

Accretion product formation from self- and cross-reactions of RO₂ radicals in the atmosphere

Torsten Berndt¹, Wiebke Scholz², Bernhard Mentler², Lukas Fischer², Hartmut Herrmann¹, Markku Kulmala³, Armin Hansel^{2,3}

¹ Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Dept. (ACD), 04318 Leipzig, Germany.
² Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria.
³ Department of Physics, University of Helsinki, Helsinki 00014, Finland.

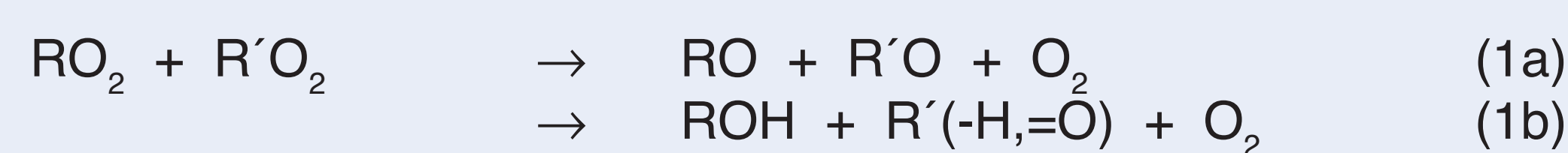
contact: berndt@tropos.de



Motivation

The global emission rate of non-methane hydrocarbons from vegetation and human activities into the atmosphere is estimated to be about 1.3×10^9 metric tons of carbon per year.¹ Their gas-phase degradation process proceeds almost exclusively via the formation of RO₂ radicals as reactive intermediates.

It is currently accepted that the main products of the self- and cross-reaction of RO₂ radicals are either the corresponding alkoxy radicals (RO), pathway (1a), or an alcohol (ROH) in conjunction with a carbonyl (R'(-H,=O)), pathway (1b):



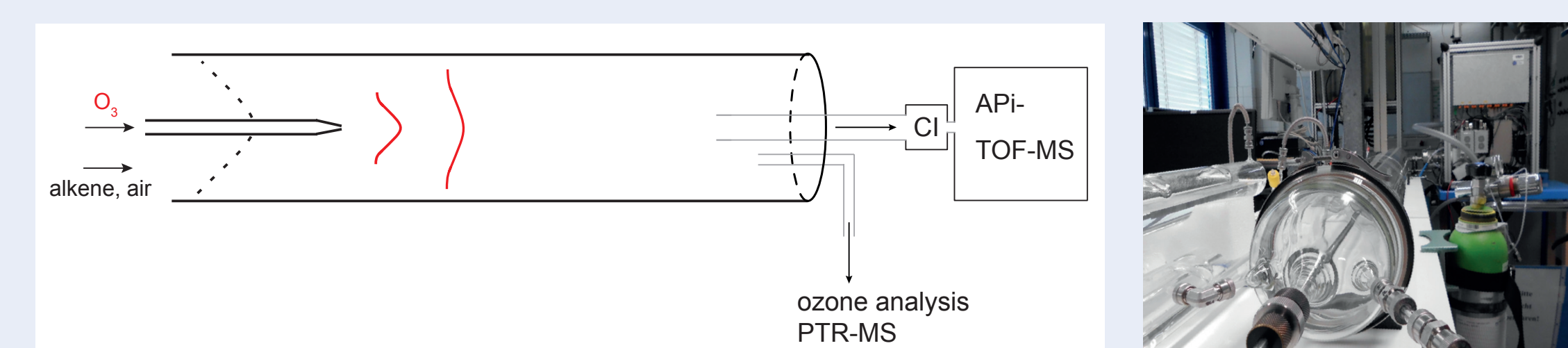
As a result of earlier studies, the formation of dialkyl peroxides has been discussed additionally, pathway (1c). Stated peroxide yields from the self-reaction of the simplest RO₂ radicals, RO₂ = R'O₂ = CH₃O₂, C₂H₅O₂ or CH₃C(O)O₂, were reported to be small.²



