

Highly oxidized RO₂ radicals and consecutive products from the ozonolysis of three sesquiterpenes

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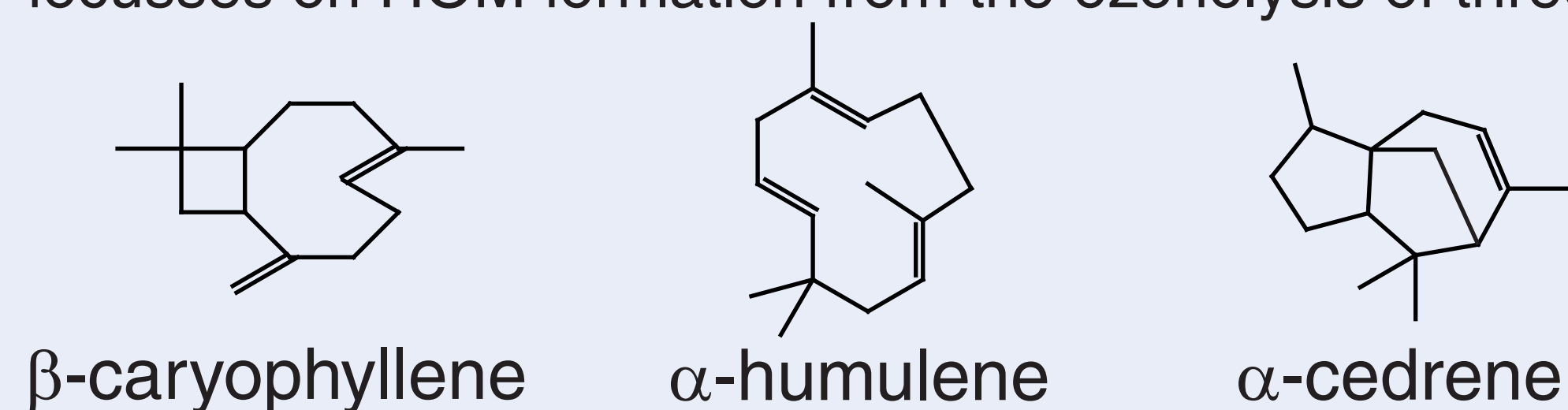
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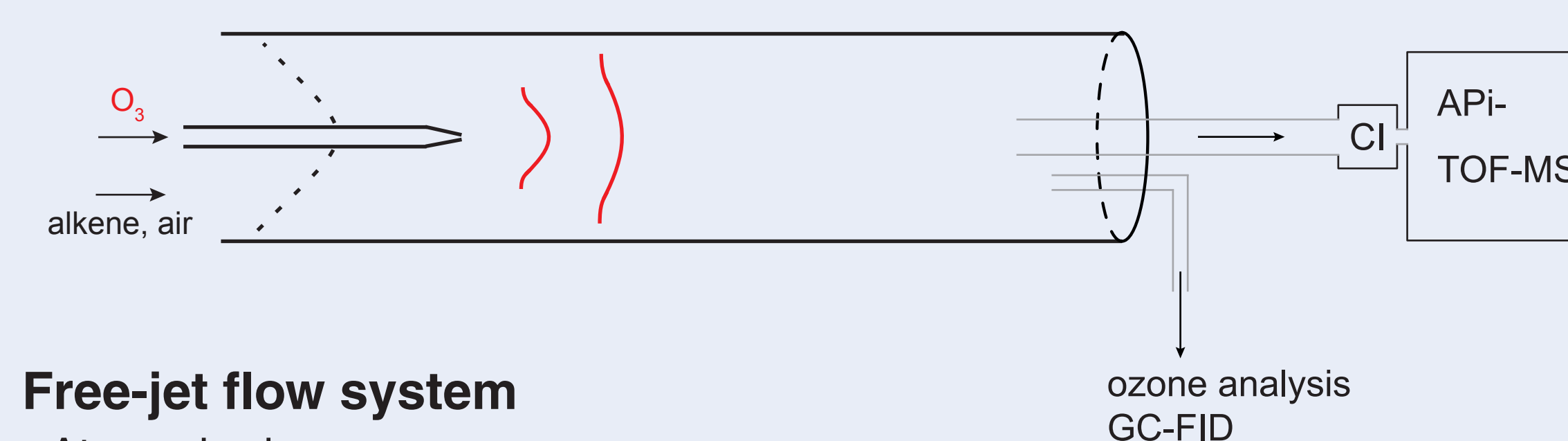
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Motivation

