

We thank the reviewer for the helpful remarks on our manuscript. Please find our point-by-point responses below.

## Reviewers' comments to author:

### Reviewer: 1

#### Comments:

The authors describe a product study of caryophyllene ozonolysis in a free jet flow tube. Experiments were performed applying acetate CI-API-TOF-MS and nitrate CI-API-TOF-MS to detect peroxy radicals and closed shell oxidation products. Labelling experiments using heavy O<sub>3</sub> and D<sub>2</sub>O helped to discriminate product classes from different reaction pathways and were used to underpin the proposed reaction scheme. This is an excellent, original study which was carefully conducted and evaluated. The proposed reaction schemes are reasonable and - wherever possible - supported with earlier findings by the authors and in the literature, although it has some speculative moments. But I see the latter as a challenge and I am wondering if the authors have ideas how a proof for the scheme in Fig 7 could look like. The paper is well written and very good to read (with a few exceptions, where formulations seem to be a little bit intricate). The results are original and new and give further deep insights into autoxidation and formation of highly oxidized molecules. This excellent manuscript should be published in ACP as it is.

**Reply:** We thank the reviewer for this comment. Unfortunately, the authors have no further idea how to proof the proposed reaction schemes in Figure 7.

#### Minor comments:

The authors may want to consider the following minor suggestions:

Figures are not addressed in sequence of their numberings in manuscript.

**Reply:** We addressed the figures now according to their numbering in the manuscript and added the following sentence:

**Changes in the text:** The number of oxygen atoms arising from the initial ozone attack was confirmed in experiments with isotopically labeled ozone (<sup>18</sup>O<sub>3</sub>) (Fig. 2).

Further possible reaction pathways of species 4b forming “norm. AutOx. and “ext. AutOx.” reaction products are proposed in Fig. 6.

page 5, line 28: “Up to now” does not seem the right intro for what is following.

**Reply:** We removed the intro “up to now” from the sentence.

page 6, line 21: Maybe it is better use “analysis” instead of “investigation” in this context.

**Reply:** We changed the text accordingly.

page 6, line 26: I think it is better to talk about “HOM signal” instead of “HOM yield”, the yield should be the same, independent of the detection scheme.

**Reply:** We changed the expression.

page 7, line 17: It may be simpler to replace “comparing by using” by “applying”.

**Reply:** The term was changed accordingly.

page 7, line 19: typo, . . . second oxygen atom from the initial ozone attack must “have been” abstracted . . .

**Reply:** .We corrected this typo.

page 7, line 28: an acylalkoxy radical “(species 15)”. Addition of species number would be helpful.

**Reply:** The species number 15 was added.

page 11, line 26: “The analysis has been done using nitrate ionization.” may be better “These measurements were performed applying nitrate ionization” ?

**Reply:** The sentence was changed according to the reviewers suggestion.

page 12, line 10: typo, “of” missing.

**Reply:** Unfortunately, we did not see, where the “of” is missing.

Figure 2, caption: Although it is explained later in the caption it confused me that there was no blue signal shown in the Figure. May be better “(in black with blue label)” or so.

**Reply:** .We changed the figure caption accordingly

Supplement line 15: “deflected” seems to be more appropriate to me than “sucked”.

**Reply:** We changed the expression.

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## Reviewers' comments to author:

### Reviewer: 2

#### Comments:

This is an interesting manuscript describing a continuation of the work from this laboratory on studying autoxidation reactions of biogenic terpenoids. The experiments seem carefully conducted with a previously described instrumentation that is especially suited for studying end product distributions of complex VOC oxidation reactions. However, number of conclusions derived in this paper, especially concerning “the extended autoxidation mechanism”, seem somewhat hastily derived - or already reported. Thereby I’m not sure if the manuscript, as it currently stands, brings enough new insight to merit it’s publication in ACP.

Most importantly, I do not see a need for “an extended autoxidation mechanism” for various reasons. Firstly, it is of obvious relevance what is understood as “the old mechanism”. If the “old mechanism” is only thought of including peroxy radical isomerization + O<sub>2</sub> addition steps, then I guess we could talk about a “new mechanism” at some level. However, the whole process is dependent on easily abstractable H-atoms and suitable molecular geometries enabling the abstractions – this is about what is clear at the moment. At the current stage it’s not unambiguously clear what kind of steps are needed to progress the autoxidation chain to reach into the most highly-oxidized products in monoterpene oxidation (recently Kurten et al. 2015 suggested that bimolecular steps might be needed to advance the  $\alpha$ -pinene oxidation). What seems intuitively clear, however, is that we’re only beginning to understand the importance and the details of the autoxidation progression. So at this level it seems very preliminary to talk about “extended autoxidation” as we do not have a clear concise picture what constitutes the “normal autoxidation” in this context. In any case, probably you cannot really isolate the different pathways, but can account for branching between pathways under different conditions. So in my humble opinion, there is no need to bring up a “new extended autoxidation mechanism” – it is all the same autoxidation, just with a few additional steps.

Secondly, the pathways suggested to represent this “extended mechanism” constitute unambiguous reaction steps – the CO<sub>2</sub> elimination and endoperoxide formation. Importantly, it does not seem to be possible to separate this CO<sub>2</sub> elimination pathway from a CO-loss pathway brought up previously in autoxidation studies (e.g., Rissanen 2014, 2015, Mentel 2015). Both of these processes occur from acyl type radicals – the CO loss before O<sub>2</sub> addition and the CO<sub>2</sub> loss after the O<sub>2</sub> addition. So while it is definitely worth to (and you should) discuss the potential of this type of reaction pathway, with current results it is impossible to be sure which type of dissociation process actually occurred. This should be made absolutely clear, and reference to papers where CO-loss was discussed should be given. Thirdly, the endoperoxide formation that is given as the explanation to account for the formation of “too less acidic hydrogens” (see D<sub>2</sub>O experiments) has already been suggested in exactly in the same context in previous literature concerning HOM formation (Rissanen et al. 2015, Kurten et al. 2015). So to sum up, it is hard to see the novelty of this paper especially as the main results of  $\beta$ -caryophyllene ozonolysis were already published previously (see Richters, et al. 2016). Hence, even though the manuscript appears to be generally well made, I cannot support its publication without severe changes in the interpretation of the mechanistic pathways and corresponding modifications for the manuscript text.

**Reply:** We thank the reviewer for the assessment of the manuscript. This main criticism is already answered in our “Short reply to RC 2”.

Minor points:

Some of the terminology seem a bit awkward. In certain places it seems useful to label where the oxygens come from (i.e., O,O-formalism), but in most cases I think it only hinders the reading. So I would propose to stick with common C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> formalism most of the time and then use the more difficult format where you are talking about the mechanism.

**Reply:** The authors prefer the use of the terminology. It allows always to illustrate the number of hydroperoxide moieties as well as the number of oxygen atoms arising from the initial ozone attack. For instance, the common C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> formalism cannot distinguish between “norm. AutOx.” and “ext. AutOx.” reaction products, which have the same molecular formula. This differentiation is possible with the O,O-formalism and we think that it helps to understand the difference between the autoxidation mechanisms.

Can there be a different detection sensitivity for the peroxy radicals in comparison with the closed-shell products? It seems somewhat counterintuitive that the RO<sub>2</sub> radicals could have such a long lifetimes under the present experimental conditions.

**Reply:** The reviewer is right that the detection sensitivity for RO<sub>2</sub> radicals might differ from the detection sensitivity of the closed-shell products. However, we cannot investigate this without having standard compounds for quantification. Standard compounds are not available for closed-shell products and it is not possible to synthesize the intermediate reaction products, RO<sub>2</sub> radicals. With our experimental setup we can almost suppress bimolecular reactions of RO<sub>2</sub> radicals and thus, the RO<sub>2</sub> radicals mainly react in rather slow unimolecular reaction pathways to form closed-shell products. The missing of bimolecular reactions can explain the rather long lifetimes of RO<sub>2</sub> radicals concerning bimolecular reactions such as with other RO<sub>2</sub> radicals under the given experimental conditions.

How was O<sub>3</sub> handled? I assume that the “<sup>18</sup>O<sub>3</sub>” flow still contains about 95 to 99% of <sup>18</sup>O<sub>2</sub> (due to O<sub>3</sub> generator generating efficiency) and thereby this could lead to significant difficulties in tracking the amount of O-atoms that are left from ozonolysis and do not result from secondary reactions after the initiation. This would be especially severe in trying to understand the contribution of different pathways (see Section 3.2.).

**Reply:** The reviewer is right that <sup>18</sup>O<sub>3</sub> was produced by passing <sup>18</sup>O<sub>2</sub>, premixed in N<sub>2</sub>, through and ozone generator (Thermo Environmental Instruments 49C). Hence, <sup>18</sup>O<sub>2</sub> will still be present in the carrier gas. However, only 10 mL min<sup>-1</sup> of <sup>18</sup>O<sub>2</sub> was used, first diluted in 4,99 L min<sup>-1</sup> of N<sub>2</sub> and later diluted in 95 L min<sup>-1</sup> purified air. Hence, 0.05% of the present oxygen in the carrier gas is supposed to be <sup>18</sup>O<sub>2</sub>. This very small amount should not influence the addition of <sup>16</sup>O<sub>2</sub> to the alkyl radicals and thus, the isotopically labeled <sup>18</sup>O atoms will stem from the ozone attack at the double bond.

**Changes in the text:** The concentration of remaining <sup>18</sup>O<sub>2</sub> in the carrier gas was about 0.05% of the total O<sub>2</sub> concentration. Hence, <sup>18</sup>O<sub>2</sub> cannot compete with <sup>16</sup>O<sub>2</sub> in the autoxidation steps. Thus, the isotopically labeled <sup>18</sup>O atoms will stem from the ozone attack at the double bond.

Page 3, Line 27: The use of CH<sub>3</sub>COOH is not mentioned. Also in Page 4 and line 13.

**Reply:** CH<sub>3</sub>COOH was used in the experiment in Figure 8 to scavenge stabilized Criegee intermediates (sCIs). This addition allows to investigate if sCIs take part in the HOM formation processes. This does not seem to be the case. An additional sentence was added to Page 3, line 27.

**Changes in the text:** The addition of  $\text{CH}_3\text{COOH}$  was used to scavenge stabilized Criegee intermediates from the ozonolysis of  $\beta$ -caryophyllene (Beck et al., 2011; Neeb et al., 1996).

Page 4, Line 3: How was caryophyllene sampling done? Did the GC and PTR methods indicate any differences in determined concentrations?

**Reply:**  $\beta$ -caryophyllene was sampled using heated PEEK capillaries (100°C) which directly sample the center air flow from the experiment to the instrument. Only GC-FID was used for quantification. Here, the air flow was resampled in a sampling loop and then injected in the GC-FID. PTR-MS was only used to monitor the caryophyllene concentration, not to quantify it.

Page 4, line 20: What is meant by mass spectrometer setting?

**Reply:** By mass spectrometer settings we mean the applied voltages and flow conditions in the CI-MS. We added this information to the main text.

**Changes in the text:** The mass spectrometer settings (applied voltages and flow rates) as well as the approach applied for the determination of HOM concentrations are equal to those described in detail by Berndt et al. (2015b).

Page 5, Line 8. The number quoted is only the estimated concentration of highly oxidized  $\text{RO}_2$ . How large do you assume is the pool of other radical species (e.g., how much are there less oxidized  $\text{RO}_2$ s and  $\text{HO}_2$ )?

**Reply:** Indeed, we can only state concentrations for  $\text{RO}_2$  radicals and closed-shell products that can be detected using CI-API-TOF mass spectrometry. Therefore, it is difficult to guess the concentrations of other  $\text{RO}_2$  radicals. The concentration of  $\text{HO}_2$  is supposed to be very low as very little OH radicals are formed in these reactions (total molar OH radical yield: 6% (Shu and Atkinson, 1994)). Furthermore, no reaction products from the bimolecular reaction of  $\text{RO}_2$  radicals with  $\text{HO}_2$  were detected (+ 1 nominal Th to the respective  $\text{RO}_2$  radical) which supports that very low  $\text{HO}_2$  concentrations are present.

Page 5, Lines 20-32: Similar H/D exchange behavior was observed and discussed in Rissanen, et al. 2015.

**Reply:** The reviewer is right that Rissanen et al. (2015) discusses this H/D exchange behavior from the ozonolysis of  $\alpha$ -pinene. However,  $\alpha$ -pinene does not contain a second double bond and thus, the H/D exchange by one nominal mass unit less than expected must arise from another reaction mechanism.

Page 6, Line 25-25: How can the yield change when changing ionization method? What you want to say is that the detection sensitivity varies between products and ionization methods. But what this means to the determined yields then? Does these yields then mean anything?

**Reply:** Indeed, the yield cannot change, but the apparent yield (detected yield) can change. With the following sentence "The change of the detection sensitivity for different HOMs (especially for those containing a single hydroperoxide moiety) leads to a different contribution of the individual product groups to the total molar HOM yield when changing from nitrate ionization to acetate ionization.", we hope, we clearly stated that the detection sensitivity varied between the reagent ions.

We still think that the relative contribution of the reaction products to the total molar yield mean something. Indeed, the numbers vary when changing from nitrate to acetate ionization, but they can show that the "norm. AutOx." reaction pathway is of minor importance for the

HOM formation from the ozonolysis of  $\beta$ -caryophyllene. We changed the text in the following way:

**Changes in the text:** Thus, the “norm. AutOx.” group contributes with 29% to the total molar HOM yield when detecting with nitrate ionization and with 35% when detecting with acetate ionization. These values are based on the lower-limit concentration calculations and on the different detection sensitivities of the different reagent ions, which are depending e.g. on the number of hydroperoxide moieties in the molecule of interest. Hence, a quantitative statement concerning the contributions of the three reaction product groups is difficult. However, the two new product groups “ext. AutOx.” and “ext. AutOx. -CO<sub>2</sub>” are crucial for the explanation of HOM formation from the ozonolysis of  $\beta$ -caryophyllene.

Page 7 (and others): Be careful with Figure and Table numbering. Currently there are “Figs.” and “Figures” which are not in numerical order.

**Reply:** Thanks for careful reading, the figures appear now in numerical order in the text.

Page 7, Line 19: Couldn't this be as well accounted for by a reaction in which 18OH (derived from VHP decomposition) starts the autoxidation sequence?

**Reply:** We conducted experiments in the presence of the OH scavenger propane and did not see a difference in the product spectrum. Furthermore, the OH radical yield from the ozonolysis of  $\beta$ -caryophyllene is very low (6% (Shu and Atkinson, 1994)) and should not influence the reaction spectrum. Thus, the influence of the OH-radical induced oxidation of  $\beta$ -caryophyllene is not supposed to play a role here.

Page 9, Line 10-15: How certain are you that the H/D exchange was 100% complete?

