Supporting Information

to

Different Pathways of the Formation of Highly Oxidized Multifunctional Organic Compounds (HOMs) from the Gas-Phase Ozonolysis of β-Caryophyllene

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S1 Experimental

S1.1 Product detection and determination of concentrations

Highly oxidized reaction products were detected using CI-APi-TOF (chemical ionization – atmospheric pressure interface – time-of-flight) mass spectrometry (Airmodus, Tofwerk) and ionization with nitrate and acetate ions. The CI-APi-TOF mass spectrometer sampled from the center flow with a rate of 10 L min^{-1} (STP) (Ehn et al., 2012; Eisele and Tanner, 1991, 1993; Jokinen et al., 2012; Junninen et al., 2010).

In experiments with nitrate ionization, 1-2 mL min^{-1} air passed over concentrated nitric acid (HNO_3) and was diluted with 35 L min^{-1} (STP) purified air to produce the HNO_3-containing sheath air. This sheath air is ionized by an americium source (^{241}Am) producing the reagent ions $(HNO_3)_nNO_3^-$ (n = 0, 1, 2) which were electrostatically sucked into the sample flow without a mixing of both flows. Highly oxidized multifunctional organic compounds (HOMs) formed stable adducts with NO_3^- which allowed their detection with high sensitivity using this approach.

For acetate ionization, 2 mL min^{-1} air passed over concentrated acetic acid and was added to the purified air flow of 35 L min^{-1} (STP) forming the reagent ions $(CH_3COOH)_mCH_3COO^-$ (m = 0, 1, 2). Either HOM adducts formed in the course of the ion-molecule reactions or negatively charged HOMs were formed via proton transfer from the target molecule to the reagent ion: (HOM-H)$^-$ (Berndt et al., 2015; Graul et al., 1990).

The first principles for the stability of the HOM adducts with nitrate and acetate ions are not yet well understood. Hyttinen et al. (2015) calculated the cluster stability of nitrate ion HOM clusters from the ozonolysis of cyclohexene and followed that “at least two hydrogen bond donor functional groups (in this case, hydroperoxide, OOH) are needed for an ELVOC molecule to be detected in a nitrate ion CI-APi-TOF”. However, also HOMs containing only one hydroperoxide moiety were detected efficiently when changing from nitrate ionization to acetate ionization (Berndt et al., 2015). Detection with acetate ionization seems to be more sensitive especially for HOMs containing only one hydroperoxide moiety. Further development of the analytical techniques and the use of different reagent ions might lead to the detection a wider range of oxidation products and a higher detection sensitivity.

HOM concentrations were calculated as described in detail by Berndt et al. (2015). The calibration of the CI-APi-TOF mass spectrometer was conducted using sulfuric acid (HSO_4^-, 96.9601 Th) detection, giving a calibration coefficient of $f = 1.85 \times 10^9$ molecules cm^{-3}. HOM concentrations were calculated using the same calibration factor which lies within the range of the calculated calibration factor. The calculation of the calibration factor assumes a reaction of the reagent ion with the HOM with a rate coefficient close to the collision limit (Berndt et al., 2015). The determination of HOM concentrations assumes a reaction of HOMs with the reagent ion at their collision frequency and a negligible loss of formed clusters within the detection unit. If this assumption is not valid, the HOM concentration would be underestimated. Accordingly, all stated concentrations (RO_2 radicals and closed-shell products) are lower limits (Berndt et al., 2015).

For nitrate ionization, the concentration of the target compound was calculated from the signal intensity, the calibration factor and the sum of the reagent ions (NO_3^-, $(HNO_3)NO_3^-$ and $(HNO_3)_2NO_3^-$) according to Eq. (1).

$$[HOM] = f\,\frac{[(HOM)NO_3^-]}{[NO_3^-]+[(HNO_3)NO_3^-]+[(HNO_3)_2NO_3^-]} \qquad (1)$$

For acetate ionization, the same calibration factor f was used (Berndt et al., 2015). The products were either detected as acetate ion adducts or deprotonated and the HOM concentration was calculated according to Eq. (2).

$$[HOM] = f\,\frac{[(HOM)CH_3COO^-]+[(HOM-H)^-]}{[CH_3COO^-]+[(CH_3COOH)CH_3COO^-]+[(CH_3COOH)_2CH_3COO^-]} \qquad (2)$$

This approach gives lower-limit HOM concentrations, as explained above. In addition, the ion transmissions of HSO_4^- and HOMs differ from each other. An uncertainty factor of two is assumed leading to a measurement uncertainty of -50/+100%. The detection limit was about 10^4 molecules cm^{-3} when applying two minutes data averaging (Berndt et al., 2015).