Recently, highly oxidized multifunctional organic compounds (HOMs) with up to twelve oxygen atoms were detected from the oxidation of monoterpenes (C₁₀H₁₆) in field and laboratory studies (Ehn, 2014; Jokinen, 2014). Monoterpenes are emitted with annual quantities of 83 million metric tons carbon representing the dominant biogenic volatile organic compound (BVOC) emissions beside isoprene (Sindelarova, 2014). The new compound class of HOMs, which thus contains a very high oxygen to carbon ratio, is assigned to extremely low-volatility organic compounds (ELVOCs). Therefore, HOMs are thought to contribute significantly to secondary organic aerosol (SOA) formation in the atmosphere. HOM formation from sesquiterpene oxidation is not yet examined. Sesquiterpenes (C₁₅H₂₄, SQT) are emitted by plants with a global emission rate of about 20 million tons per year which correspond to 2.4% of the global BVOC emission (Sindelarova, 2014). Their oxidation products are believed to have very low vapor pressure and they contribute to SOA formation. Therefore, this study focusses on HOM formation from the ozonolysis of three atmospherically relevant SQT:



Experimental



Free-jet flow system

- Atmospheric pressure
- Temperature: 297 ± 1 K
- Residence time: 7.9 s
- Carrier gas: purified air (99.999999 vol%)
- [Sesquiterpene] = (2.3 - 700) · 10¹⁰ molecule cm⁻³
- [O₃] = (4.5 - 1020) · 10⁹ molecule cm⁻³
- [C₃H₈] = (1.2 - 2.5) · 10¹⁶ molecule cm⁻³ (OH scavenger)
- Detection method:
 - Chemical ionization - atmospheric pressure interface - time-of-flight (CI-API-TOF) mass spectrometry
 - Ionization techniques: nitrate and acetate ionization