**Reply:** We added sufficient D<sub>2</sub>O that the H/D exchange from the acid-reagent ion clusters ((HNO<sub>3</sub>)<sub>1,2</sub>NO<sub>3</sub><sup>-</sup> and (CH<sub>3</sub>COOH)<sub>1,2</sub>CH<sub>3</sub>COO<sup>-</sup>) was complete. Furthermore, we performed the same H/D exchange experiments from the ozonolysis of cyclohexene and  $\alpha$ -cedrene (two alkenes containing only one double bond). Here, the whole signals were shifted by the number of expected acidic H atoms. This shows that enough D<sub>2</sub>O was added to ensure a complete H/D exchange. Furthermore, we also increased the D<sub>2</sub>O concentration from 8 to 25 % r.h. and did not see a change in the intensities of the two signals that are separated in the presence of D<sub>2</sub>O.

For example, in Rissanen et al. 2015 and incomplete H/D shift as seen in reagent ions was shown to result in partial H/D shifts in products too. So how accurate is the determination of the importance of different pathways, based on H/D shift?

**Reply:** As stated above, we made sure that enough D<sub>2</sub>O was added to the experiments to have a complete H/D exchange. This was made adding more D<sub>2</sub>O and by using other alkenes which contain only one double bond using the same experimental setup.

Page 10: Would make sense to change section 3.4. to 3.1. to improve the readability.

**Reply:** The authors agree that it might be challenging in some parts to understand the classification in three reaction product groups in 3.1. However, such an introduction is necessary to understand the experimental results and we prefer to show the experimental results before presenting the proposed reaction mechanisms.



Page 11, Line 11: Similar epoxide formation is well-known from atmospheric isoprene oxidation (e.g. Paulot et al. 2009)

**Reply:** Indeed, Paulot et al., 2009 proposed an epoxide formation. However, they proposed the attack of an O atom from a hydroperoxide moiety, releasing an OH radical. This proposed mechanism is different from the attack of a RO<sub>2</sub> radical under formation of an epoxide and an acylalkoxy radical.

Page 11, Line 16: RO<sub>2</sub> + RO<sub>2</sub> is usually considered as progression, not termination.

**Reply:** The reaction of an RO<sub>2</sub> radical with another RO<sub>2</sub> radical can either lead to progression, e.g. forming RO radicals, or to termination, e.g. forming a carbonyl compound and a hydroxyl moiety. Therefore, we exchange the word “termination” by “bimolecular” in this sentence.

Page 11, Line 27: Is this the first time nitrate ionization has been reported to see simple carboxylic acids?

**Reply:** In these experiments, the concentrations of CH<sub>3</sub>COOH are high enough to detect acetic acid as a nitrate cluster. For a concentration of [CH<sub>3</sub>COOH] = 10<sup>14</sup> molecules cm<sup>-3</sup>, a calculated concentration of [(CH<sub>3</sub>COOH)NO<sub>3</sub>] = 10<sup>7</sup> molecules cm<sup>-3</sup> was detected. This shows the very low sensitivity for these simple carboxylic acids.

Conclusions first sentence: Rather “end-product analysis was used to infer oxidation pathways”.

**Reply:** We mainly investigated RO<sub>2</sub> radicals which are early intermediate reaction products and not “end products”. We changed the text to the following sentence:

**Changes in the text:** Early reaction intermediates (mainly highly oxidized RO<sub>2</sub> radicals) from the ozonolysis of β-caryophyllene were investigated in a free-jet flow system at ambient pressure and a temperature of 295 ± 2 K to study the formation mechanisms of highly oxidized multifunctional organic compounds (HOMs).

Page 12, Line 26: I think the discussion on VOC sources etc. should be moved to discussion, after all it's not what was studied in this work.

**Reply:** We agree with the reviewer and deleted the sentences about VOC sources and the main oxidant from the conclusion.

Page 13, Line 1: “These, up to now undiscovered reaction pathways...” This sentence is an overstatement and simply not true. (In Line 10 a more appropriate wording is used).

**Reply:** We changed the sentence to the following:

**Changes in the text:** These new insights in RO<sub>2</sub> radical reaction pathways were investigated in a free-jet flow system...

Figure 7: I find it a bit odd that at the same time it's stated that the abstraction is “an example only” and then resulting species are said to be detected in the spectra. And the assumed epoxide structure seems questionable.

**Reply:** In the mass spectrometer, we can only detect the chemical composition of substances, the molecular structure in Figure 7 is just a proposed structure based on the

experimental results. Therefore, we cannot state which H atom was abstracted during the oxidation and hence, it represents an example only. However, we were able to detect a reaction product which contains the chemical composition, the number of acidic H atoms and the number of oxygen atoms from the initial ozone attack of the proposed molecule. The epoxide structure is a proposed structure and we state ourselves that: "The epoxide formation cannot be proven and represents only a proposed reaction pathway in order to explain the experimental results."

#### References:

- T. Kurtén, et al., *J. Phys. Chem. A*, 2015, 119, 11366.  
T. Mentel, et al. *Atmos. Chem. Phys.* 2015, 15, 2791.  
F. Paulot, et al. 2009, *Science*, 325, 730.  
S. Richters, et al. *Environ. Sci. Technol.* 2016, 50, 2354.  
M. Rissanen, et al., *J. Am. Chem. Soc.* 2014, 136, 15596.  
M. Rissanen, et al., *J. Phys. Chem. A*, 2015, 119, 4633.

#### References:

- Beck, M., *et al.*: (2011), *Phys. Chem. Chem. Phys.* **13**, 10970-11001.  
Neeb, P., *et al.*: (1996), *Int. J. Chem. Kin.* **28**, 721-730.  
Shu, Y. G. and Atkinson, R.: (1994), *Int. J. Chem. Kinet.* **26**, 1193-1205.  
Berndt, T., et al., *J. Phys. Chem. A*, 119, 10336-10348, 2015.



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## Reviewers' comments to author:

### Reviewer: 3

#### Comments:

The manuscript, "Different Pathways..." by Richters et al. is well written, presents thorough experimental work and detailed spectral analyses that allowed the authors to identify three different pathways by which the Criegee intermediates formed by the ozonolysis of beta-caryophyllene undergo isomerization to become HOMs. The authors utilized a CI-API-ToF-MS with acetate as well as nitrate ionization coupled to a flow-tube. The use of isotopically labeled ozone and water vapor allowed robust identification of the ways in which the various RO<sub>2</sub> peroxy radicals are formed, mainly, that a diene (presumably larger than a certain size) can undergo auto-oxidation in a few different ways to form unique molecular products. The branching ratios of these three pathways are also quantified. The work presented will be a significant contribution to the growing body of research on these HOM species, thus, should be published in ACP with some clarifications.

The D<sub>2</sub>O experiment (highlighted by figure 3 and SI figure 1) is key to differentiating "norm. AutoOx." and "ext. AutoOx." since the byproducts of each channel normally (in the absence of D<sub>2</sub>O) have the same molecular composition. The shift in mass by 1 amu between the y=1 and x=2 products (similarly, y = 2 and x=3) in the D<sub>2</sub>O experiment allows their distinction. How efficient or fast is the H/D exchange for these acidic H/D atoms? Is it possible that the y=1 peak is really "norm AutoOx." product but with just one of the -OOH groups that has undergone H/D exchange?

**Reply:** The H/D exchange is always an equilibrium exchange and thus, we have to make sure that we add D<sub>2</sub>O in excess to enable a complete H/D exchange. We checked that by increasing the D<sub>2</sub>O concentration in the carrier gas to up to 25% relative humidity. No change in the signal intensities were visible when increasing from 8 to 25% r.h.. Furthermore, the reagent ions-acid clusters ((HNO<sub>3</sub>)<sub>1-2</sub>NO<sub>3</sub><sup>-</sup>) are completely shifted to ((DNO<sub>3</sub>)<sub>1-2</sub>NO<sub>3</sub><sup>-</sup>). Accordingly, D<sub>2</sub>O was added in excess and all acidic H atoms were exchanged by D atoms. We conducted the same experiments with cyclohexene (Berndt et al., 2015) and α-cedrene (Richters et al., 2016). For these alkenes, which contain one double bond, the whole signals were shifted by the number of acidic H atoms assumed from the "normal" autoxidation mechanism. Hence, we can assume that the experimental conditions allow a complete H/D exchange and that the signal shift by one nominal mass unit less must arise from the missing of one acidic H atom giving reaction products from the "ext. AutoOx." product group.

It appears that (in figures S1 and figure 3) that the red and blue peaks (y=1 and x=2) add up more-or-less to the corresponding black peak (no D<sub>2</sub>O). Would you expect this to be the case given that a compound with an endoperoxide group should have a different sensitivity (i.e. possess different ion cluster stability) compared to a compound with just hydroperoxide groups? The fact that red and blue add up to black would then suggest y=1 is really x=2 with one less H/D exchange.

**Reply:** The reviewer is right that HOMs with an endoperoxide moiety could be detected with a lower sensitivity than "norm. AutoOx. HOMs. But we cannot prove or even quantify this. However, yes we would expect that the "norm. AutoOx." (red) and "ext. AutoOx." (blue) peaks add up to the corresponding black peak (no D<sub>2</sub>O). If we assume that the sensitivity does not change when exchanging acidic H atoms with D atoms, we expect that the black signal must always represent the sum of the "red" and "blue" signal. If the black signal was only

composed of the “norm. AutOx.” signal and the split-up was only due to an incomplete H/D exchange, the red and blue peaks should add up to the black peak. But this should also be the case, if the blue peak represents the “ext. AutOx.” RO<sub>2</sub> radical. In the latter case, the black peak is composed of contributions from the “norm. AutOx” and the “ext. AutOx.” product groups. Independent of the sensitivity, this signal should then be split up to the “red” and the “blue” signal and the intensities should add up to the intensity of the black signal. Furthermore, we checked that for HOMs from the ozonolysis of alkenes containing only one double bond, the signals are completely shifted by the expected number of D atoms (see answer above).

Given a reaction time of 7.9 seconds would you expect H/D exchange to be complete? Was there a time dependence experiment conducted (as in section 3.6) with D<sub>2</sub>O that demonstrates that the peak height for y=1 relative to x=2 does not change with residence or reaction time? If not, perhaps state in the manuscript that a peak where y=1 would reside was not observed for alpha-cedrene (monoalkene) in Richters et al [2016 ES&T figure 3]. Was [D<sub>2</sub>O] » [H<sub>2</sub>O] such that at equilibrium essentially all –OOH groups would be present as -OOD?

**Reply:** We did not conduct a time dependence experiment with D<sub>2</sub>O but changed the D<sub>2</sub>O concentration in the carrier gas. Here, no relative peak height changes between y = 1 and x = 2 were detectable. Thus, we expect that D<sub>2</sub>O was added in such an excess, that all acidic H atoms were exchanged by D atoms in this equilibrium reaction giving only –OOD groups. Indeed, the peak of y = 1 was not observed for α-cedrene and this statement was added to the text as proposed by the reviewer.

**Changes in the text:** A signal which corresponds to the “ext. AutOx.” RO<sub>2</sub> radical O<sub>2</sub>C<sub>15</sub>H<sub>23-y</sub>(OO)(OOH)<sub>y</sub>O<sub>2</sub> with y = 1 was not detected as a product from the ozonolysis of α-cedrene (a sesquiterpene with one double bond). Instead, the whole signal was shifted by the expected number of acidic H atoms, here two for O<sub>2</sub>C<sub>15</sub>H<sub>23-x</sub>(OOH)<sub>x</sub>O<sub>2</sub> with x = 2. Accordingly, the concentration of heavy water was high enough to enable a complete exchange of acidic H atoms by D atoms.

As reported in lines 15-20 on page 6, the sensitivity (or ion cluster stability) difference between acetate and nitrate ionization to these HOMs (particularly those with one -OOH moiety) is quite large. It is reported (lines 21-30 page 6) that the “norm. AutOx” accounts for “between 29 and 35%” of HOM RO<sub>2</sub> formation. This assertion is less than convincing. The two values do not really represent a range. It is two numbers from two different ionization schemes, each of which detects these compounds with varying efficiencies. There is a factor of 2-3 difference in these branching ratios for the “ext. AutoOx” and “ext. AutoOx -CO<sub>2</sub>” pathways for the two ionization schemes. Given such large discrepancy, how is reliable or informative are the 29 and 35% numbers or any of these numbers? A discussion is needed on how the varying sensitivities of the ionization schemes are reconciled for this to be quantitative in any way. Moreover, though quantifying an absolute HOM yield is not the objective of this work, I find it uncomfortable that a single sensitivity value obtained from an inorganic acid (H<sub>2</sub>SO<sub>4</sub>) is applied to all of these multifunctional organic hydroperoxides and endoperoxides. Though this approach now has become routine, I strongly urge the authors to consider a more robust technique in the future to account for the varying sensitivities (depending on size, ring number, functional group, etc.) to these organics.

**Reply:** We agree with the reviewer that 29 and 35% are just two numbers and do not represent a range. Furthermore, all HOM concentrations represent lower limits and the determined concentrations using two different ionization techniques do only show that all reaction pathways are of importance. We changed the text in the following way:

**Changes in the text:** Thus, the “norm. AutOx.” group contributes with 29% to the total molar HOM yield when detecting with nitrate ionization and with 35% when detecting with acetate ionization. These values are based on the lower-limit concentration calculations and on the different detection sensitivities of the different reagent ions, which are depending e.g. on the number of hydroperoxide moieties in the molecule of interest. Hence, a quantitative statement concerning the contributions of the three reaction product groups is difficult. However, the two new product groups “ext. AutOx.” and “ext. AutOx. -CO<sub>2</sub>” are crucial for the explanation of HOM formation from the ozonolysis of β-caryophyllene.

Furthermore, we agree that a single calibration factor should not be used to quantify all different HOMs. However, we decided to use this specific value only because it agreed with the calculations of the calculation factor. This calculation is described in detail in the literature (Berndt et al., 2015) and assumes an ideal and inlet system with a 12% diffusion loss in the inlet tube and a reaction time of 0.2-0.3 s (Berndt et al., 2015). The result of this calculation was a range of the calibration factor between  $(1.5 - 2.8) \times 10^9$  molecule cm<sup>-3</sup>. The calculation and the good agreement of the calculation with the experimental value ( $1.85 \times 10^9$  molecule cm<sup>-3</sup>) indicated that ionization reactions can be described properly. Therefore, we decided to use the experimental calibration factor, but this factor was checked using a general calculation.

Are the authors able to rule out pathways other than the three reported here? Are all peaks in the spectra accounted for by the three pathways? If not, what fraction of the observed peaks (at least the ones that can be reasonably identified as 1st generation products) are attributed to the three pathways? Is the alkoxy radical (RO dot) formation and subsequent degradation/isomerization relevant at all here?

**Reply:** With the three reported pathways, we are able to assign all intense signals in the mass spectra. There are additional small signals which we cannot assign, but these signals are of minor importance and do not influence the total molar HOM yield. The alkoxy radical formation needs bimolecular reaction mechanisms, these bimolecular reactions are almost completely suppressed within the setup and are not relevant here.

Please include a brief discussion on variables that may affect the branching ratios of the three pathways. Ambient pressure/temperature? Carbon number? The number of rings? Would MT or isoprene undergo "ext. AutoOx" and "ext. AutoOx. -CO<sub>2</sub>"?

**Reply:** The reaction mechanisms were only investigated at one Temperature ( $T = 295 \pm 2$  K) and at ambient pressure. The influence of temperature and pressure was experimentally not studied.

