the RO<sub>2</sub> functionalization. Attractive forces from donor-acceptor

relationships between functional groups of the two reacting RO<sub>2</sub> radicals are probably a necessary driving force for the rapid accretion product formation via pathway (1c). It can be speculated at this point that based on hydrogen bonds, carbonyl or endo-peroxide groups as acceptor and hydroxyl or carboxylic groups as donor, a more stable thus longer living reactive complex is generated that finally forms the covalently bound accretion product after O<sub>2</sub> elimination.

Finally, the formed accretion products ROOR' can be treated as a source for secondary organic aerosol (SOA) due to their expected low vapour pressure in the case of functionalized ROOR'. Consequently, this process of accretion product formation can help to explain missing SOA sources in the atmosphere.

## References

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