Results and Discussion

HOM mass spectra from α-cedrene ozonolysis

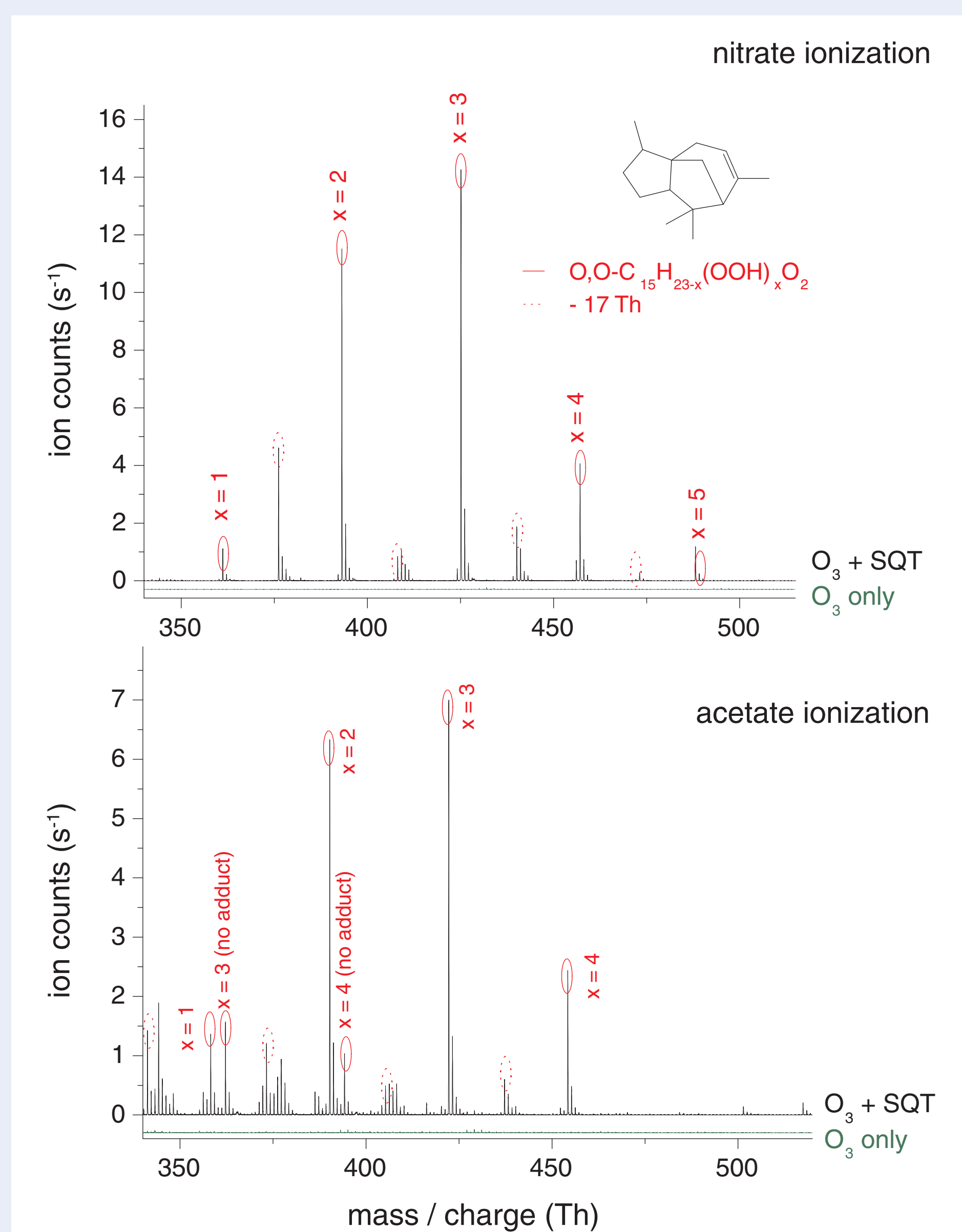


Figure 1: Ozonolysis of α-cedrene: Highly oxidized RO₂ radicals (O₂O-C₁₅H_{23-x}(OOH)_xO₂, x = 1 - 5, in red) and corresponding C₁₅-closed-shell products (C₁₅H₂₂O₇₋₁₃, red dotted lines) detected by means of nitrate (upper spectrum) and acetate (lower spectrum) ionization. [α-Cedrene] = (6.5 - 7) · 10¹², [O₃] = 1.02 · 10¹² molecule cm⁻³, reaction time: 7.9 s.

Highly oxidized RO₂ radicals and corresponding closed-shell products with up to 14 oxygen atoms (x = 5) were detected from the ozonolysis of α-cedrene using two different ionization techniques. The same HOMs were detected in both spectra as adducts of the charger ions. In the case of acetate ionization, also dehydrated products ("no adducts") were detectable.

References

- M. Ehn et al., Nature, 506, 476-479, 2014
 T. Jokinen et al., Angew. Chem. Int. Ed., 53, 14596-14600, 2014.
 K. Sindelarova et al., Atmos. Chem. Phys., 14, 9317-9341, 2014.
 I. V. Berezin, E. T. Denisov, and N.M. Emanuel, The Oxidation of Cyclohexane, Pergamon Press, 1996.