All proposed reaction mechanisms are unimolecular reaction mechanisms. Here, a change in the pressure can only influence the rate coefficients if the reaction is not in its high-pressure limit. In our case, we cannot know if the investigated unimolecular reactions are in their high-pressure limit.

The unimolecular reactions have energy barriers. Thus, these reactions are supposed to be temperature dependent and the temperature dependence can have a strong influence on the specific unimolecular reaction and thus, on the branching ratios of the three pathways. However, we cannot state, which reaction pathway might be preferred when increasing the temperature.

The carbon number itself is not supposed to influence the rate coefficients however, structure and steric hindrance (and thus the number of rings) should influence the rate coefficients of the three reaction pathways. The number of weakly-bond H atoms in the precursor molecule and the presence of a second double bond are crucial for the importance of the pathways. For instance, the endoperoxide formation should be favored if five- or six-membered rings can be formed.

Accordingly, also monoterpenes should be able to undergo “ext. AutOx.” and “ext. AutOx. -CO<sub>2</sub>” if a second double bond is available or can be formed (e.g. for limonene). For isoprene, Vereecken and Peeters (2004) already proposed an endoperoxide formation starting from the OH radical initiated oxidation of isoprene.

We think that the discussion of a pressure, temperature, and structure dependence of the rate coefficients of the unimolecular reaction pathways is out of the scope of this manuscript, especially because we cannot provide experimental results for changing one of these variables. Thus, we did not add an additional paragraph to the manuscript and hope to answer the reviewer’s question adequately.

In the future, the authors may want to consider not using the blue/red color combination since many have trouble distinguishing the two.

**Reply:** The reviewer is right that it can be hard to distinguish between these colors and the authors will consider a change in the future.

The term "acidic H atoms" is a bit vague. Please re-word in way that doesn't imply that these are H atoms from acid functional groups only. Perhaps "non-alkyl H atoms"?

**Reply:** The authors prefer to stay with “acidic H atoms” because this term does explain the chemical nature of these H atoms in the best way. Non-alkyl H atoms are not necessary acidic, e.g. if they are bond to another heteroatom.

Line 5 of page 9: "...three or two..." to "...three and two..."

**Reply:** We changed the text accordingly.

SI figure is really informative and deserves to be in manuscript not SI. Possible to combine with figure 3 or replace figure 3?

**Reply:** We agree with the reviewer and added the SI figure as Figure 4 to the main text.

#### References:

- Berndt, T., *et al.*: (2015), *J. Phys. Chem. A* **119**, 10336-10348.  
Richters, S., *et al.*: (2016), *Environ. Sci. Technol.* **50**, 2354-2362.  
Vereecken, L. and Peeters, J.: (2004), *J. Phys. Chem. A* **108**, 5197-5204.

# Different Pathways of the Formation of Highly Oxidized Multifunctional Organic Compounds (HOMs) from the Gas-Phase Ozonolysis of $\beta$ -Caryophyllene

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**Abstract.** The gas-phase mechanism of the formation of highly oxidized multifunctional organic compounds (HOMs) from the ozonolysis of  $\beta$ -caryophyllene was investigated in a free-jet flow system at atmospheric pressure and a temperature of  $295 \pm 2$  K. Reaction products, mainly highly oxidized  $\text{RO}_2$  radicals, containing up to 14 oxygen atoms were detected using  
10 chemical ionization – atmospheric pressure interface – time-of-flight mass spectrometry with nitrate and acetate ionization. These highly oxidized  $\text{RO}_2$  radicals react with  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HO}_2$  and other  $\text{RO}_2$  radicals under atmospheric conditions forming the first-generation HOM closed-shell products.

Mechanistic information on the formation of the highly oxidized  $\text{RO}_2$  radicals ~~are~~is based on results obtained with isotopically labeled ozone ( $^{18}\text{O}_3$ ) in the ozonolysis reaction and from H/D exchange experiments of acidic H atoms in the products. The  
15 experimental findings indicate that HOM formation in this reaction system is considerably influenced by the presence of a double bond in the  $\text{RO}_2$  radicals primarily formed from the  $\beta$ -caryophyllene ozonolysis. Three different reaction types for HOM formation can be proposed allowing to explain the detected main products, i.e. i) the simple autoxidation, corresponding to the repetitive reaction sequence of intramolecular H-abstraction of a  $\text{RO}_2$  radical,  $\text{RO}_2 \rightarrow \text{QOOH}$ , and subsequent  $\text{O}_2$  addition forming a next peroxy radical,  $\text{QOOH} + \text{O}_2 \rightarrow \text{R}'\text{O}_2$ , ii) an extended autoxidation mechanism additionally involving the internal  
20 reaction of a  $\text{RO}_2$  radical with a double bond forming most likely an endoperoxide, and iii) an extended autoxidation mechanism including  $\text{CO}_2$  elimination. The individual reaction steps of the reaction types ii) and iii) are uncertain at the moment. From the product analysis it can be followed that the simple autoxidation mechanism accounts only for about one third of the formed HOMs.

Time-dependent measurements showed that the HOM formation proceeds at a timescale of 3 seconds or less under the  
25 concentration regime applied here.

The new reaction pathways represent an extension of the mechanistic understanding of HOM formation via autoxidation in the atmosphere, as recently discovered from laboratory investigations on monoterpene ozonolysis.

## 1 Introduction

The emission of biogenic volatile organic compounds (BVOCs) from vegetation to the troposphere and their oxidation in the gas phase is subject of intense research (Calvert et al., 2000; Guenther et al., 2012; Ziemann and Atkinson, 2012).

Sesquiterpenes (SQTs, C<sub>15</sub>H<sub>24</sub>) with an annual emission of 18-24 million metric tons carbon (Messina et al., 2015; Sindelarova et al., 2014) contribute with up to 3 % to the annual global BVOC emission of 720-1150 million metric tons of carbon (Guenther et al., 1995; Guenther et al., 2012; Lathièrè et al., 2005; Sindelarova et al., 2014). They are emitted by a large variety of plants and fungi and their emission pattern depends strongly on the region and the season (Ciccioli et al., 1999; Duhl, 2008; Geron and Arnts, 2010; Horváth et al., 2011; Jardine et al., 2011). Biotic stress can drastically increase SQT emissions (Mentel et al., 2013).  $\beta$ -Caryophyllene emissions were calculated to account for 25 % of global SQT emissions (Guenther et al., 2012) and can contribute 70 % to the regional BVOC emissions, e.g. in orange orchards (Ciccioli et al., 1999; Duhl, 2008). The oxidation products are expected to have a very low vapor pressure making them important for the process of secondary organic aerosol (SOA) formation (Jaoui et al., 2013; Zhao et al., 2015).

$\beta$ -Caryophyllene is mainly oxidized by ozone under atmospheric conditions having a lifetime  $\tau_{(O_3)} = 2$  min for an average ozone concentration of  $[O_3] = 7 \times 10^{11}$  molecules cm<sup>-3</sup> (Finlayson-Pitts and Pitts, 1986) and a rate coefficient  $k_{(296\text{ K})} = 1.1 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Richters et al., 2015; Shu and Atkinson, 1994). Gas-phase product formation from the ozonolysis of  $\beta$ -caryophyllene was already studied in a series of laboratory investigations (Calogirou et al., 1997; Grosjean et al., 1993; Jaoui et al., 2003; Lee et al., 2006; Winterhalter et al., 2009) and by means of theoretical calculations (Nguyen et al., 2009). A large variety of carbonyl, epoxide and carboxyl compounds containing up to five oxygen atoms were experimentally observed using different detection techniques. The total carbon yield, comprising gas- and particle phase products, accounts for up to 64 % (Jaoui et al., 2003). A summary of available data in the literature is given by Winterhalter et al. (2009). DFT quantum chemical calculations were conducted accompanying the experimental work by Winterhalter et al. (2009) with special attention to the first oxidation steps. The fraction of stabilized Criegee intermediates at atmospheric pressure was calculated to be 74 %, slightly higher than the experimental value of 60 %. Furthermore, the calculations support the proposed uni- and bimolecular reaction pathways of the Criegee intermediates as proposed from the experimental work. The main reaction product was stated to be the secondary ozonide with a yield of 64 %. The formation of acids should account for 8 %, dominated by the formation of caryophyllonic acid (Nguyen et al., 2009). This value is slightly lower than the overall gas- and aerosol phase yield of 13.5 % for caryophyllonic acid measured by Jaoui et al. (2003).

Recently, Ehn et al. (2012); (2014) detected highly oxidized multifunctional organic compounds (HOMs) from the oxidation of  $\alpha$ -pinene in field and laboratory studies. These HOMs contain up to twelve oxygen atoms and are supposed to have a very low vapor pressure, which led to their classification as extremely low-volatility organic compounds (ELVOCs) and as important candidates-precursors for SOA formation (Ehn et al., 2014).

Other experimental work on HOM formation from the ozonolysis of monoterpenes (Jokinen et al., 2014; Mentel et al., 2015) and model substances, such as cyclohexene (Berndt et al., 2015b; Mentel et al., 2015; Rissanen et al., 2014), led to the



development of an autoxidation mechanism based on RO<sub>2</sub> radical chemistry. In this process, an RO<sub>2</sub> radical internally abstracts an H atom forming an alkyl radical with a hydroperoxide moiety (RO<sub>2</sub> → QOOH). Subsequent oxygen addition forms a next R'O<sub>2</sub> radical (QOOH + O<sub>2</sub> → R'O<sub>2</sub>) (Berndt et al., 2015b; Crouse et al., 2013; Ehn et al., 2014; Jokinen et al., 2014; Rissanen et al., 2014), which can repeat this reaction sequence. The overall process results in a repetitive oxygen insertion into the molecules on a time scale of seconds (Jokinen et al., 2014). The principle of autoxidation is well known from the liquid phase since more than hundred years (Berezin et al., 1996; Jazukowitsch, 1875) and was recently extended to atmospheric gas-phase reactions (Crouse et al., 2013).

For alkenes with multiple double bonds, such as β-caryophyllene, this mechanism can become more complex caused by the variety of possible reaction pathways of unsaturated RO<sub>2</sub> radicals formed as the intermediates. A recent study from this laboratory showed that the HOM formation from the ozonolysis of α-cedrene (a SQT that contains only a single double bond) was completely explainable by the autoxidation mechanism initiated by the ozone attack at the double bond (Richters et al., 2016). On the other hand, in the case of the analogous reaction of β-caryophyllene (containing two double bonds), the product spectrum was more complex and not fully in line with an autoxidation mechanism (RO<sub>2</sub> → QOOH, QOOH + O<sub>2</sub> → R'O<sub>2</sub>). This fact points to additional reaction pathways for HOM generation most likely caused by the presence of a second double bond.

The scope of the present work is the mechanistic elucidation of possible, new reaction pathways of HOM formation starting from the ozonolysis of β-caryophyllene. Experiments with heavy water (D<sub>2</sub>O) and isotopically labeled ozone (<sup>18</sup>O<sub>3</sub>) were conducted in order to obtain additional information on elementary reaction pathways needed to explain the observed products. This approach allowed to develop an extended mechanism for the HOM formation from the ozonolysis of β-caryophyllene.

## 20 **2 Experimental**

The gas-phase ozonolysis of β-caryophyllene was investigated in a free-jet flow system at a temperature of 295 ± 2 K and a pressure of 1 bar purified air. The experimental approach is described in detail in the literature (Berndt et al., 2015a; 2015b; Richters et al., 2016) and only a brief summary will be given here.

Experiments in the free-jet flow system (outer tube: length: 200 cm, 15 cm inner diameter and a moveable inner tube: 9.5 mm outer diameter with a nozzle) were conducted under conditions of negligible wall-loss of products and with a reaction time of 3.0-7.9 s (Berndt et al., 2015a). The inner flow of 5 L min<sup>-1</sup> (STP), containing varying ozone concentrations, was injected through a nozzle to the outer air flow of 95 L min<sup>-1</sup> (STP) which contained β-caryophyllene and CH<sub>3</sub>COOH if needed. The addition of CH<sub>3</sub>COOH was used to scavenge stabilized Criegee intermediates from the ozonolysis of β-caryophyllene (Beck et al., 2011; Neeb et al., 1996). Turbulent gas mixing downstream the nozzle rapidly generates a homogeneously mixed reactant gas.



Ozone was produced by passing air or  $^{18}\text{O}_2$ , premixed in  $\text{N}_2$ , through an ozone generator (UVP OG-2) and was measured at the outflow of the reactor by a gas monitor (Thermo Environmental Instruments 49C). All gas flows were set by calibrated gas flow controllers (MKS 1259/1179).  $\beta$ -Caryophyllene was stored in flasks maintained at 278 K, carried along with 38-48  $\text{cm}^3 \text{min}^{-1}$  (STP) nitrogen, and diluted with the air stream just before entering the flow system. Gas chromatography with a flame – ionization detector (GC-FID; Agilent 6890) as well as proton transfer reaction – mass spectrometry (PTR-MS; HS PTR-QMS 500, Ionicon) served as the analytical techniques for  $\beta$ -caryophyllene detection.

The absolute  $\beta$ -caryophyllene concentrations were determined using the “effective carbon-number approach” from GC-FID analysis using a series of reference substances with known concentrations (Scanlon and Willis, 1985). The reference substances were  $\alpha$ -pinene,  $\beta$ -pinene and limonene. The ratio of the effective carbon numbers (equal to the signal ratio for identical sample concentrations) of  $\beta$ -caryophyllene with respect to these monoterpenes is 1.5 (Helmig et al., 2003; Scanlon and Willis, 1985). Before each measurement series, the concentration was determined using GC-FID analysis measuring the  $\beta$ -caryophyllene signal as well as the signals of the reference substances with known concentrations simultaneously. The  $\beta$ -caryophyllene concentration in the flow system was continuously monitored throughout the experiments by PTR-MS measurements following the ion traces at 205, 147 and 137 amu.

The  $\beta$ -caryophyllene conversion was varied by changing the initial ozone concentration for otherwise constant reaction conditions. The needed gas mixture of  $\text{CH}_3\text{COOH}$  was prepared in a gas-mixing unit.

The reactant gases used had the following purities:  $\beta$ -caryophyllene (98.5 %; Aldrich),  $\text{CH}_3\text{COOH}$  (Aldrich; 99.5 %),  $\text{N}_2$  (Air Products; 99,9992 %),  $^{18}\text{O}_2$  (euriso-top, isotopic enrichment 96 %). Air was taken from a PSA (Pressure Swing Adsorption) unit with further purification by activated charcoal and 4Å molecular sieve. If needed, humidified air was produced by passing a part of the air flow through water saturators filled with  $\text{D}_2\text{O}$  (Aldrich, 99.9 atom %).

Reaction products were detected and quantified by means of chemical ionization – atmospheric pressure interface – time-of-flight (CI-APi-TOF) mass spectrometry (Airmodus, Tofwerk) using nitrate ions and acetate ions for chemical ionization. The mass spectrometer settings ([applied voltages and flow rates](#)) as well as the approach applied for the determination of HOM concentrations are equal to those described in detail by Berndt et al. (2015b). All stated concentrations represent lower limits (Berndt et al., 2015b). The calculation of HOM concentrations and information about detection limitations and the mass axis calibration are given in the supplementary information.