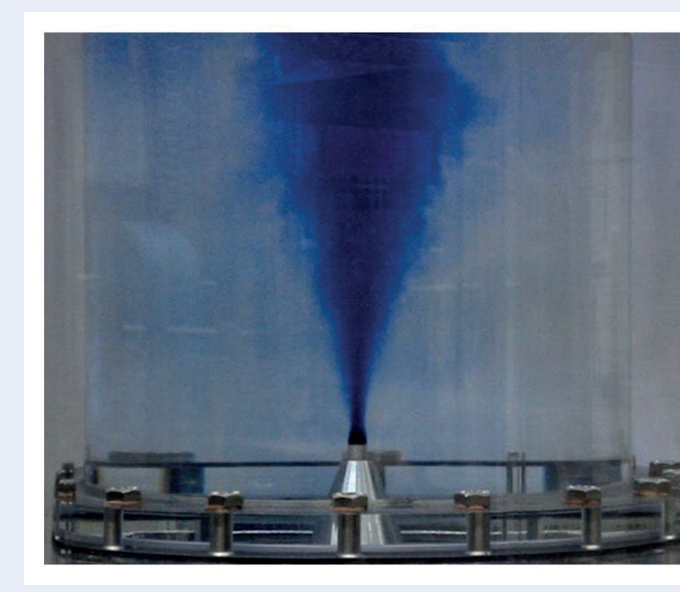
The relevance of pathway (1c) has not been investigated yet for RO₂ radicals other than for the small model RO₂ radicals and is currently not considered in atmospheric modelling. However, recent experimental findings, especially from gas-phase ozonolysis of cyclohexene and terpenes, point to accretion product formation that could be at least partly explained by a process according to pathway (1c). Here we report on an experimental study focusing on the formation of accretion products with the chemical composition ROOR' that can be explained via pathway (1c).³

Experiment

Free-jet flow system



- Atmospheric pressure
- Temperature: 295 ± 2 K
- Residence time: 2.9 - 7.9 sec.
- Flown: 100 L/min. (STP) air or N₂/O₂ mixtures
- Formation of RO₂ radicals or other intermediates without secondary chemistry
- *Benefit*: wall-free conditions



Detection of RO₂ radicals and closed-shell products

- CI-API-TOF (chemical ionization - atmospheric pressure interface - time-of-flight) mass spectrometry (Airmodus, Tofwerk AG)
reagent ions: CH₃COO⁻, C₃H₇NH₃⁺
- NH₄⁺-CI3-TOF (University Innsbruck)