The experimental data were analyzed using the MATLAB-based software TofTools which is described in literature (Ehn et al., 2012; Junninen et al., 2010; Schobesberger et al., 2013).

The mass axis was calibrated for each experiments using first the reagent ions NO_3^- (61.9884 Th), $(HNO_3)NO_3^-$ (124.9840 Th) and $(HNO_3)_2NO_3^-$ (187.9797 Th) for nitrate ionization or CH_3COO^- (59.0139 Th), $(CH_3COOH)CH_3COO^-$ (119.0350 Th) and $(CH_3COOH)_2CH_3COO^-$ (179.0561 Th) for acetate ionization. The mass-to-charge ratios of these reagent ions are all below 200 Th and cannot reliably calibrate the mass axis in the product range of the HOM adducts (340-500 Th). Thus, two of the most intense product signals (here at 393.1277 Th and 425.1175 Th for nitrate ionization and 390.1531 Th and 422.1430 Th for acetate ionization) were used to extend the calibration range. For this approach, the correctness of the assignment of these signals to molecular formulas has to be assumed.

S2 Results

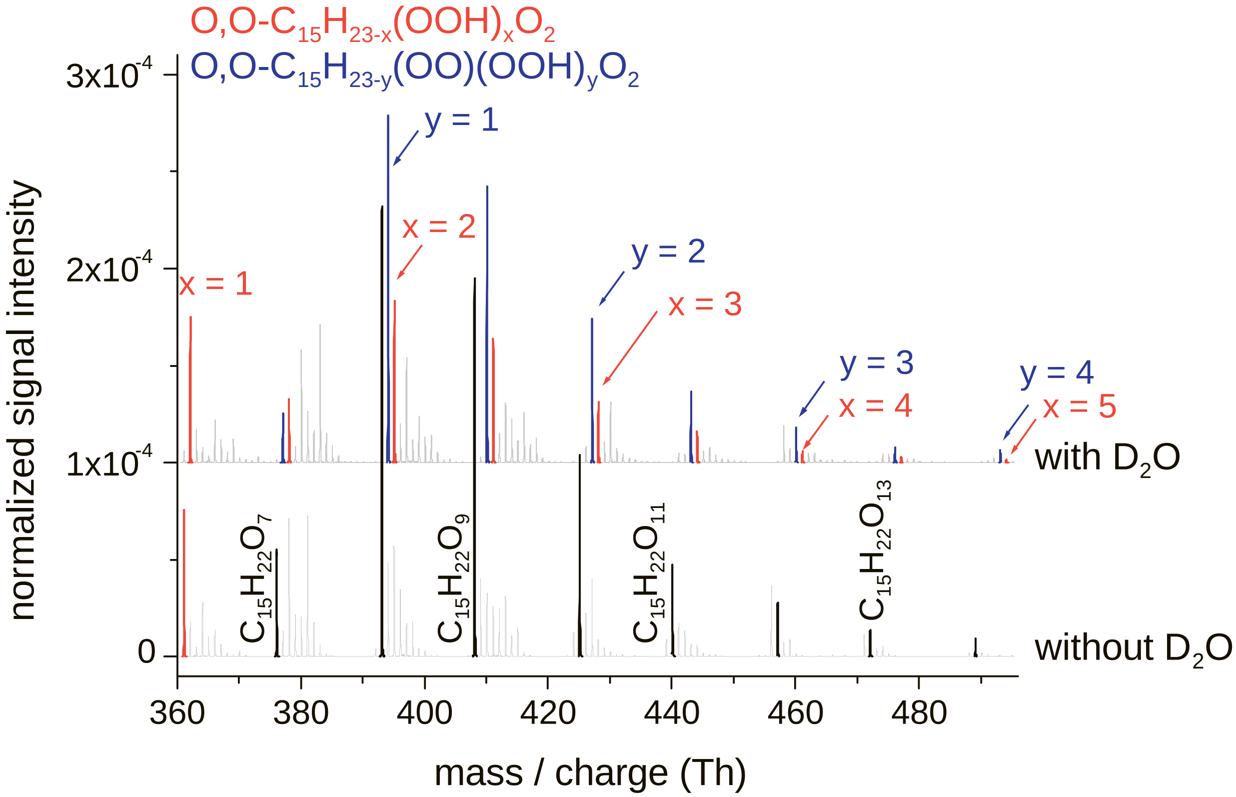

Figure S1. Ozonolysis of β-caryophyllene, in absence (lower part) and presence (upper part) of D_2O applying nitrate ionization in the analysis. Signals highlighted in black stand for the sum of signals in absence of D_2O from highly oxidized RO_2 radicals of the product groups "norm. AutOx.", $O,O\text{-}C_{15}H_{23\text{-}x}(OOH)_xO_2$ with x = 2-5, and "ext. AutOx.", $O,O\text{-}C_{15}H_{23\text{-}y}(OO)(OOH)_yO_2$, with y = 1-4, and the corresponding closed-shell product $C_{15}H_{22}O_7$, $C_{15}H_{22}O_9$, $C_{15}H_{22}O_{11}$, $C_{15}H_{22}O_{15}$. The addition of D_2O leads to an H/D exchange of all acidic H atoms present in the molecule. With that, signals from the two product groups are separated by their number of acidic H atoms and the split-up signals are highlighted in red for the "norm. AutOx." group and in blue for the "ext. AutOx." group. The signal at nominal 361 Th can be completely assigned to the RO_2 radical $O,O\text{-}C_{15}H_{23\text{-}x}(OOH)_xO_2$ with x = 1 and is highlighted in red. [β-caryophyllene] = 8.3 x 10^{10}; [O_3] = 1.02 x 10^{12} molecules cm^{-3}; reaction time: 7.9 s.

References