The initial concentrations were (unit: molecules  $\text{cm}^{-3}$ ): [ $\beta$ -caryophyllene] = (8.3-8.6)  $\times 10^{10}$ ; [ $\text{O}_3$ ] = (4.7-102)  $\times 10^{10}$  and [ $\text{CH}_3\text{COOH}$ ] = (0-1.4)  $\times 10^{14}$ .

### 3 Results and Discussion

A series of different experiments was conducted in order to investigate the product formation from the ozonolysis of  $\beta$ -caryophyllene in more detail. In Sect. 3.1, three different groups of products are proposed as a result of the identified signals

from mass spectra recorded from runs with nitrate and acetate ionization. The experimental findings utilized for the signal assignment to the different product groups are described in the following sections. Section 3.2 discusses results from experiments with normal ( $^{16}\text{O}_3$ ) or isotopically labeled ozone ( $^{18}\text{O}_3$ ) that allow to distinguish between the origin of the O-atoms in the reaction products arising either from attacking ozone or from air- $\text{O}_2$ . Experiments with  $\text{D}_2\text{O}$  addition in the carrier gas provide information about the total number of acidic H atoms in each reaction product, being equal to the number of OH and OOH groups, see Sect. 3.3.

### 3.1 Three groups of highly oxidized products

Figure 1 shows two product mass spectra from  $\beta$ -caryophyllene ozonolysis in the mass-to-charge range 345-505 Th, recorded a) with acetate ionization and b) with nitrate ionization. The products appear as adducts with the reagent ion (Ehn et al., 2014). Here, a signal of the same product shows a shift by three nominal mass units comparing acetate ion adducts (+59 nominal mass units) with nitrate ion adducts (+62 nominal mass units). Mainly  $\text{RO}_2$  radicals were detected as reaction products because the  $\text{RO}_2$  radical concentrations did not exceed  $9 \times 10^6$  molecules  $\text{cm}^{-3}$  and bimolecular reactions of the formed  $\text{RO}_2$  radicals were less efficient for a reaction time of 3.0-7.9 s in these experiments. Therefore, the discussion is mainly focused on  $\text{RO}_2$  radicals. The observed product signals were classified in three product groups. The position of the dominant signals in each product group differs by 32 nominal mass units each due to the stepwise insertion of oxygen molecules.

Signals of the first group, the so-called normal autoxidation group, “norm. AutOx.” appear at the same positions in the mass spectrum as observed from the HOM formation of  $\alpha$ -cedrene ozonolysis (an SQT with only one double bond, but with the same chemical formula  $\text{C}_{15}\text{H}_{24}$  like  $\beta$ -caryophyllene) (Richters et al., 2016). The  $\text{RO}_2$  radicals from this group were summarized by the general formula  $\text{O}_2\text{O}-\text{C}_{15}\text{H}_{23-x}(\text{OOH})_x\text{O}_2$  with  $x = 1-5$  (Jokinen et al., 2014; Richters et al., 2016). Here,  $x$  stands for the number of hydroperoxide moieties in the molecule, the two oxygen atoms “ $\text{O}_2\text{O}$ ” arise from the initial ozone attack and the final  $\text{O}_2$  stands for the  $\text{RO}_2$  radical functional group (Jokinen et al., 2014). The carbon skeleton of 15 carbon atoms is retained and up to 14 oxygen atoms are inserted in the products. The number of oxygen atoms arising from the initial ozone attack was confirmed in experiments with isotopically labeled ozone ( $^{18}\text{O}_3$ ) (Fig. 2).

The second product group, the extended autoxidation group “ext. AutOx.”, comprises the signals of  $\text{RO}_2$  radicals with the general formula  $\text{O}_2\text{O}-\text{C}_{15}\text{H}_{23-y}(\text{OO})(\text{OOH})_y\text{O}_2$  with  $y = 1-4$ . Here, “(OO)” stands - most likely - for an endoperoxide group. Reactions leading to this insertion step are discussed in the reaction mechanisms in Sect. 3.4.  $\text{RO}_2$  radicals from the “norm. AutOx.” group with  $\text{O}_2\text{O}-\text{C}_{15}\text{H}_{23-x}(\text{OOH})_x\text{O}_2$  have the same chemical composition, and consequently the same position in the mass spectrum like the  $\text{RO}_2$  radicals from the “ext. AutOx.” group. A distinction is possible measuring the number of acidic H atoms in the molecules (equal to the number of OOH groups) applying H/D exchange experiments with heavy water (Fig. 3, 4) (Rissanen et al., 2014). Products of the “ext. AutOx.” group contain one acidic H atom less than the corresponding product from “norm. AutOx.” with the same composition, for instance for  $\text{C}_{15}\text{H}_{23}\text{O}_8$ :  $\text{O}_2\text{O}-\text{C}_{15}\text{H}_{23-y}(\text{OO})(\text{OOH})_y\text{O}_2$  with  $y = 1$  and  $\text{O}_2\text{O}-\text{C}_{15}\text{H}_{23-x}(\text{OOH})_x\text{O}_2$  with  $x = 2$ . ~~Up to now,~~ H/D exchange experiments were successfully conducted in order to elucidate the

~~structure-number of OOH groups in the~~ highly oxidized reaction product from the ozonolysis of cyclohexene which represents a model compound for cyclic monoterpenes (Berndt et al., 2015b; Rissanen et al., 2014). In the case of cyclohexene ozonolysis, the formation of HOMs strictly followed the normal autoxidation mechanism and the results of H/D exchange experiments confirmed the expected number of hydroperoxide moieties in the products.

5 The third product group (extended autoxidation with CO<sub>2</sub> elimination) named “ext. AutOx -CO<sub>2</sub>”, includes the signals of HOMs with a C<sub>14</sub> skeleton formed by CO<sub>2</sub> elimination in the course of their formation. Based on experiments with isotopically labeled ozone (<sup>18</sup>O<sub>3</sub>) (Fig. 2) and heavy water (Fig. 45), highly oxidized RO<sub>2</sub> radicals of this product group were assigned to the general formula O-C<sub>14</sub>H<sub>23-α</sub>(O)(OOH)<sub>α</sub>O<sub>2</sub> with α = 1-3. Here, only one oxygen atom from the ozone attack “O-“ is retained in the HOM. An additional oxygen atom “(O<sub>2</sub>)” is inserted into the molecule arising from air-O<sub>2</sub>. It is assumed that this “(O)” exists in an epoxide ring. A possible reaction sequence leading to epoxide formation is discussed in Sect. 3.4.

10 Closed-shell products in all three product groups were detected at minus 17 nominal mass units compared with the position of the respective RO<sub>2</sub> radical in the mass spectrum. The formation of closed-shell products as a result of consecutive, uni- or bimolecular reactions of the RO<sub>2</sub> radicals can be explained by a formal loss of one oxygen and one hydrogen atom from the RO<sub>2</sub> radical, see proposed reaction pathways as given by Jokinen et al. (2014).

15 The same reaction products (RO<sub>2</sub> radicals and closed-shell products) were detected by means of both ionization methods and all signal assignments were supported by the exact mass-to-charge ratio of the signals (resolving power at 393 Th: 4100 Th/Th). The detected signal intensity (normalized by the reagent ion intensity) of the same HOM measured by both ionization techniques is not necessarily identical caused by possible differences of the cluster ion stability (Berndt et al., 2015b; Hyttinen et al., 2015). As a result of our analysis, acetate ionization is more sensitive especially for the detection of HOMs that contain only one hydroperoxide moiety, O,O-C<sub>15</sub>H<sub>23-x</sub>(OOH)<sub>x</sub>O<sub>2</sub> with x = 1 and O-C<sub>14</sub>H<sub>23-α</sub>(O)(OOH)<sub>α</sub>O<sub>2</sub> with α = 1. A similar observation has been already done for reaction products from the ozonolysis of cyclohexene (Berndt et al., 2015b). The signals of the HOMs with only one hydroperoxide moiety dominate the spectrum recorded with acetate ionization (Fig. 1a) but are of minor importance in the case of nitrate ionization (Fig. 1b). Table 1 summarizes the nominal mass-to-charge ratios of the detected signals and their assignments.

25 The investigation analysis of the signal intensities points to an important role of reaction products from the “ext. AutOx.” and “ext. AutOx. -CO<sub>2</sub>” groups for the total HOM formation from the ozonolysis of β-caryophyllene. The relative contribution of reaction products from the “ext. AutOx.” group to the total molar HOM yield, investigated in the presence of D<sub>2</sub>O using nitrate ionization, was determined to be 49 %. The “norm. AutOx.” group contribute with 29 % and the “ext. AutOx. -CO<sub>2</sub>” with 22 % to the total molar HOM yield. The change of the detection sensitivity for different HOMs (especially for those containing a single hydroperoxide moiety) leads to a different contribution of the individual product groups to the total ~~molar-HOM yield~~ signal intensities when changing from nitrate ionization to acetate ionization. For acetate ionization, the “ext. AutOx. -CO<sub>2</sub>” group contributes with 50 %, the “norm. AutOx.” group with 35 % and the “ext. AutOx.” group only with 15 % to the total molar HOM yield. Thus, the “norm. AutOx.” group contributes with 29% to the total molar HOM yield when detecting with nitrate ionization and with 35% when detecting with acetate ionization. These values are based on the lower-limit concentration

calculations and on the different detection sensitivities of the different reagent ions, which are depending e.g. on the number of hydroperoxide moieties in the molecule of interest. Hence, a quantitative statement concerning the contributions of the three reaction product groups is difficult. However, the ~~on average only with 29-35 % to the total molar HOM yield.~~ The two new product groups “ext. AutOx.” and “ext. AutOx. -CO<sub>2</sub>” are crucial for the explanation of HOM formation from the ozonolysis of β-caryophyllene.

### 3.2 Experiments with isotopically labeled ozone (<sup>18</sup>O<sub>3</sub>)

The signal assignment of the three reaction product groups was supported by experiments using isotopically labeled ozone, <sup>18</sup>O<sub>3</sub>. When changing from <sup>16</sup>O<sub>3</sub> to <sup>18</sup>O<sub>3</sub> in the ozonolysis, the product signals in the mass spectra were shifted by two nominal mass units for each oxygen arising from the initial ozone attack (Jokinen et al., 2014). The concentration of remaining <sup>18</sup>O<sub>2</sub> in the carrier gas was about 0.05% of the total O<sub>2</sub> concentration. Hence, <sup>18</sup>O<sub>2</sub> cannot compete with <sup>16</sup>O<sub>2</sub> in the autoxidation steps. Thus, the isotopically labeled <sup>18</sup>O atoms will stem from the ozone attack at the double bond.

For example, Figure 2 shows a comparison of results from an experiment using either <sup>18</sup>O<sub>3</sub> or <sup>16</sup>O<sub>3</sub> in the ozonolysis reaction for otherwise constant reaction conditions. The spectra in the range 340-400 Th are dominated by four signals of RO<sub>2</sub> radicals at the nominal mass-to-charge ratio of 346, 358, 378 and 390 Th representing signals of all three product groups. The signals at nominal 358 and 390 Th were shifted by four nominal mass units when changing from <sup>16</sup>O<sub>3</sub> to <sup>18</sup>O<sub>3</sub>. This shift indicates the presence of two oxygen atoms in these reaction products from the initial ozone reaction. The signal at nominal 358 Th is attributed to a RO<sub>2</sub> radical from the “norm. AutOx.” group, the signal at nominal 390 Th contains contributions from products of the “norm. AutOx.” as well as the “ext. AutOx.” group. (A further differentiation by means of H/D exchange experiments is described later.) The signal shift by four nominal mass units shows that reaction products from both product groups contain two oxygen atoms from the initial ozone attack, “O,O”, as stated in the general formulas O,O-C<sub>15</sub>H<sub>23-x</sub>(OOH)<sub>x</sub>O<sub>2</sub> with x = 1-5 (“norm. AutOx.”) and O,O-C<sub>15</sub>H<sub>23-y</sub>(OO)(OOH)<sub>y</sub>O<sub>2</sub> with y = 1-4 (“ext. AutOx.”). The third oxygen atom from the attacking ozone is the oxygen atom of the OH radical that was split-off from the Criegee intermediate forming the alkyl radicals **4a-4c**; see as shown in the first steps of the ozonolysis mechanism in Fig. 56. Further possible reaction pathways of species **4b** forming “norm. AutOx. and “ext. AutOx.” reaction products are proposed in Fig. 7.

The signals at nominal 346 and 378 Th were shifted by two nominal mass units ~~comparing the results using~~ applying either <sup>16</sup>O<sub>3</sub> or <sup>18</sup>O<sub>3</sub>. Consequently, only one oxygen atom from the initial ozone attack remains in these reaction products and a second oxygen atom from the initial ozone attack must ~~be~~ have been abstracted in the course of the product formation. The position and the exact mass-to-charge ratio of these RO<sub>2</sub> signals in the mass spectra suggest that the RO<sub>2</sub> radicals contain only 14 carbon atoms. The loss of one carbon atom and one more oxygen atom from the initial ozone attack points to an elimination of CO or CO<sub>2</sub> in these molecules. The elimination of CO from highly oxidized RO<sub>2</sub> radicals was proposed for reaction products from the ozonolysis of cyclohexene (Berndt et al., 2015b). The corresponding reaction products from the ozonolysis of β-

caryophyllene including  $\alpha$ -CO elimination were detected in small yields at nominal 365, 397 and 429 Th using nitrate ionization and were not further investigated here.

On the other hand, the formation of reaction products from the third product group is supposed to involve  $\alpha$ -CO<sub>2</sub> elimination starting from species **7** in Fig. [78](#). Species **7** contains an acylperoxy radical functional group which might react with the double bond under formation of an acylalkoxy radical **15**. From this acylalkoxy radical, CO<sub>2</sub> can easily be released (Jaoui et al., 2003; Winterhalter et al., 2009). Therefore, the reaction product at nominal 346 Th can be explained by an elimination of CO<sub>2</sub> (-44 nominal mass units) and a subsequent O<sub>2</sub> addition (+32 nominal mass units). Reaction products with signals at nominal 378 and 420 Th can be formed by further O<sub>2</sub> insertion via autoxidation starting from **17**, see Fig. [78](#). Based on these results,  $\alpha$ -CO<sub>2</sub> elimination was proposed for reaction products from the third product group, named “ext. AutOx. -CO<sub>2</sub>”. Products of this group can be explained by the general formula O-C<sub>14</sub>H<sub>23- $\alpha$</sub> (O)(OOH) <sub>$\alpha$</sub> O<sub>2</sub> with  $\alpha$  = 1-3. Here, “O-” stands for the remaining oxygen atom from the reacting ozone. The proposed reaction mechanism for the formation of the first member of the “ext. AutOx. -CO<sub>2</sub>” group with  $\alpha$  = 1 is given in Fig. [78](#), **7** → **15** → **16** → **17**. It includes tentatively the formation of an epoxide ring. The corresponding oxygen atom is marked as “(O)” in the general formula O-C<sub>14</sub>H<sub>23- $\alpha$</sub> (O)(OOH) <sub>$\alpha$</sub> O<sub>2</sub>. The marked oxygen atom “(O)” could also belong to an aldehyde or  $\alpha$ -ketone. However, it was not possible to explain the formation of a carbonyl functional group together with the CO<sub>2</sub> elimination using known reaction mechanisms in the literature (Jaoui et al., 2003; Winterhalter et al., 2009). On the other hand, epoxide formation was already postulated for the OH radical-initiated oxidation of aromatic compounds (Andino et al., 1996; Bartolotti and Edney, 1995; Berndt and Böge, 2006; Ghigo and Tonachini, 1999; Suh et al., 2003). The explanation of the oxygen atom “(O)” by a hydroxide moiety can be excluded, because this would imply the presence of two more hydrogen atoms in the product and hence an increase by two nominal mass units in the mass spectrum. Furthermore, the possible presence of a hydroxyl moiety would provide an additional acidic H atom in the molecule, which was not detected in [heavy-water H/D exchange](#) experiments [with heavy water](#) (see Sect. 3.3).