Results and Discussion

Reaction of OH radicals with mesitylene OH formation via TME ozonolysis

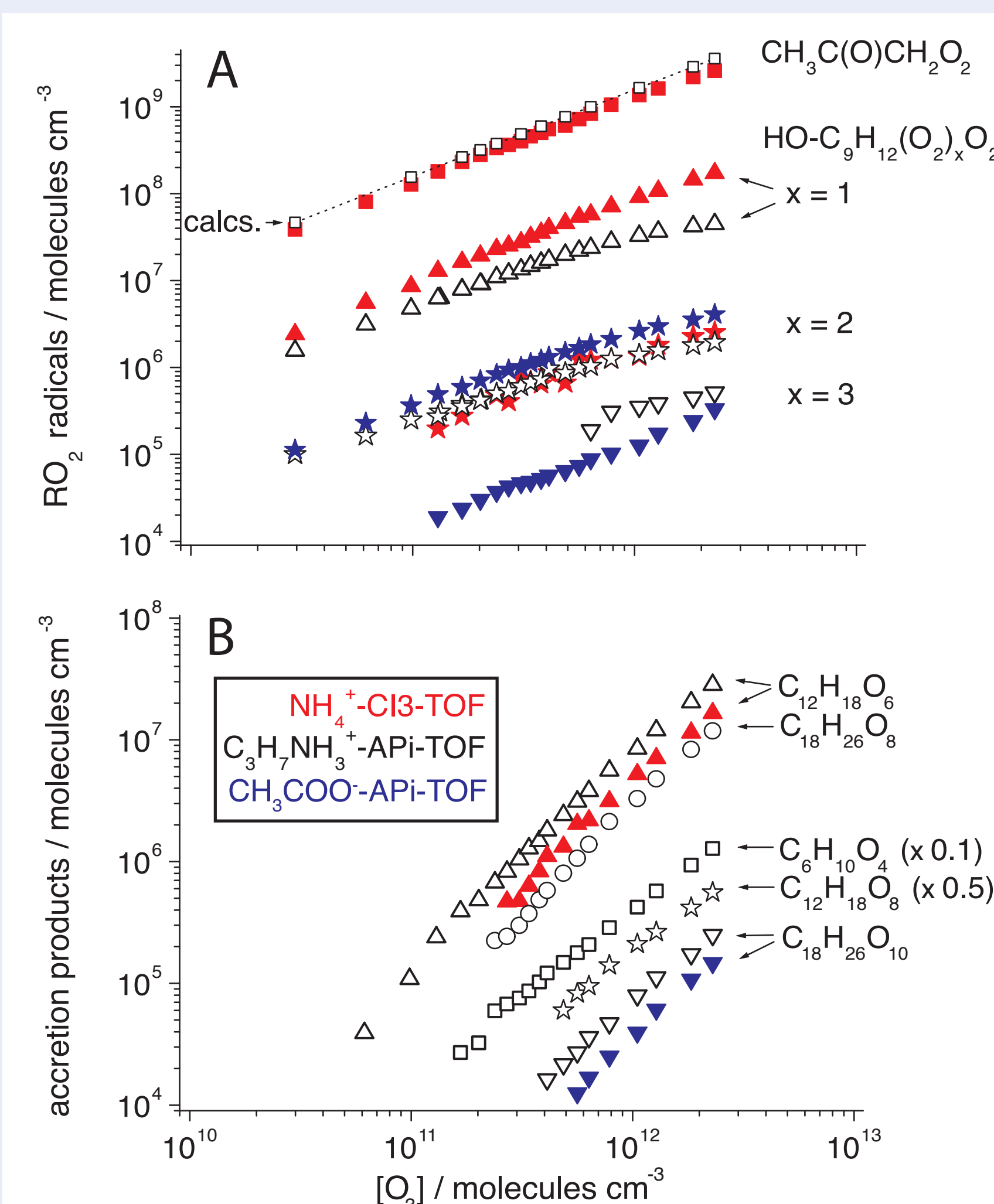


Fig.1: RO₂ radicals **A** and accretion products **B** from the reaction OH + mesitylene using OH radical formation via TME ozonolysis. [TME] = 2.0×10^{11} and [mesitylene] = 4.06×10^{12} molecules cm⁻³.