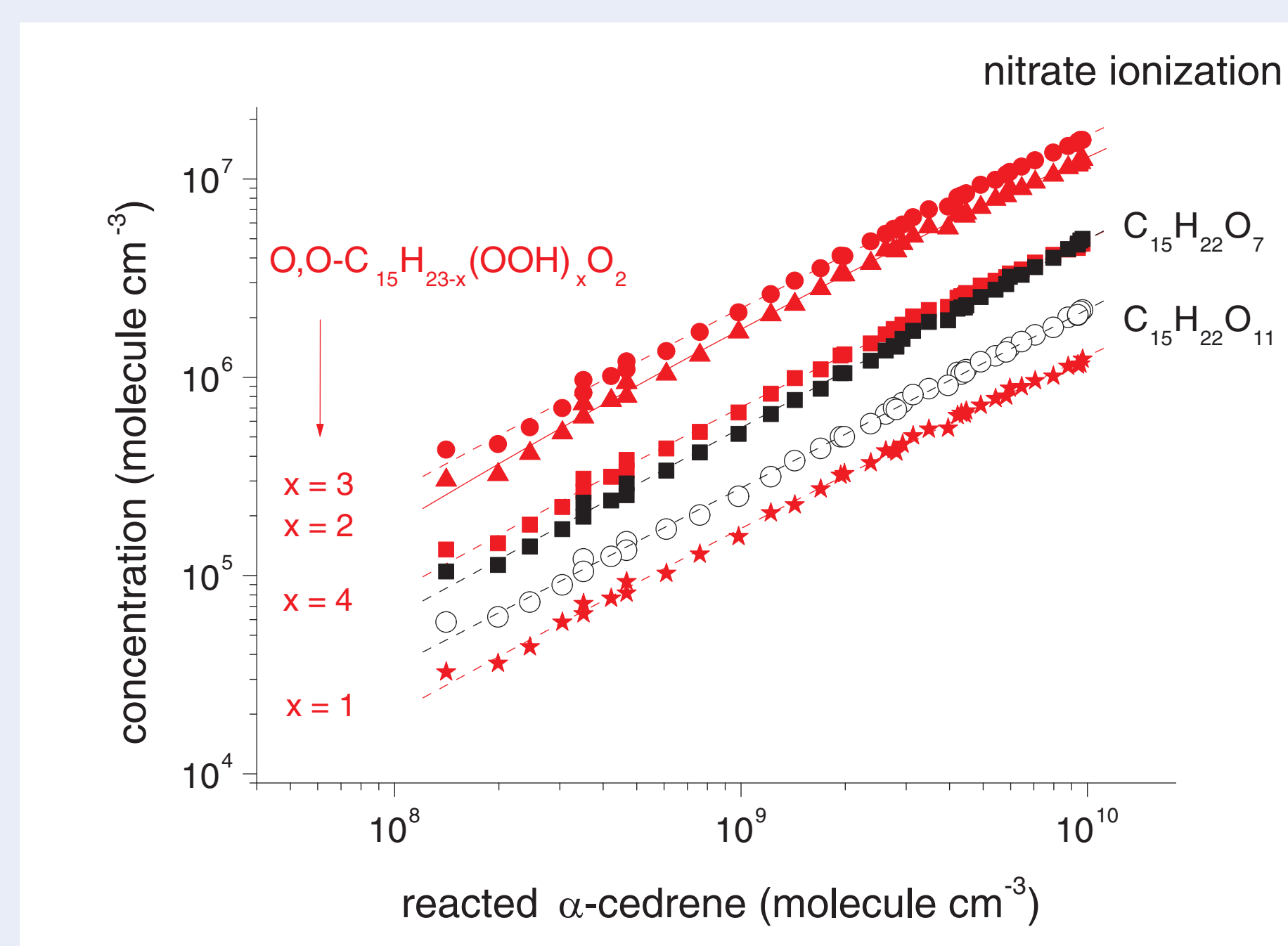
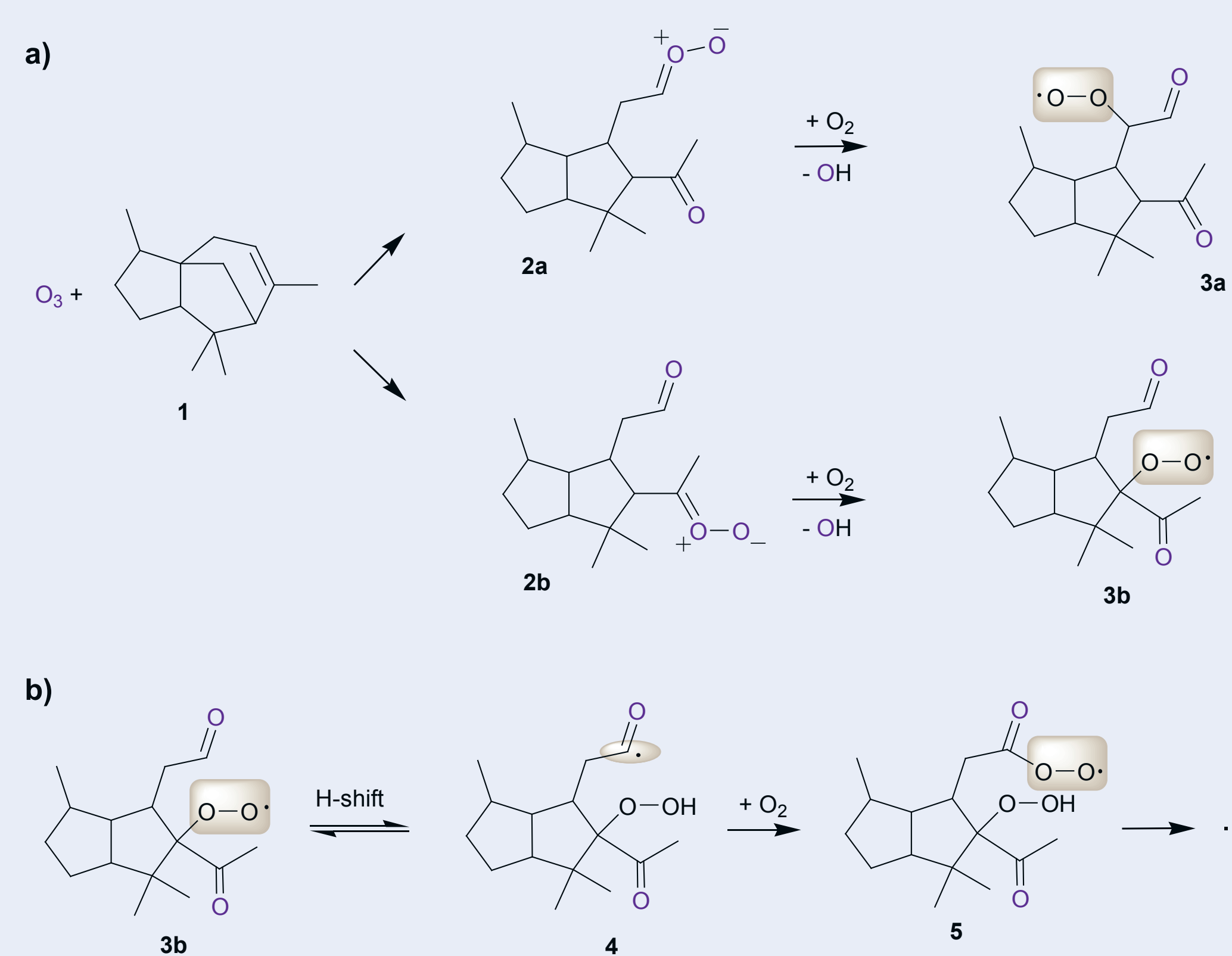