### 3.3 Experiments with heavy water (D<sub>2</sub>O)

A next set of experiments was conducted in presence of heavy water (D<sub>2</sub>O), applying nitrate ionization, see Fig. [3](#), [4](#), and [45](#). The addition of D<sub>2</sub>O leads to an H/D exchange of all acidic H atoms present in the molecule (Rissanen et al., 2014) and thus, to a signal shift in the mass spectrum by a certain number of nominal mass units being equal to the number of acidic H atoms in the molecule. For HOMs following the normal autoxidation process, all oxygen molecules inserted into the molecule, except the RO<sub>2</sub> radical functional group, are present as hydroperoxide moieties. The resulting signal shift in the presence of D<sub>2</sub>O corresponds to the number of hydroperoxide moieties as shown for the HOMs from the ozonolysis of cyclohexene (Berndt et al., 2015b; Rissanen et al., 2014) and  $\alpha$ -cedrene (Richters et al., 2016).

Figure 3 shows mass spectra in the presence and absence of D<sub>2</sub>O focusing on the signals at nominal 393, 408 and 425 Th which were assigned to reaction products of the “norm. AutOx.” and “ext. AutOx.” groups. The full spectra in the nominal mass-to-charge range 360-495 Th are shown in Fig. [S14](#). In presence of D<sub>2</sub>O, all three signals were split up into two signals according

to their numbers of acidic H atoms in the molecules. This behavior indicates that two different reaction products contribute to each signal. The signal at nominal 393 Th corresponds to the RO<sub>2</sub> radical C<sub>15</sub>H<sub>23</sub>O<sub>8</sub> and was shifted by one or two nominal mass units when adding D<sub>2</sub>O. Two of the eight oxygen atoms arise from the initial ozone attack (see Sect. 3.2) and two oxygen atoms represent the RO<sub>2</sub> radical functional group. Consequently, two oxygen molecules (four oxygen atoms) at the maximum can exist in hydroperoxide groups indicated by a signal shift of two nominal mass units. The corresponding product belongs to the “norm. AutOx.” group, O<sub>2</sub>O-C<sub>15</sub>H<sub>23-x</sub>(OOH)<sub>x</sub>O<sub>2</sub> with x = 2, species **11** in Fig. 78. The signal intensity of the signal shifted by two nominal mass units accounts for 31 % of the total signal intensity, see the red peak at nominal 395 Th. On the other hand, the signal shift by one nominal mass unit less, blue peak at nominal 394 Th, can only be explained by an oxygen molecule insertion without forming a hydroperoxide group. This insertion is tentatively explained by an endoperoxide formation from the internal reaction of a RO<sub>2</sub> radical with the second, still intact, double bond in the molecule, see reaction sequence **5'** → **8** → **9** in Fig. 6-7 and **7'** → **13** → **14** in Fig. 78. The signal intensity of this reaction product from the extended autoxidation mechanism “ext. AutOx.”, O<sub>2</sub>O-C<sub>15</sub>H<sub>23-y</sub>(OO)(OOH)<sub>y</sub>O<sub>2</sub> with y = 1, accounts for 69 % of the total intensity of the shifted peaks. The group “(OO)” in the formula stands for the inserted oxygen molecule appearing as the postulated endoperoxide, see species **14** in Fig. 78.

The signal of the RO<sub>2</sub> radical at nominal 425 Th was shifted by three ~~or~~ and two nominal mass units accounting for 29 % and 71 % of the total signal intensity, respectively. Here, compared to the reaction products appearing at nominal 393 Th, a next oxygen molecule was inserted in the products resulting in a third hydroperoxide group in “norm. AutOx.”, O<sub>2</sub>O-C<sub>15</sub>H<sub>23-x</sub>(OOH)<sub>x</sub>O<sub>2</sub> with x = 3, and a second hydroperoxide group in “ext. Autox.”, O<sub>2</sub>O-C<sub>15</sub>H<sub>23-y</sub>(OO)(OOH)<sub>y</sub>O<sub>2</sub> with y = 1. The signal of the corresponding closed-shell product to the RO<sub>2</sub> radical at nominal 425 Th is visible at nominal 408 Th. It shows the same signal shift as its corresponding RO<sub>2</sub> radical by three or two nominal mass units. The signal intensity of the closed-shell product from the “norm. AutOx.” group, O<sub>2</sub>O-C<sub>15</sub>H<sub>22-x</sub>O(OOH)<sub>x</sub> with x = 3 accounts for 30 % of the total signal intensity of the shifted peaks (red peak at nominal 411 Th), the signal intensity of the reaction product from the “ext. AutOx.” group, O<sub>2</sub>O-C<sub>15</sub>H<sub>22-y</sub>O(OO)(OOH)<sub>y</sub>O<sub>2</sub> with y = 2 (blue peak at 410 Th) accounts for 70 %.

The relative contributions of the two product groups to the total signal intensity for all signals are summarized in Table 1. With the exception of the signal at nominal 376 Th, the ratio of the contributions of the two product groups is “norm.AutOx.” / “ext. AutOx.” = 3/7-2/8. This ratio shows, that the extended autoxidation mechanism is more important than the normal autoxidation mechanism for reaction products from the ozonolysis of β-caryophyllene.

Figure 4-5 shows a comparison of spectra in the nominal mass-to-charge range 345-385 Th recorded in the presence and absence of D<sub>2</sub>O. The detected signals at nominal 349, 364 and 381 Th are assigned to the third product group “ext. AutOx -CO<sub>2</sub>”. The signal at nominal 349 Th was shifted by one nominal mass unit when adding D<sub>2</sub>O which indicates the presence of one hydroperoxide moiety in this reaction product. This signal has the molecular formula C<sub>14</sub>H<sub>23</sub>O<sub>6</sub> and one of the six oxygen atoms arises from the initial ozone attack as observed from the experiments with isotopically labeled ozone, see Sect. 3.2. Two oxygen atoms are assigned to the RO<sub>2</sub> radical functional group. The signal shift by one nominal mass unit from the H/D exchange experiment indicates that two of the three remaining oxygen atoms form a hydroperoxide moiety. The third,



residual oxygen atom must be inserted into the molecule without generating an additional acidic H atom, illustrated by “(O)” in the general formula  $O-C_{14}H_{23-\alpha}(O)(OOH)_\alpha O_2$ . The chemical nature of this “(O)” in the product is still uncertain and was tentatively attributed to an epoxide formation at the second double bond, see **7'**  $\rightarrow$  **15** in Fig. 7-8 and the discussion in the Sect. before (3.2). The position of the RO<sub>2</sub> radical signal of  $O-C_{14}H_{23-\alpha}(O)(OOH)_\alpha O_2$  with  $\alpha = 2$  at nominal 381 Th and its corresponding closed-shell product C<sub>14</sub>H<sub>22</sub>O<sub>7</sub> at nominal 364 Th were shifted by two nominal mass units in presence of D<sub>2</sub>O. The insertion of a next oxygen molecule leads to the formation of the RO<sub>2</sub> radical  $O-C_{14}H_{23-\alpha}(O)(OOH)_\alpha O_2$  with  $\alpha = 3$  detected at nominal 413 Th, and its closed-shell product at nominal 396 Th. Both signals were shifted by three nominal mass units in presence of D<sub>2</sub>O. Signals of reaction products from the “ext. AutOx. -CO<sub>2</sub>” group with more than ten oxygen atoms and more than three hydroperoxide moieties were not detected.

### 10 3.4 Mechanism of HOM formation

Figures 5-6-7-8 show the proposed initial reaction steps of the ozonolysis of  $\beta$ -caryophyllene with a focus on the HOM formation. The reaction is initiated by the ozone attack at the more reactive, endocyclic double bond of  $\beta$ -caryophyllene **1** marked by the orange oval in Fig. 5-6. The rate coefficient of the reaction of ozone with the endocyclic double bond is about 100 times higher than that of the exocyclic double bond (Winterhalter et al., 2009). Therefore, the reaction of ozone with the exocyclic double bond is neglected here. The reaction of ozone with a double bond is exothermic and forms carbonyl oxides, the so-called Criegee intermediates (CIs), **2a** and **2b** (Criegee, 1975). Due to the reaction exothermicity, the CIs exist initially with a large amount of excess energy (chemically activated CIs), which is stepwise lost by collisions with the bath gas molecules (Kroll et al., 2001). CIs with an internal energy below a definite threshold energy, needed for prompt decomposition, are called stabilized CIs (Vereecken and Francisco, 2012). Both, stabilized and chemically activated CIs, can undergo unimolecular reactions or can be further collisionally stabilized by the bath gas (Kroll et al., 2001; Vereecken et al., 2012). Stabilized CIs can also react in a variety of bimolecular reactions depending on their molecular structure (Vereecken et al., 2012). An important unimolecular isomerization step gives the corresponding vinyl hydroperoxide **3a**, **3b** and **3c** (Drozd et al., 2011; Kroll et al., 2001; Vereecken et al., 2012) that further decomposes under OH radical release and formation of the alkyl radicals **4a**, **4b** and **4c**. For simplicity, the reaction scheme does not differentiate between excited and stabilized molecules.

Figure 6-7 focuses on further reaction pathways of the alkyl radical **4b**. It is supposed that **4a** and **4c** are reacting similarly. Molecular oxygen rapidly adds to **4b** forming the first RO<sub>2</sub> radical **5**. Species **5** can either react via an intramolecular H-transfer, **5**  $\rightarrow$  **6**, followed by O<sub>2</sub> addition forming the RO<sub>2</sub> radical **7** from the product group “norm. AutOx.”,  $O,O-C_{15}H_{23-x}(OOH)_x O_2$  with  $x = 1$ , or **5** can internally attack the remaining double bond forming an endoperoxide and an alkyl radical, **5**  $\rightarrow$  **5'**  $\rightarrow$  **8**, and after O<sub>2</sub> addition the RO<sub>2</sub> radical **9**. This cyclisation leads to an O<sub>2</sub> insertion without forming a hydroperoxide moiety, indicated by “(OO)” in the formula  $O,O-C_{15}H_{23-y}(OO)(OOH)_y O_2$  of the product group “ext. AutOx.”. “(OO)” represents the endoperoxide group. The RO<sub>2</sub> radical **9** can be further oxidized via the autoxidation mechanism forming



RO<sub>2</sub> radicals belonging to the product group “ext. AutOx.”, O,O-C<sub>15</sub>H<sub>23-y</sub>(OO)(OOH)<sub>y</sub>O<sub>2</sub> with y = 1-4, not shown here. A similar endoperoxide formation was already predicted for the OH radical-initiated oxidation of aromatic compounds (Andino et al., 1996; Bartolotti and Edney, 1995; Berndt and Böge, 2006; Ghigo and Tonachini, 1999; Suh et al., 2003). Berndt et al. (2015b) validated the formation of endoperoxide-group containing RO<sub>2</sub> radicals from the OH radical-initiated oxidation of mesitylene (1,3,5-trimethylbenzene) based on the detection of accretion products of these RO<sub>2</sub> radicals. Endoperoxide formation was also proposed from theoretical investigations for the reaction of OH radicals with the monoterpenes α- and β-pinene (Vereecken et al., 2007; Vereecken and Peeters, 2004; Vereecken and Peeters, 2012) and tentatively confirmed in chamber experiments (Eddingsaas et al., 2012).

Figure 7-8 shows the further reaction pathways of the RO<sub>2</sub> radical **7** from the “norm. AutOx.” group, O,O-C<sub>15</sub>H<sub>23-x</sub>(OOH)<sub>x</sub>O<sub>2</sub> with x = 1. The step **7** → **10a** → **11** is an intramolecular H-transfer with subsequent O<sub>2</sub> addition under formation of the RO<sub>2</sub> radical **11**, O,O-C<sub>15</sub>H<sub>23-x</sub>(OOH)<sub>x</sub>O<sub>2</sub> with x = 2 (“norm. AutOx.”). Furthermore, the closed-shell product **12** can be formed via intramolecular H-transfer and subsequent OH radical elimination, **7** → **10b** → **12**. The formation of HOMs from the “ext. AutOx.” group can be explained by the internal RO<sub>2</sub> radical reaction with the remaining double bond. This might lead to the cyclization product **13** that subsequently adds O<sub>2</sub> forming the next RO<sub>2</sub> radical **14**, O,O-C<sub>15</sub>H<sub>23-y</sub>(OO)(OOH)<sub>y</sub>O<sub>2</sub> with y = 1. The formation of HOMs from the product group “ext. AutOx. -CO<sub>2</sub>” is uncertain at the moment. A possible reaction sequence starting from the RO<sub>2</sub> radical **7** is shown in Fig. 7-8, **7** → **7'** → **15** → **16** → **17**. In this reaction mechanism an epoxidation step is proposed, **7'** → **15**. Subsequently, CO<sub>2</sub> is eliminated from the acylalkoxy radical functional group, **15** → **16**, resulting in an alkyl radical **16** that rapidly adds O<sub>2</sub> forming the RO<sub>2</sub> radical **17**. This new RO<sub>2</sub> radical **17**, O-C<sub>14</sub>H<sub>23-α</sub>(O)(OOH)<sub>α</sub>O<sub>2</sub> with α = 1, can further react via autoxidation, i.e. intramolecular H-transfer and subsequent O<sub>2</sub> addition, forming the next RO<sub>2</sub> radicals of the “ext. AutOx. -CO<sub>2</sub>” group with α = 2 and 3.

The epoxide formation cannot be proven and represents only a proposed reaction pathway in order to explain the experimental results. A similar epoxide formation step was postulated for the OH radical-initiated oxidation of aromatic compounds (Bartolotti and Edney, 1995; Glowacki et al., 2009; Motta et al., 2002; Pan and Wang, 2014; Suh et al., 2003; Yu and Jeffries, 1997). Possible reaction products, e.g. epoxide carbonyls, were detected in small quantities using GC-MS analysis (Glowacki et al., 2009; Yu and Jeffries, 1997).