Berndt, T., Richters, S., Kaethner, R., Voigtländer, J., Stratmann, F., Sipilä, M., Kulmala, M., and Herrmann, H.: Gas-phase ozonolysis of cycloalkenes: formation of highly oxidized RO_2 radicals and their reactions with NO, NO_2, SO_2, and other RO_2 radicals, J. Phys. Chem. A, 119, 10336-10348, 2015.

Ehn, M., Kleist, E., Junninen, H., Petäjä, T., Lönn, G., Schobesberger, S., Dal Maso, M., Trimborn, A., Kulmala, M., Worsnop, D. R., Wahner, A., Wildt, J., and Mentel, T. F.: Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air, Atmos. Chem. Phys., 12, 5113-5127, 2012.

Eisele, F. L. and Tanner, D. J.: Ion-assisted tropospheric OH measurements, J. Geophys. Res., 96, 9295-9308, 1991.

Eisele, F. L. and Tanner, D. J.: Measurement of the gas phase concentration of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, J. Geophys. Res., 98, 9001-9010, 1993.

Graul, S. T., Schnute, M. E., and Squires, R. R.: Gas-phase acidities of carboxylic acids and alcohols from collision-induced dissociation of dimer cluster ions, Int. J. Mass Spectrom., 96, 181-198, 1990.

Hyttinen, N., Kupiainen-Määttä, O., Rissanen, M. P., Muuronen, M., Ehn, M., and Kurtén, T.: Modeling the charging of highly oxidized cyclohexene ozonolysis products using nitrate-based chemical ionization, J. Phys. Chem. A, 119, 6339-6345, 2015.

Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin, R. L., Kulmala, M., and Worsnop, D. R.: Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF, Atmos. Chem. Phys., 12, 4117-4125, 2012.

Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition, Atmos. Meas. Tech., 3, 1039-1053, 2010.

Schobesberger, S., Junninen, H., Bianchi, F., Lönn, G., Ehn, M., Lehtipalo, K., Dommen, J., Ehrhart, S., Ortega, I. K., Franchin, A., Nieminen, T., Riccobono, F., Hutterli, M., Duplissy, J., Almeida, J., Amorim, A., Breitenlechner, M., Downard, A. J., Dunne, E. M., Flagan, R. C., Kajos, M., Keskinen, H., Kirkby, J., Kupc, A., Kürten, A., Kurtén, T., Laaksonen, A., Mathot, S., Onnela, A., Praplan, A. P., Rondo, L., Santos, F. D., Schallhart, S., Schnitzhofer, R., Sipilä, M., Tomé, A., Tsagkogeorgas, G., Vehkamäki, H., Wimmer, D., Baltensperger, U., Carslaw, K. S., Curtius, J., Hansel, A., Petäjä, T., Kulmala, M., Donahue, N. M., and Worsnop, D. R.: Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules, Proc. Natl. Acad. Sci. U.S.A, 110, 17223-17228, 2013.