Figure 2: Ozonolysis of α-cedrene: Concentration of highly oxidized RO₂ radicals (O₂O-C₁₅H_{23-x}(OOH)_xO₂, x = 1 - 4, in red) and the corresponding C₁₅-closed-shell products (C₁₅H₂₂O₇, C₁₅H₂₂O₁₁, in black) as a function of the α-cedrene conversion, nitrate ionization. [α-cedrene] = 7 · 10¹², [O₃] = (1.5 - 102) · 10¹⁰ molecule cm⁻³, reaction time: 7.9 s.

Highly oxidized RO₂ radicals and corresponding closed-shell products increase linearly with α-cedrene conversion. The concentrations represent lower-limit values.



Scheme 1: Formation of RO₂ radicals from the ozone initiated oxidation of α-cedrene. First steps of ozonolysis (a) and an example of a reversible intra-molecular H-abstraction starting from molecules 3b followed by subsequent O₂ addition (b).

Summary

- Highly oxidized multifunctional organic compounds (HOMs) were investigated as products from the ozonolysis of three sesquiterpenes (α-cedrene, β-caryophyllene, and α-humulene).
- Molar HOM yields between 0.5 and 1.8% were detected from SQT ozonolysis however, these yields depended on the ionization technique. For β-caryophyllene, it increased by a factor of 3.6 when switching from nitrate to acetate ionization.
- These rather low yields lead to a limited contribution of sesquiterpene HOM to global SOA formation (monoterpene HOM formation prevailing). However, SQT HOM might control SOA formation on a regional scale where SQT emission predominate.