The Figures 5-6-7-8 show the proposed reaction paths leading to the first RO<sub>2</sub> radicals of all three product groups. Consecutive oxidation processes lead to the next RO<sub>2</sub> radicals in competition to termination-bimolecular reactions like RO<sub>2</sub> + R'O<sub>2</sub>, or RO<sub>2</sub> + NO. The formation of first-generation closed-shell products from highly oxidized RO<sub>2</sub> radicals is discussed by Jokinen et al. (2014) and is not included here.

### 30 3.5 Experiment with addition of the sCI scavenger CH<sub>3</sub>COOH

A measurement series in the presence of acetic acid (CH<sub>3</sub>COOH) has been conducted in order to get an indication whether the HOM formation starts from the chemically activated CI or from the collisionally stabilized CI (sCI), species **2a** and **2b** in Fig.

89. Small organic acid were found to efficiently react with sCIs (Beck et al., 2011; Neeb et al., 1996) while chemically activated CIs exclusively react via unimolecular reactions, and bimolecular reactions with other species (such as acids) can be neglected (Vereecken and Francisco, 2012) , see also Sect. 3.4.

Figure 8-9 shows the concentrations of three highly oxidized RO<sub>2</sub> radicals from the three product groups as a function of the acetic acid (CH<sub>3</sub>COOH) concentration in the reaction gas. ~~These measurements were performed applying nitrate ionization. The analysis has been done using nitrate ionization.~~ Additionally, also acetic acid was detectable by the (CH<sub>3</sub>COOH)NO<sub>3</sub><sup>-</sup> adduct. The stated (lower limit) adduct concentrations are by a factor of 2 x 10<sup>7</sup> smaller than the acetic acid concentration in the reaction gas. Even for the highest CH<sub>3</sub>COOH concentrations of 1.4 x 10<sup>14</sup> molecules cm<sup>-3</sup>, no influence of the HOM concentrations on the acid concentration was detected, ~~see (Fig. 89).~~

The absolute rate coefficient of the reaction of acetic acid with sCIs (CH<sub>2</sub>OO or CH<sub>3</sub>CHOO) was measured at 4 torr and 298 K to (1.2-2.5) x 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Welz et al., 2014). Assuming a value of 2 x 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the rate coefficient of the reaction of acetic acid with the sCIs from β-caryophyllene ozonolysis, a sCI lifetime with respect to this reaction of 3.6 x 10<sup>-5</sup> s ~~at using~~ [CH<sub>3</sub>COOH] = 1.4 x 10<sup>14</sup> molecules cm<sup>-3</sup> follows. The sCI lifetime with respect to the unimolecular reactions, **2a** → **3a** and **2b** → **3b/c**, is substantial longer with 4 x 10<sup>-3</sup> s assuming the kinetic data for the largest sCI ((CH<sub>3</sub>)<sub>2</sub>COO) available ~~in the literature~~ (Olzmann et al., 1997). That means that ~~at for~~ [CH<sub>3</sub>COOH] > 10<sup>13</sup> molecules cm<sup>-3</sup>, the fate of the sCIs is ~~most likely~~ dominated by the reaction with CH<sub>3</sub>COOH and the formation of **3a-3c**, the expected precursors species of the HOMs, is suppressed. The absence of any effect of the HOM concentrations on the acetic acid concentration is taken as an indicator, that the sCIs are not involved in the HOM formation. Consequently, the HOM formation is ~~provisionally tentatively~~ attributed to reactions starting from the chemically activated Criegee intermediates.

### 20 3.6 Time dependence of RO<sub>2</sub> radical formation

All previous experiments were conducted with a reaction time of 7.9 s. A variation of the reaction time allowed to examine the possible time dependence of the reaction processes.

Therefore, the reaction time was varied for constant initial conditions in the time range of 3.0-7.9 s using acetate ionization and the concentration changes of RO<sub>2</sub> radical from all three product groups were investigated, see Fig. 910. All RO<sub>2</sub> radical concentrations increased proportionally with time. That shows first, that no significant RO<sub>2</sub> radical consumption occurred at these reaction conditions. Secondly, the interconversion of all RO<sub>2</sub> radicals, including the RO<sub>2</sub> radicals from the “ext. AutOx” group with a proposed endoperoxide formation and those from the “ext. AutOx. -CO<sub>2</sub>” group with ~~a the~~ proposed CO<sub>2</sub> elimination, proceeds at a time scale of seconds, i.e. with a rate coefficient ≥ 1 s<sup>-1</sup>. The RO<sub>2</sub> concentrations increased by a factor of 2.3-2.7 from the shortest to the longest reaction time which is ~~close almost identical~~ to the ~~time~~ increase of the reaction time ~~by a~~ factor of 2.6. This finding differs from the results of an investigation of cyclohexene ozonolysis using the same experimental setup where a concentration increase by a factor of 20-35 was detected when extending the reaction time from 1.5 to 7.9 s (Berndt et al., 2015b). This strong increase was explained by the presence a rate limited entrance channel for the

highly oxidized RO<sub>2</sub> radicals detected from the cyclohexene ozonolysis. A similar behavior was not observed for the formation of highly oxidized RO<sub>2</sub> radicals from β-caryophyllene ozonolysis.

#### 4 Conclusion

5 Early reaction intermediates (mainly highly oxidized RO<sub>2</sub> radicals) from the ozonolysis of β-caryophyllene were investigated  
in a free-jet flow system at ambient pressure and a temperature of 295 ± 2 K to study the formation mechanisms of highly  
oxidized multifunctional organic compounds (HOMs).~~The mechanism of the formation of highly oxidized multifunctional~~  
~~organic compounds (HOMs) from the ozonolysis of β-caryophyllene was investigated in a free jet flow system at atmospheric~~  
~~pressure and a temperature of 295 ± 2 K. β-Caryophyllene is globally the most emitted sesquiterpene, responsible for up to 70~~  
~~% of regional biogenic volatile organic compound emissions, e.g. in orange orchards (Ciccioli et al., 1999). It is mainly~~  
10 ~~oxidized by ozone under atmospheric conditions.~~ The HOM formation from this reaction was recently studied in this laboratory  
(Richters et al., 2016). Different reaction products were detected, that could not be assigned to the class of highly oxidized  
RO<sub>2</sub> radicals formed via the “normal” autoxidation mechanism (Jokinen et al., 2014; Richters et al., 2016). This behavior was  
attributed to the presence of a second double bond in β-caryophyllene which enables further reaction channels. These, ~~up to~~  
~~now undiscovered reaction pathways~~ new insights in RO<sub>2</sub> radical reaction pathways were investigated with the help of labeling  
15 experiments using heavy water and isotopically labeled ozone (<sup>18</sup>O<sub>3</sub>). The experimental results allowed to tentatively postulate  
extended autoxidation mechanisms including i) the formation of an endoperoxide moiety in the RO<sub>2</sub> radicals (“ext. AutOx”  
group) and ii) a CO<sub>2</sub> elimination in presence of an unsaturated peroxy acyl radical (“ext. AutOx -CO<sub>2</sub>” group).  
Time-dependent investigations of the formation of highly oxidized RO<sub>2</sub> radicals showed that all RO<sub>2</sub> radicals are formed on a  
time scale of less than three seconds. Experiments with acetic acid, serving as a scavenger of stabilized Criegee intermediates,  
20 indicated that HOM formation most likely proceeds via reactions of the chemically excited Criegee intermediates formed as  
an early reaction product from the ozonolysis of β-caryophyllene.  
In conclusion, this study provides insights in new reaction pathways that extend the autoxidation mechanism for unsaturated  
RO<sub>2</sub> radicals in the gas phase. About two thirds of the total molar HOM yield from the ozonolysis of β-caryophyllene can be  
explained with the help of these new reaction pathways. Further work is needed to validate the proposed reaction steps of the  
25 extended autoxidation mechanism.

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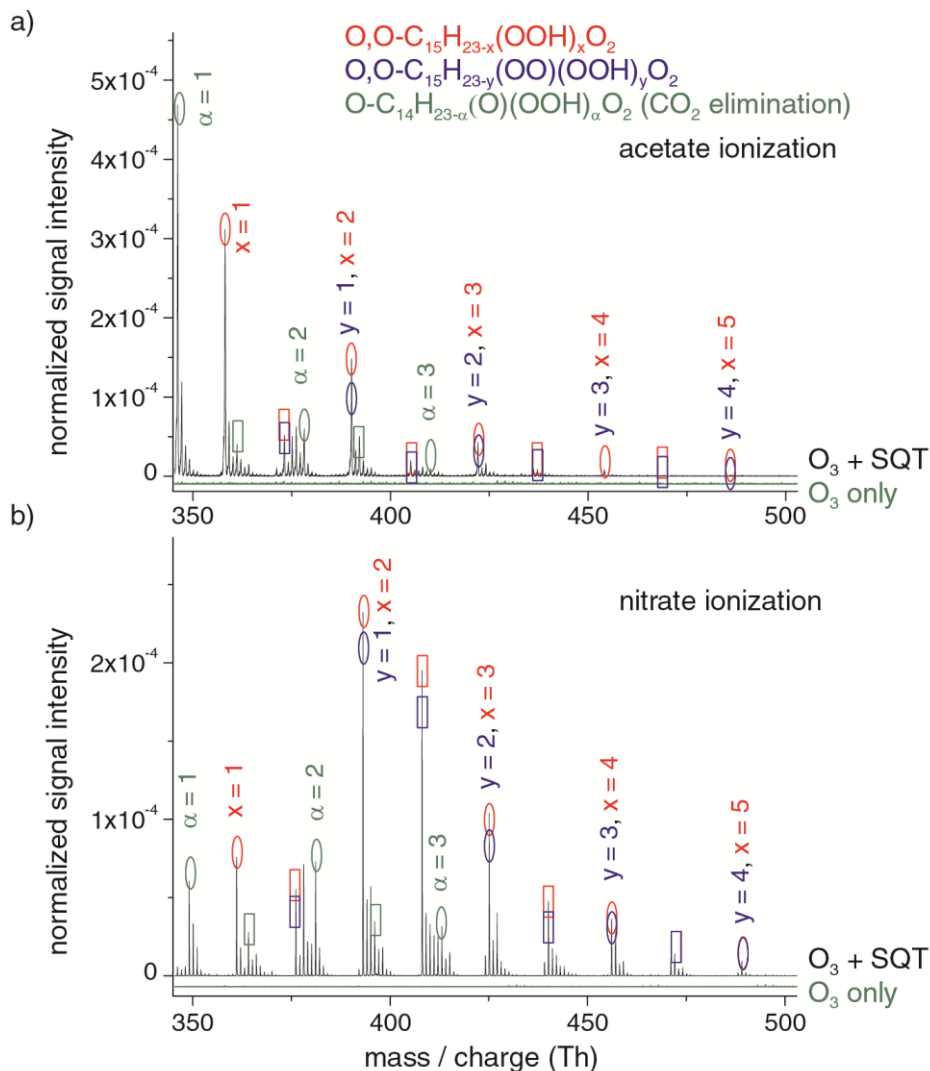
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**Table 1.** Highly oxidized reaction products from the ozonolysis of  $\beta$ -caryophyllene detected as nitrate ion adducts and acetate ion adducts using CI-API-TOF mass spectrometry. Products were categorized into three product groups, i.e. “norm. AutOx.”, “ext. AutOx.” and “ext. AutOx. -CO<sub>2</sub>”. Signals from the “norm. AutOx.” and “ext. AutOx.” groups were detected at the same mass-to-charge ratio. The percentages indicate the contribution of a signal to the different product groups, “norm. AutOx.” and “ext. AutOx.”, as elucidated by H/D exchange experiments using nitrate ionization.