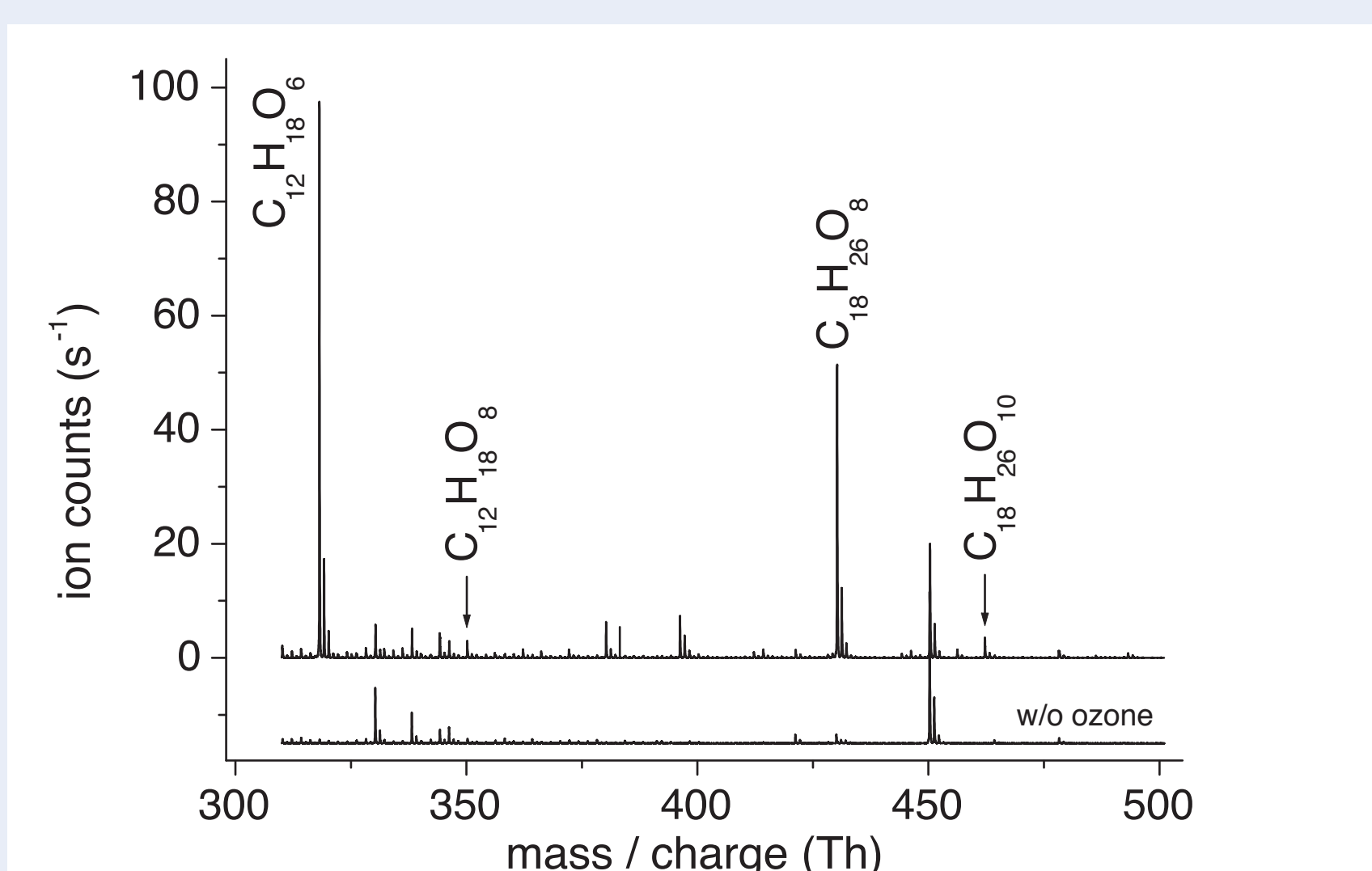