HOM yields from sesquiterpene ozonolysis

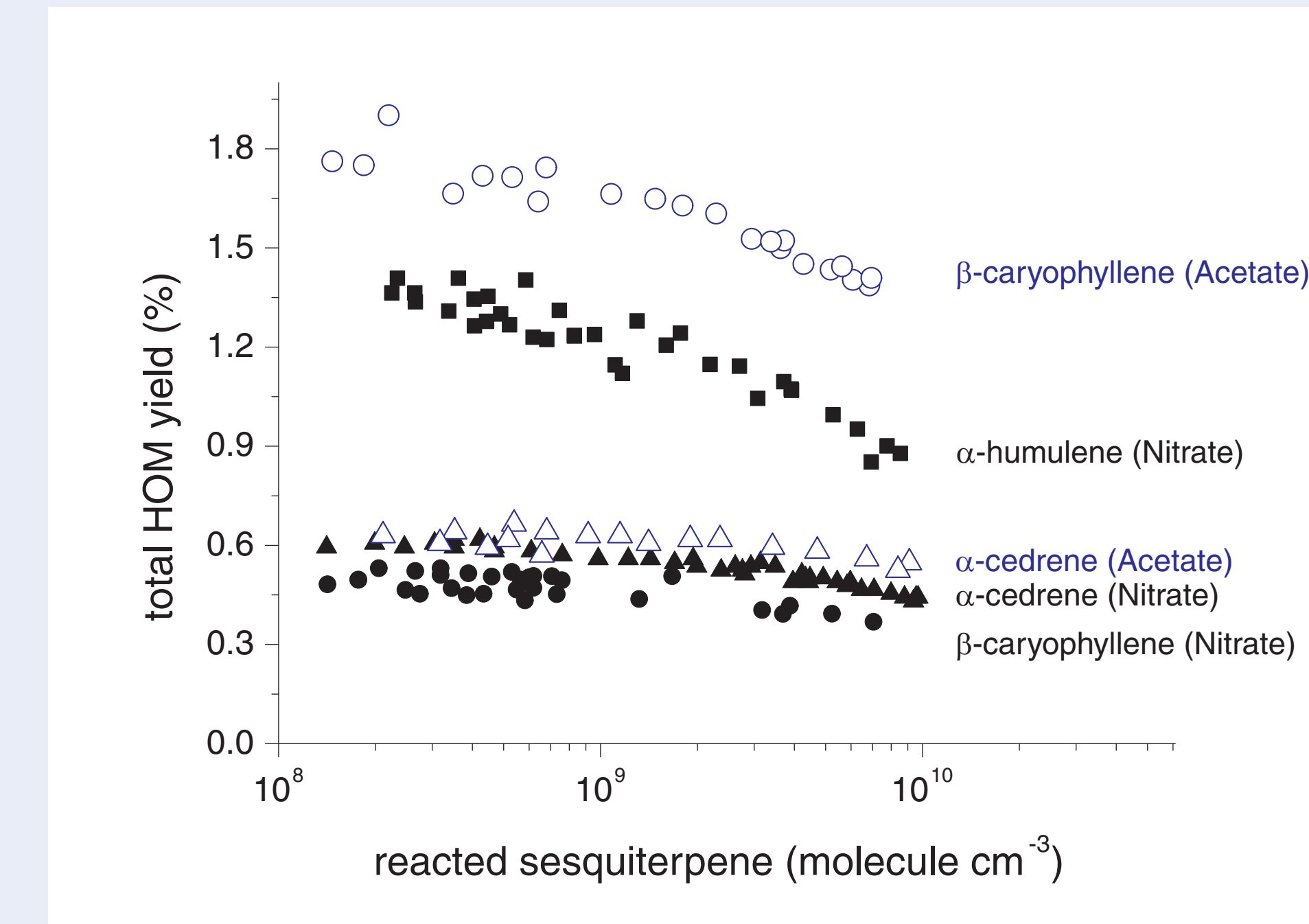


Figure 3: Total HOM yield from the ozonolysis of the three sesquiterpenes α-cedrene, β-caryophyllene and α-humulene. α-Cedrene and β-caryophyllene were investigated with two different charger ions for ionization (nitrate and acetate). [α-cedrene] = (6.5 - 7) · 10¹²; [β-caryophyllene] = (8.3 - 8.6) · 10¹⁰; [α-humulene] = (2.3 - 9.1) · 10¹⁰; [O₃] = (4.5 - 1020) · 10⁹ molecule cm⁻³, reaction time: 7.9 s.

Molar HOM yields from SQT ozonolysis lay between 0.6 and 1.8%. These yields were slightly lower than HOM yields from monoterpene ozonolysis: 3 - 7% (Ehn, 2014; Jokinen, 2014). Therefore, HOM formation from monoterpene oxidation will dominate under atmospheric conditions because of the much higher emission rate of monoterpenes. Thus, sesquiterpene HOM formation will play a minor role for global SOA formation. However, it is supposed to predominate SOA formation on a regional scale, e.g. close to orange orchards or tobacco plantations, where SQT emission prevail. HOM yields were depending on the ionization technique: The HOM yield from β-caryophyllene ozonolysis detected by means of acetate ionization was 3.6 times higher than detected via nitrate ionization. The measured yields represent lower-limit values. Improvements of the analytical techniques might further increase the molar HOM yields.

Highly oxidized RO₂ radicals were formed via intra-molecular H-abstraction and subsequent O₂ addition. This process generates hydroperoxide moieties in the molecule and proceeds similar to the well-known autoxidation processes in the liquid phase (Berezin, 1996). The amount of hydroperoxide moieties present in the molecule equals the value of x.