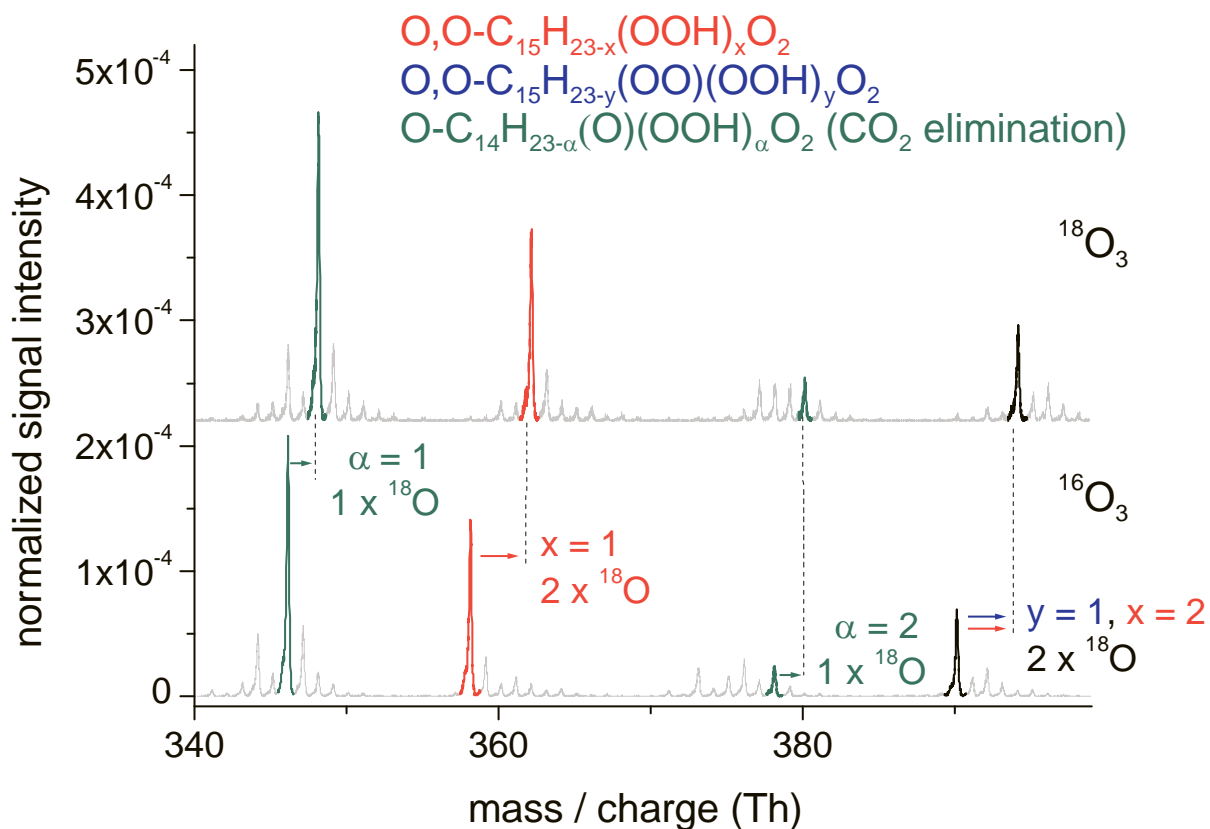
Nominal mass-to-charge ratio		Molecular formula	Product group (contribution to the total signal (%))		RO <sub>2</sub> radical	Closed-shell product
nitrate ion adducts	acetate ion adducts					
349	346	C <sub>14</sub> H <sub>23</sub> O <sub>6</sub>	ext. AutOx. -CO <sub>2</sub>		O-C <sub>14</sub> H <sub>22</sub> (O)(OOH)O <sub>2</sub>	
361	358	C <sub>15</sub> H <sub>23</sub> O <sub>6</sub>	norm. AutOx.		O,O-C <sub>15</sub> H <sub>22</sub> (OOH)O <sub>2</sub>	
364	361	C <sub>14</sub> H <sub>22</sub> O <sub>7</sub>	ext. AutOx. -CO <sub>2</sub>			O-C <sub>14</sub> H <sub>20</sub> O(O)(OOH) <sub>2</sub>
376	373	C <sub>15</sub> H <sub>22</sub> O <sub>7</sub>	norm. AutOx.	(56 %)		O,O-C <sub>15</sub> H <sub>20</sub> O(OOH) <sub>2</sub>
		C <sub>15</sub> H <sub>22</sub> O <sub>7</sub>	ext. AutOx.	(44 %)		O,O-C <sub>15</sub> H <sub>21</sub> O(OO)(OOH)
381	378	C <sub>14</sub> H <sub>23</sub> O <sub>8</sub>	ext. AutOx. -CO <sub>2</sub>		O-C <sub>14</sub> H <sub>21</sub> (O)(OOH) <sub>2</sub> O <sub>2</sub>	
393	390	C <sub>15</sub> H <sub>23</sub> O <sub>8</sub>	norm. AutOx.	(31 %)	O,O-C <sub>15</sub> H <sub>21</sub> (OOH) <sub>2</sub> O <sub>2</sub>	
			ext. AutOx.	(69 %)	O,O-C <sub>15</sub> H <sub>22</sub> (OO)(OOH)O <sub>2</sub>	
396	393	C <sub>14</sub> H <sub>22</sub> O <sub>9</sub>	ext. AutOx. -CO <sub>2</sub>			O-C <sub>14</sub> H <sub>19</sub> O(O)(OOH) <sub>3</sub>
408	405	C <sub>15</sub> H <sub>22</sub> O <sub>9</sub>	norm. AutOx.	(30 %)		O,O-C <sub>15</sub> H <sub>19</sub> O(OOH) <sub>3</sub>
		C <sub>15</sub> H <sub>22</sub> O <sub>9</sub>	ext. AutOx.	(70 %)		O,O-C <sub>15</sub> H <sub>20</sub> O(OO)(OOH) <sub>2</sub>
413	410	C <sub>14</sub> H <sub>23</sub> O <sub>10</sub>	ext. AutOx. -CO <sub>2</sub>		O-C <sub>14</sub> H <sub>20</sub> (O)(OOH) <sub>3</sub> O <sub>2</sub>	
425	422	C <sub>15</sub> H <sub>23</sub> O <sub>10</sub>	norm. AutOx.	(29 %)	O,O-C <sub>15</sub> H <sub>20</sub> (OOH) <sub>3</sub> O <sub>2</sub>	
		C <sub>15</sub> H <sub>22</sub> O <sub>9</sub>	ext. AutOx.	(71 %)	O,O-C <sub>15</sub> H <sub>21</sub> (OO)(OOH) <sub>2</sub> O <sub>2</sub>	
440	437	C <sub>15</sub> H <sub>22</sub> O <sub>11</sub>	norm. AutOx.	(29 %)		O,O-C <sub>15</sub> H <sub>18</sub> O(OOH) <sub>4</sub>
		C <sub>15</sub> H <sub>22</sub> O <sub>11</sub>	ext. AutOx.	(71 %)		O,O-C <sub>15</sub> H <sub>19</sub> O(OO)(OOH) <sub>3</sub>
457	454	C <sub>15</sub> H <sub>23</sub> O <sub>12</sub>	norm. AutOx.	(25 %)	O,O-C <sub>15</sub> H <sub>19</sub> (OOH) <sub>4</sub> O <sub>2</sub>	
		C <sub>15</sub> H <sub>23</sub> O <sub>12</sub>	ext. AutOx.	(75 %)	O,O-C <sub>15</sub> H <sub>20</sub> (OO)(OOH) <sub>3</sub> O <sub>2</sub>	
472	469	C <sub>15</sub> H <sub>22</sub> O <sub>13</sub>	norm. AutOx.	(22 %)		O,O-C <sub>15</sub> H <sub>17</sub> O(OOH) <sub>5</sub>
		C <sub>15</sub> H <sub>22</sub> O <sub>13</sub>	ext. AutOx.	(78 %)		O,O-C <sub>15</sub> H <sub>18</sub> O(OO)(OOH) <sub>4</sub>
489	486	C <sub>15</sub> H <sub>23</sub> O <sub>14</sub>	norm. AutOx.	(22 %)	O,O-C <sub>15</sub> H <sub>18</sub> (OOH) <sub>5</sub> O <sub>2</sub>	
		C <sub>15</sub> H <sub>23</sub> O <sub>14</sub>	ext. AutOx.	(78 %)	O,O-C <sub>15</sub> H <sub>19</sub> (OO)(OOH) <sub>4</sub> O <sub>2</sub>	



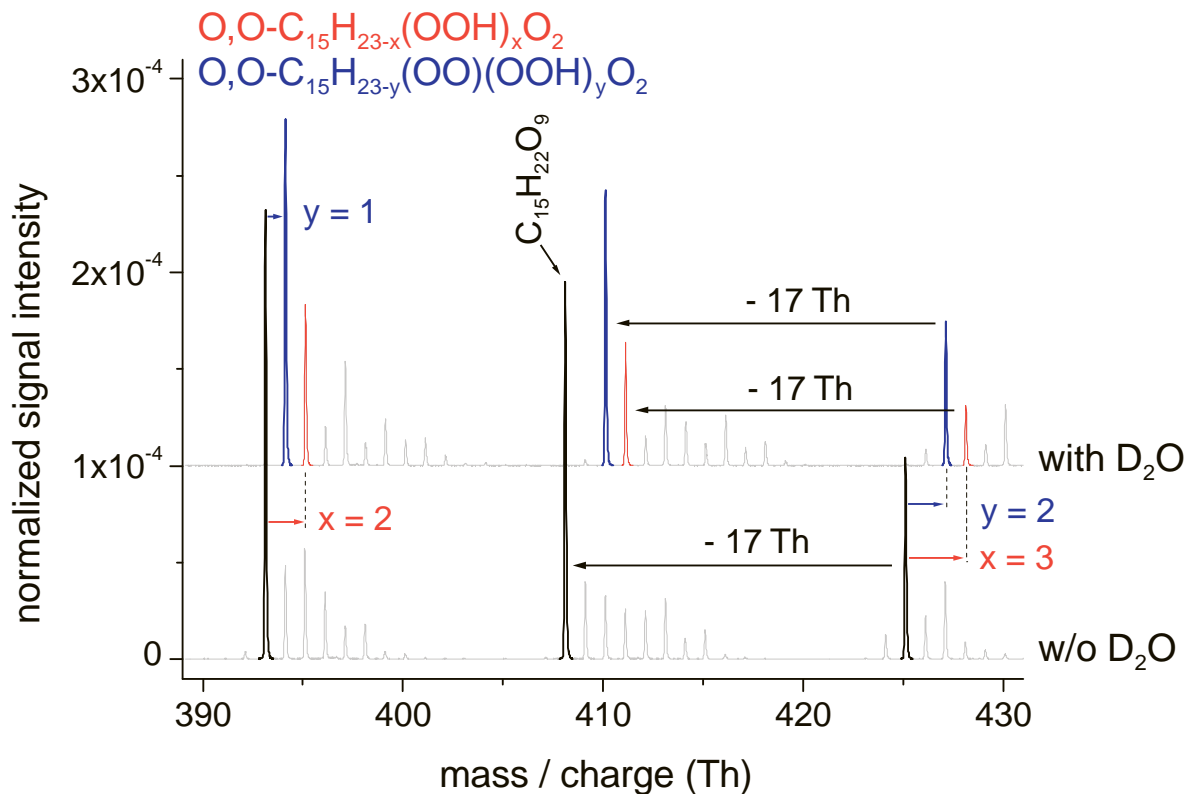


**Figure 1.** Highly oxidized RO<sub>2</sub> radicals of the three product groups “norm. AutOx.”, O<sub>3</sub>O-C<sub>15</sub>H<sub>23-x</sub>(OOH)<sub>x</sub>O<sub>2</sub> with x = 1-5 (in red), “ext. AutOx.”, O<sub>3</sub>O-C<sub>15</sub>H<sub>23-y</sub>(OO)(OOH)<sub>y</sub>O<sub>2</sub> with y = 1-4 (in blue) and “ext. AutOx. -CO<sub>2</sub>”, O-C<sub>14</sub>H<sub>23-α</sub>(O)(OOH)<sub>α</sub>O<sub>2</sub> with α = 1-3 (in green), and corresponding closed-shell products (rectangular lines) appearing at -17 nominal mass units regarding the corresponding RO<sub>2</sub> radical. The products were detected by means of a) acetate ionization and b) nitrate ionization. The same molecule gives a signal shifted by three nominal mass units comparing the acetate ion adducts (+59 nominal mass units) with the nitrate ion adducts (+62 nominal mass units). The mass spectra were normalized by their reagent ion counts. Signals from the “norm. AutOx.” group and the “ext. AutOx.” group were detected at the same mass-to-charge ratio. The green spectrum lines (O<sub>3</sub> only) shows the background experiments in which only ozone (no SQT) was present. The data of Fig. 1b was taken from Richters et al. (2016). [β-caryophyllene] = 8.6 × 10<sup>10</sup> (acetate ionization);

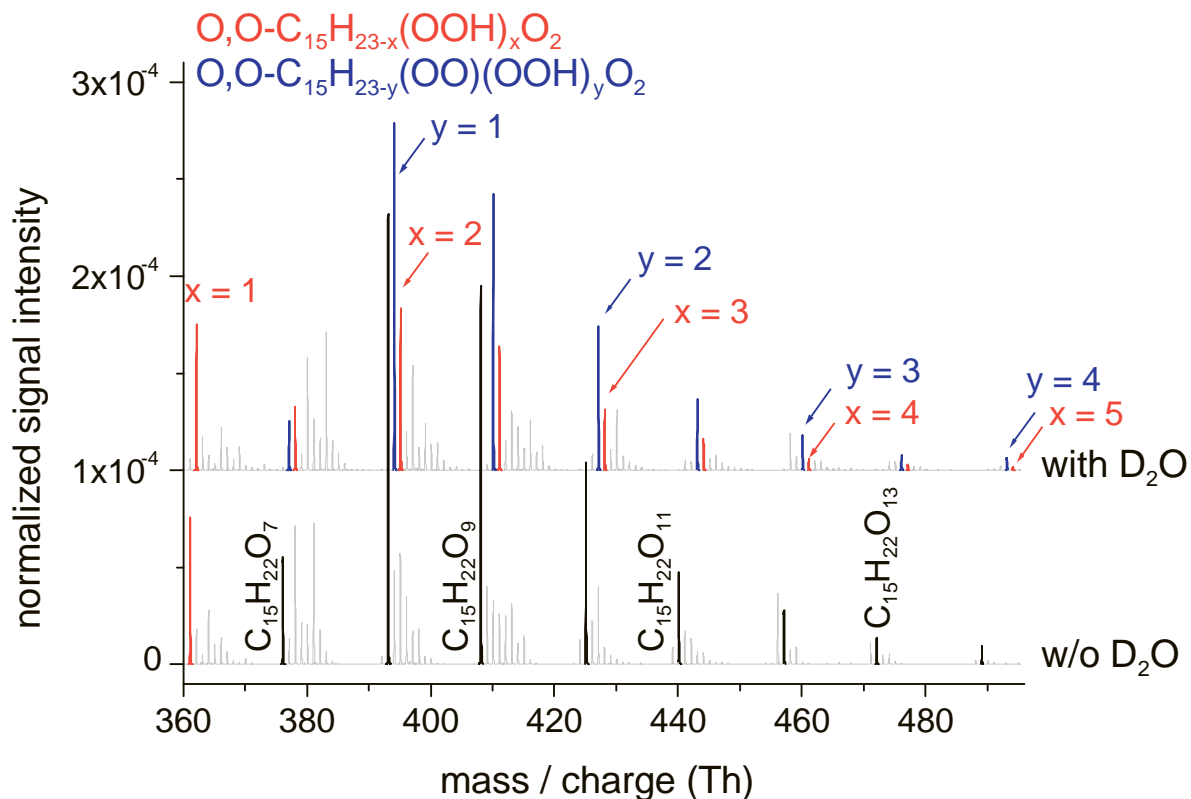
10 [β-caryophyllene] = 8.3 × 10<sup>10</sup> (nitrate ionization); [O<sub>3</sub>] = 1.02 × 10<sup>12</sup> molecules cm<sup>-3</sup>; reaction time: 7.9 s.



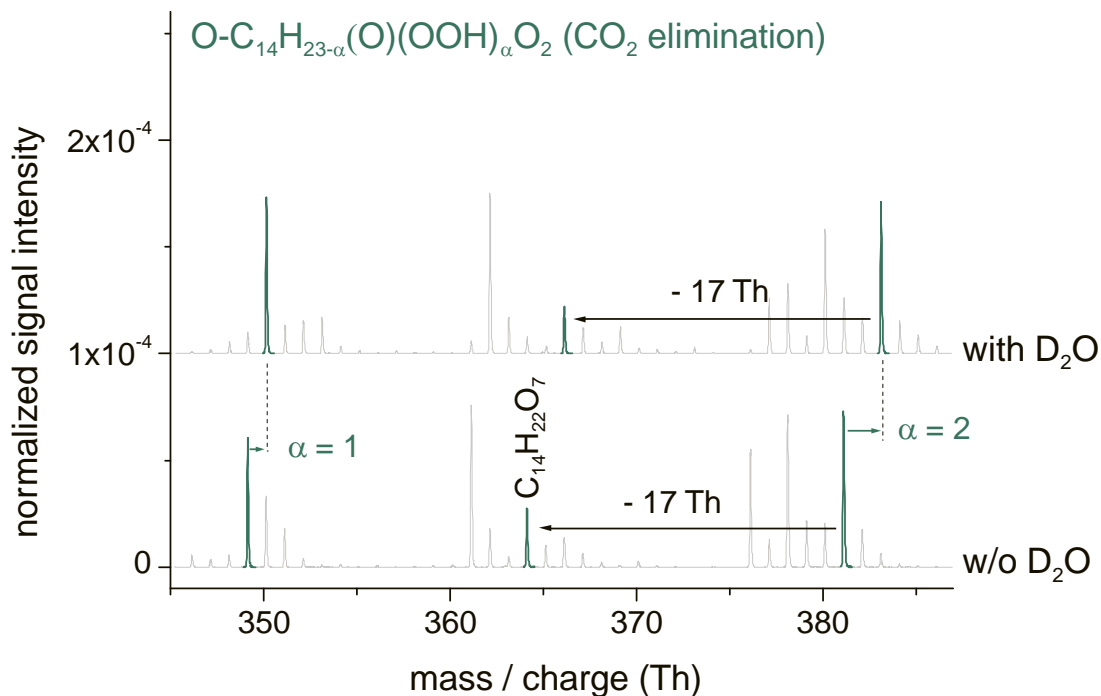
**Figure 2.** Ozonolysis of  $\beta$ -caryophyllene using  $^{16}O_3$  (lower part) and  $^{18}O_3$  (upper part) and applying acetate ionization in the analysis. Highly oxidized  $RO_2$  radicals of the three product groups “norm. AutOx.”,  $O,O-C_{15}H_{23-x}(OOH)_xO_2$  with  $x = 1$  and 2 (in red), “ext. AutOx.”,  $O,O-C_{15}H_{23-y}(OO)(OOH)_yO_2$  with  $y = 1$  (in black signal with blue label) and “ext. AutOx - $CO_2$ ”,  $O-C_{14}H_{23-\alpha}(O)(OOH)_\alpha O_2$  with  $\alpha = 1$  and 2 (in green) were detected. The black colored signals at nominal 390 Th ( $^{16}O_3$ ) and nominal 394 Th ( $^{18}O_3$ ) stand for the sum of the signal from the “norm. AutOx.”  $RO_2$  radical  $O,O-C_{15}H_{23-x}(OOH)_xO_2$  with  $x = 2$  and from the “ext. AutOx.”  $RO_2$  radical  $O,O-C_{15}H_{23-y}(OO)(OOH)_yO_2$  with  $y = 1$ . Only the arrows and inscriptions ( $y = 1; x = 2$ ) indicate the colors of the product groups. When exchanging  $^{16}O_3$  by  $^{18}O_3$ , the signals were shifted by two nominal mass units for each oxygen atom arising from the initial ozone attack. [ $\beta$ -caryophyllene] =  $8.6 \times 10^{10}$ ; [ $O_3$ ] =  $8.8 \times 10^{11}$  molecules  $cm^{-3}$ ; reaction time: 7.9 s.