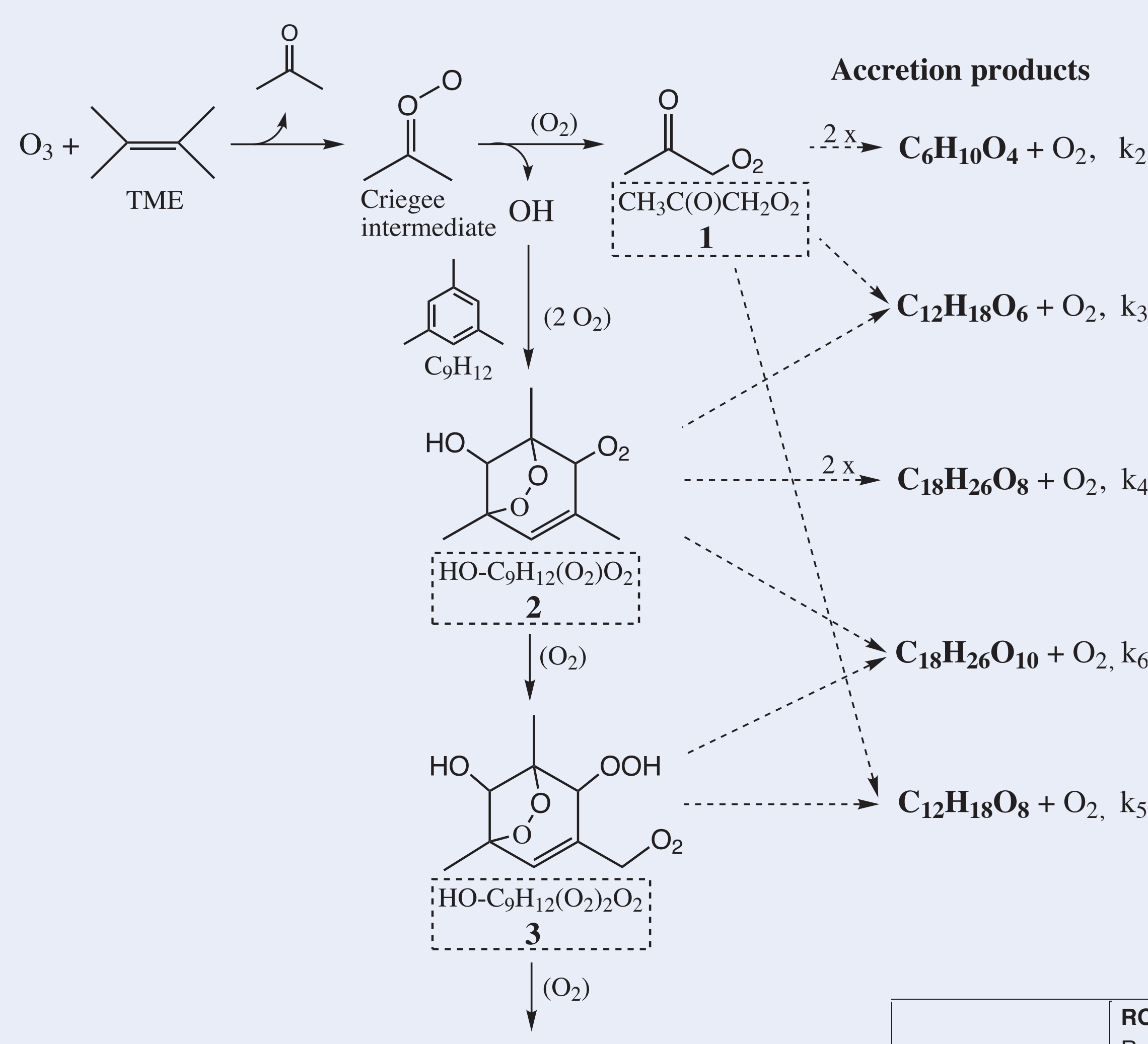


Fig.2: Obtained product mass spectra in the range of 300 - 500 Th measured by C₃H₇NH₃⁺-API-TOF.

Proposed mechanism



OH via isopropyl nitrite photolysis

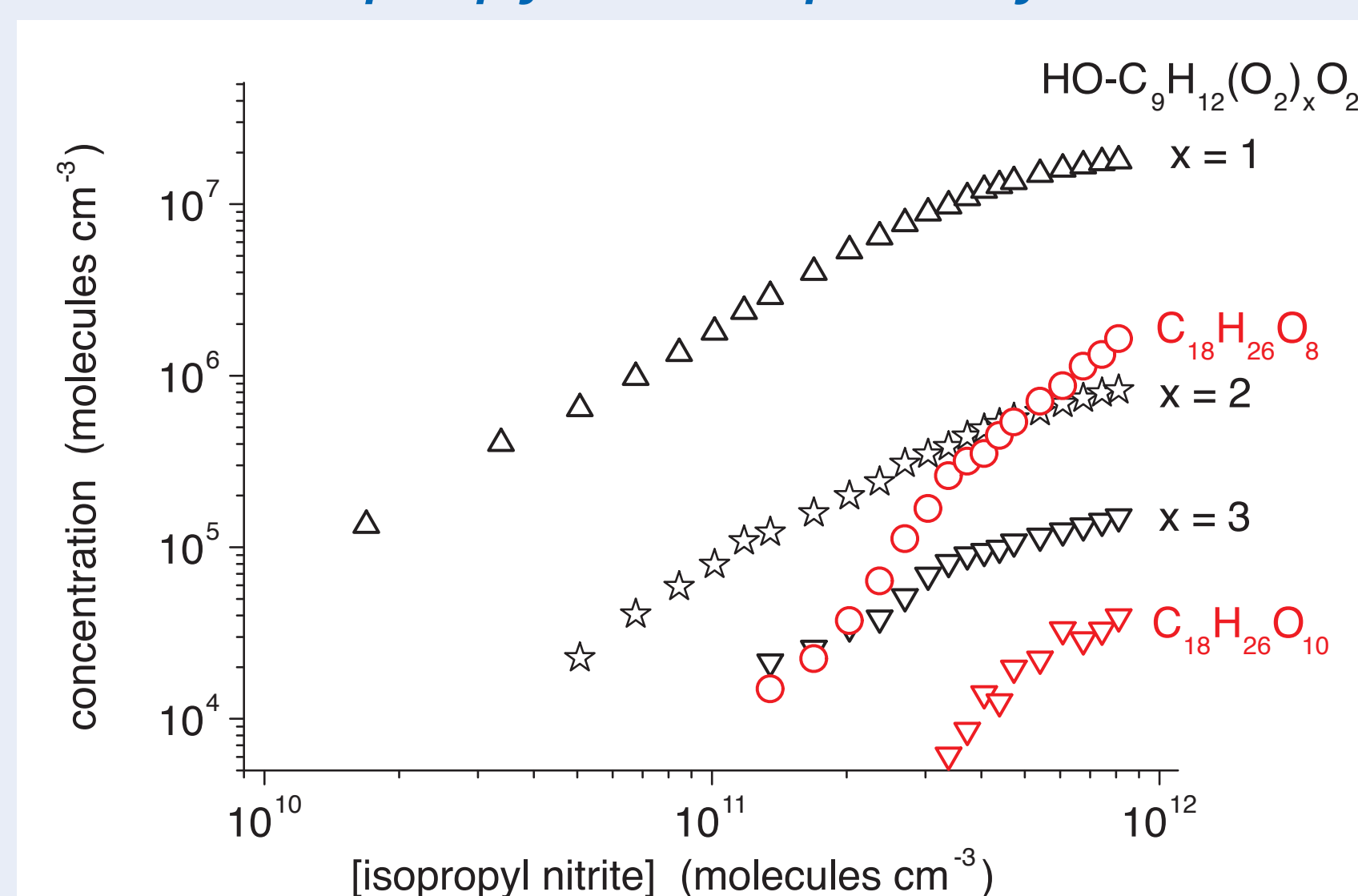


Fig.3: RO₂ radicals, HO-C₉H₁₂(O₂)_xO₂ with x = 1 - 3, and accretion products, C₁₂H₁₈O₆ and C₁₈H₂₆O₁₀, from the reaction OH + mesitylene using OH radical formation via isopropyl nitrite photolysis.

Kinetic analysis of ROOR' formation via pathway (1c)

- constant RO₂ radical formation rates
- RO₂ radical concentrations increase linearly with time
- rate coefficients k_{1c} can be estimated according to equation (I) using the measured concentrations of ROOR' and RO₂ radicals at reaction time t:

$$k_{1c} = \frac{[\text{ROOR}'_t]}{[\text{RO}_2]_t \times [\text{R}'\text{O}_2]_t} \frac{3}{t} \quad (I)$$

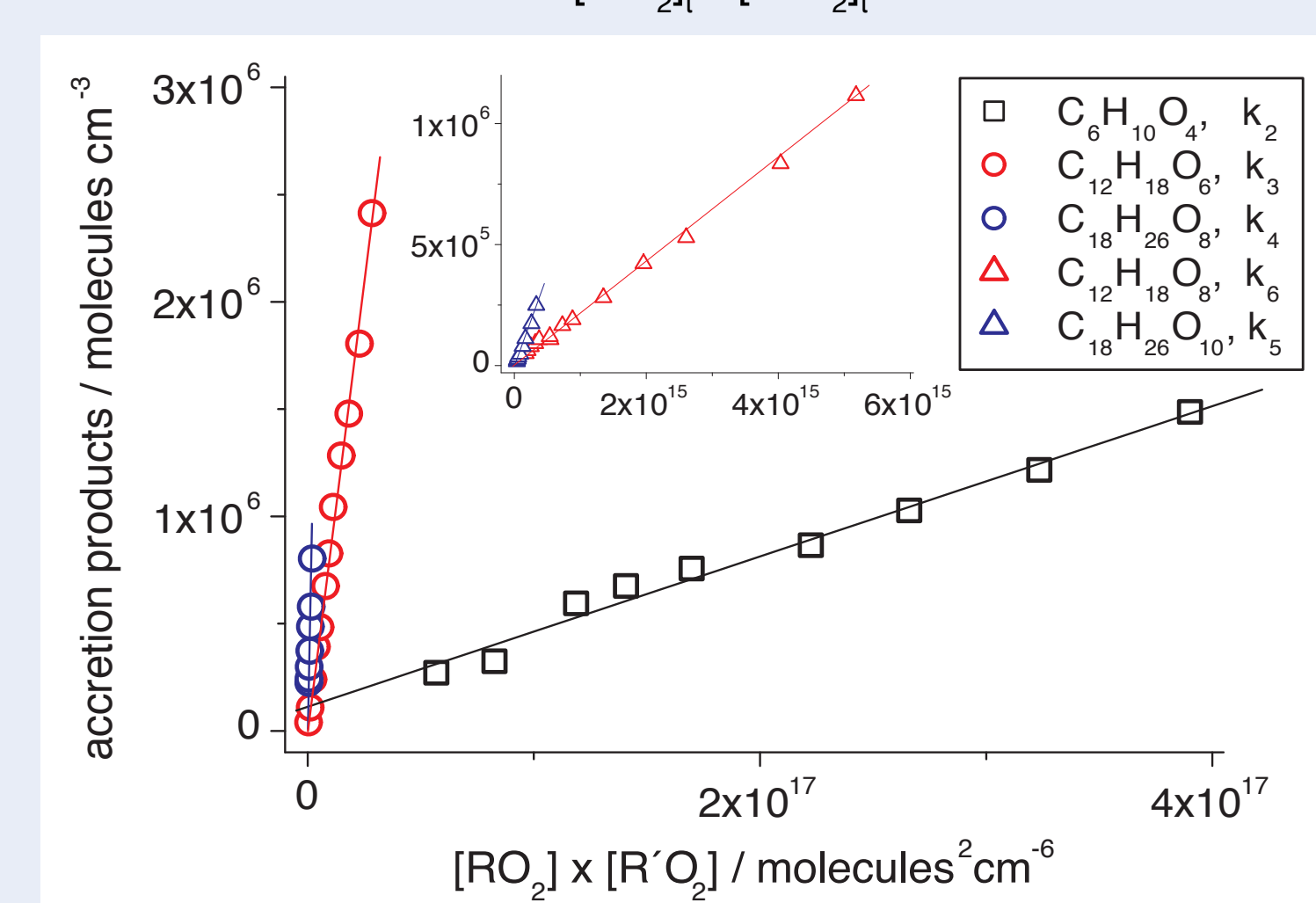


Fig.4: Kinetic analysis of accretion product formation according to equation (I).

	RO ₂ + R'O ₂ → ROOR' + O ₂ Rate coefficient (cm ³ molecule ⁻¹ s ⁻¹) T = 295 ± 2 K		
RO ₂ :	CH ₃ C(O)CH ₂ O ₂ 1	HO-C ₉ H ₁₂ (O ₂) ₂ O ₂ 2	HO-C ₉ H ₁₂ (O ₂) ₂ O ₂ 3
CH ₃ C(O)CH ₂ O ₂ 1	(k ₂) 1.3 × 10 ⁻¹²	-	-
HO-C ₉ H ₁₂ (O ₂) ₂ O ₂ 2	(k ₃) (3.7-5.5) × 10 ⁻¹¹ a	(k ₄) 1.4 × 10 ⁻¹⁰ (1.7-2.5) × 10 ⁻¹⁰ a 1.7 × 10 ⁻¹⁰ b	-
HO-C ₉ H ₁₂ (O ₂) ₂ O ₂ 3	(k ₅) 8.0 × 10 ⁻¹¹	(k ₆) 2.6 × 10 ⁻¹⁰	n.d.

Tab.1: Rate coefficients of accretion product formation via pathway (1c) from the reaction OH + mesitylene using OH radical formation via TME ozonolysis that also forms CH₃C(O)CH₂O₂. The uncertainty of the k-values is assumed to be not higher than a factor of 2 - 3.
 a from NO experiments assuming k(NO+RO₂) = 10⁻¹¹ cm³ molecule⁻¹ s⁻¹
 b from experiments using isopropyl nitrite photolysis
 n.d.: not determined

Reaction of OH radicals with 1-butene, isoprene, n-hexane or methane (OH formation via TME ozonolysis)

- in each case the corresponding accretion products from the self- and cross-reactions of OH-reaction derived RO₂ radicals, i.e. HO-C₄H₈O₂, HO-C₅H₈O₂, C₆H₁₃O₂ or CH₃O₂, and CH₃C(O)CH₂O₂ have been identified
- only small signals for CH₃OOCH₃ from the CH₃O₂ radical self-reaction in line with earlier observations²

References

- (1) A. H. Goldstein, I. E. Galbally, *Environ. Sci. Technol.* **2007**, *41*, 1514-1521.
- (2) a) J. Weaver, et al., *J. Photochem.* **1975**, *4*, 341-360. b) C. Anastasi, et al., *J. Chem. Soc., Faraday Trans. 1*, **1983**, *79*, 505-516. c) C. A. McDowell, et al., *Can. J. Chem.* **1963**, *41*, 300-307.
- (3) T. Berndt, et al., *Angew. Chem. Int. Ed.*, **2018**, *57*, 3820-3824.

Summary

- ⇒ The gas-phase reaction of two RO₂ radicals produce accretion products composed of the carbon backbone of both reactants.
- ⇒ RO₂ radicals bearing functional groups show fast accretion product formation rates competing with those of the corresponding reactions with NO and HO₂.
- ⇒ This pathway, not considered yet in the modelling of atmospheric processes, can be important, or even dominant for the fate of RO₂ radicals in all areas of the atmosphere.