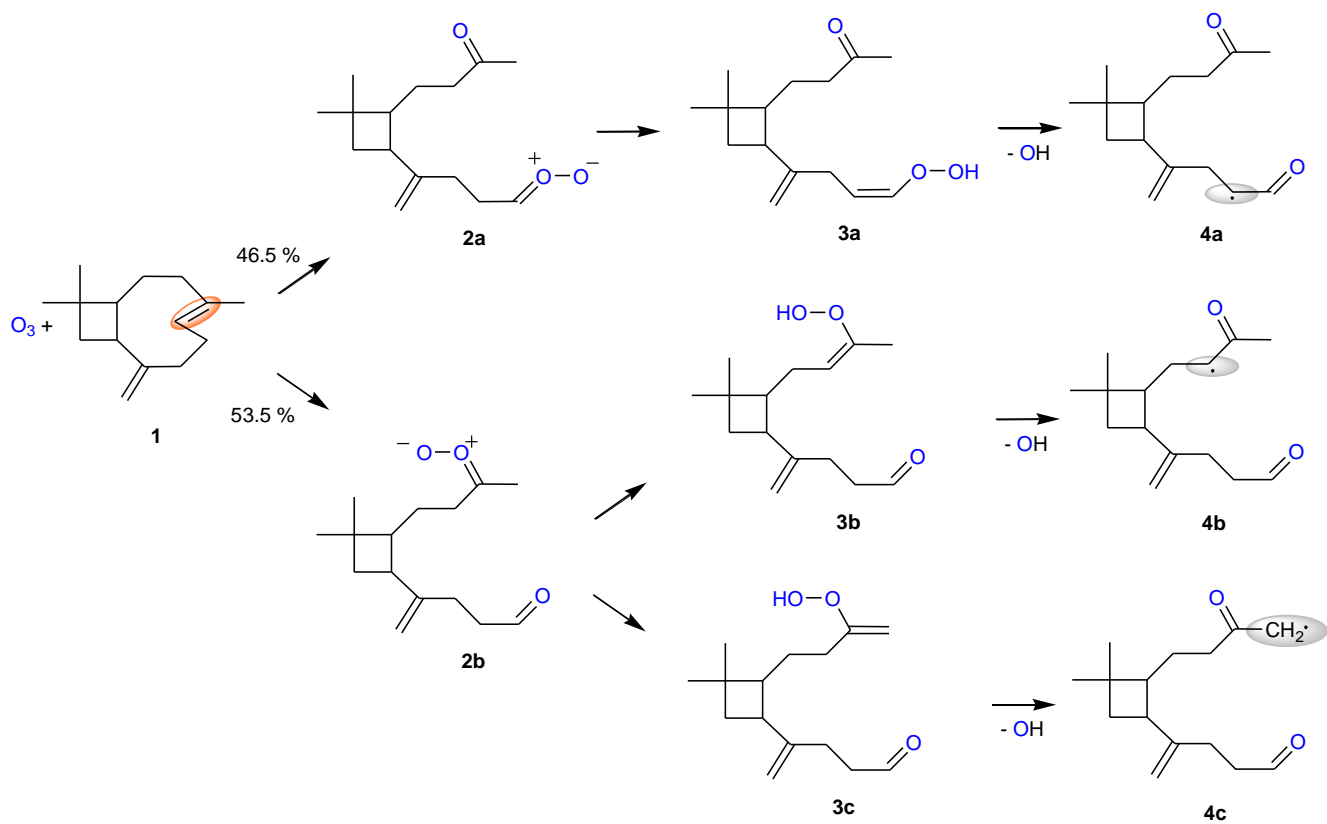
**Figure 3.** Ozonolysis of  $\beta$ -caryophyllene, in the absence (lower part) and presence (upper part) of  $D_2O$  applying nitrate ionization in the analysis. Signals highlighted in black stand for the sum of signals in the absence of  $D_2O$  from highly oxidized  $RO_2$  radicals of the product groups “norm. AutOx.”,  $O_1O-C_{15}H_{23-x}(OOH)_xO_2$  with  $x = 2$  and 3, and “ext. AutOx.”,  $O_1O-C_{15}H_{23-y}(OO)(OOH)_yO_2$ , with  $y = 1$  and 2, and the corresponding closed-shell product  $C_{15}H_{22}O_9$  of the  $RO_2$  radicals for  $x = 3$  or  $y = 2$ . The addition of  $D_2O$  leads to an H/D exchange of all acidic H atoms present in the molecule. ~~With that~~ Accordingly, 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.  $[\beta\text{-caryophyllene}] = 8.3 \times 10^{10}$ ;  $[O_3] = 1.02 \times 10^{12} \text{ molecules cm}^{-3}$ ; reaction time: 7.9 s.



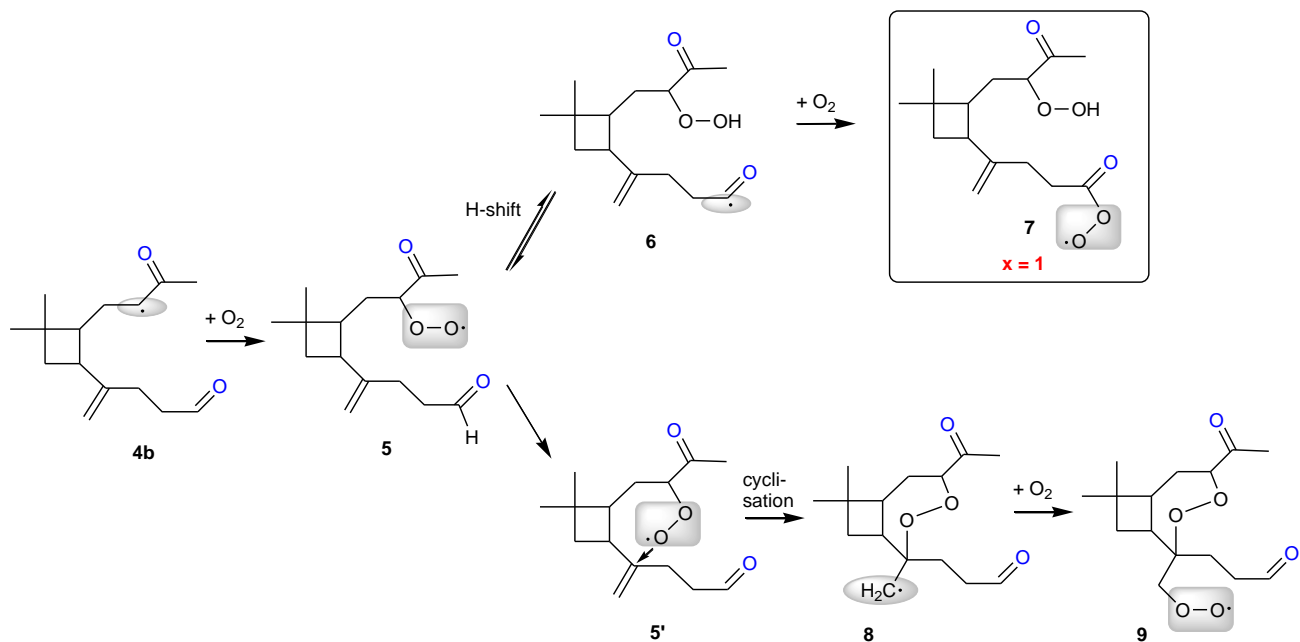
**Figure 4.** Ozonolysis of  $\beta$ -caryophyllene, in the absence (lower part) and presence (upper part) of  $D_2O$  applying nitrate ionization in the analysis. Signals highlighted in black stand for the sum of signals in the absence of  $D_2O$  from highly oxidized  $RO_2$  radicals of the product groups “norm. AutOx.”,  $O,O-C_{15}H_{23-x}(OOH)_xO_2$  with  $x = 2-5$ , and “ext. AutOx.”,  $O,O-C_{15}H_{23-y}(OO)(OOH)_yO_2$ , 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. Accordingly, 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  $O,O-C_{15}H_{23-x}(OOH)_xO_2$  with  $x = 1$  and is highlighted in red.  $[\beta\text{-caryophyllene}] = 8.3 \times 10^{10}$ ;  $[O_3] = 1.02 \times 10^{12}$  molecules  $cm^{-3}$ ; reaction time: 7.9 s.



**Figure 54.** Ozonolysis of  $\beta$ -caryophyllene in the absence (lower part) and presence (upper part) of  $\text{D}_2\text{O}$  applying nitrate ionization in the analysis. Highly oxidized  $\text{RO}_2$  radicals of the product group “ext. AutOx.  $-\text{CO}_2$ ”,  $\text{O-C}_{14}\text{H}_{23-\alpha}(\text{O})(\text{OOH})_{\alpha}\text{O}_2$  with  $\alpha = 1$  and 2 and the corresponding closed-shell product ( $\text{C}_{14}\text{H}_{22}\text{O}_7$ ) of the  $\text{RO}_2$  radical with  $\alpha = 2$  are highlighted in green. The addition of  $\text{D}_2\text{O}$  leads to an H/D exchange of the acidic H atoms being equal to the number of hydroperoxide groups in the molecules, i.e. a shift by one nominal mass unit for  $\alpha = 1$  or a shift by two nominal mass units for  $\alpha = 2$  (including the corresponding closed-shell product). [ $\beta$ -caryophyllene] =  $8.3 \times 10^{10}$ ; [ $\text{O}_3$ ] =  $1.02 \times 10^{12}$  molecules  $\text{cm}^{-3}$ ; reaction time: 7.9 s.

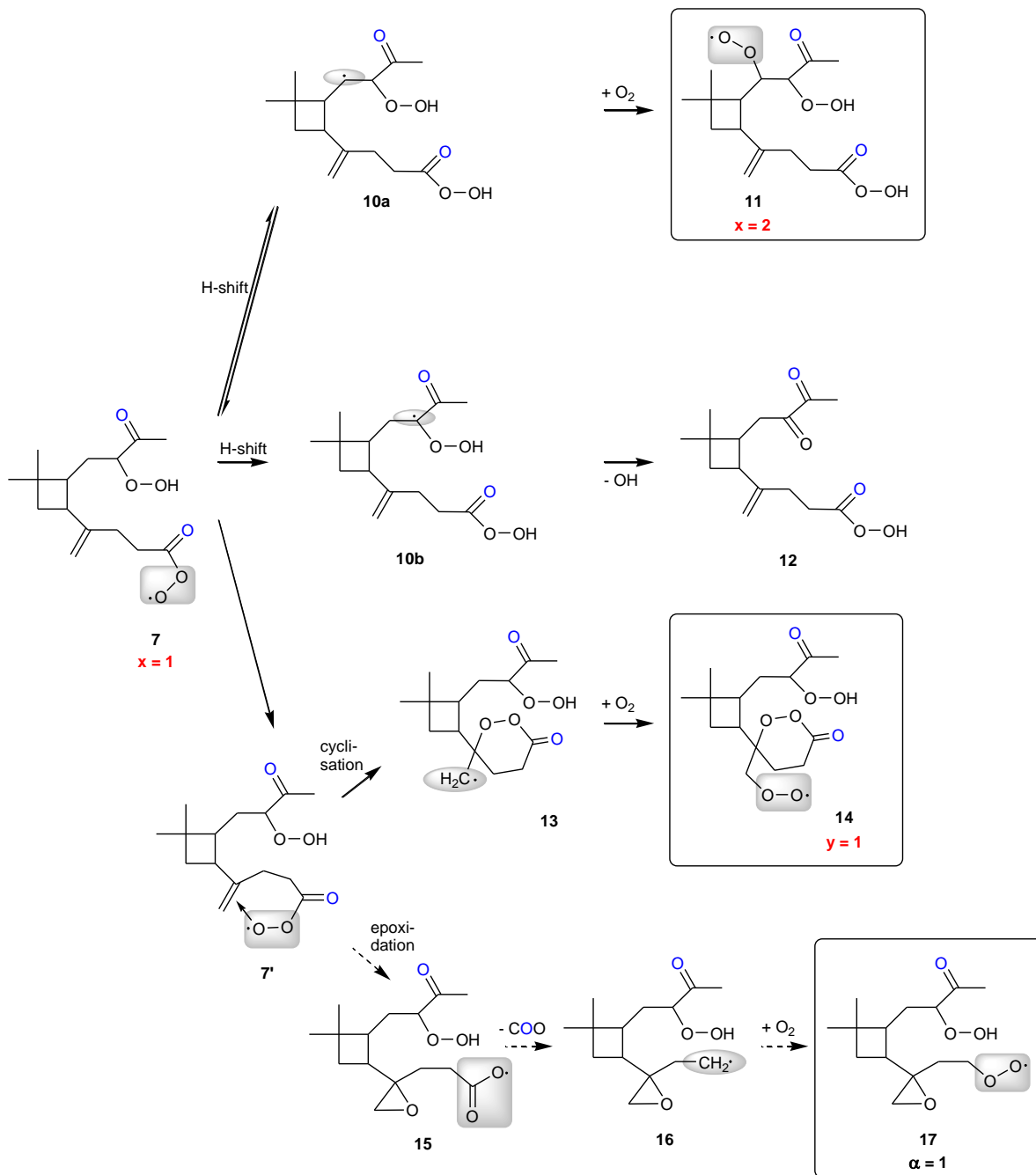


**Figure 65.** First reaction steps of the ozonolysis of  $\beta$ -caryophyllene. The attack of the more reactive endocyclic double bond (highlighted in orange) is exclusively demonstrated. Oxygen atoms arising from the attacking ozone are highlighted in blue, the alkyl radical functional groups with a shaded oval.

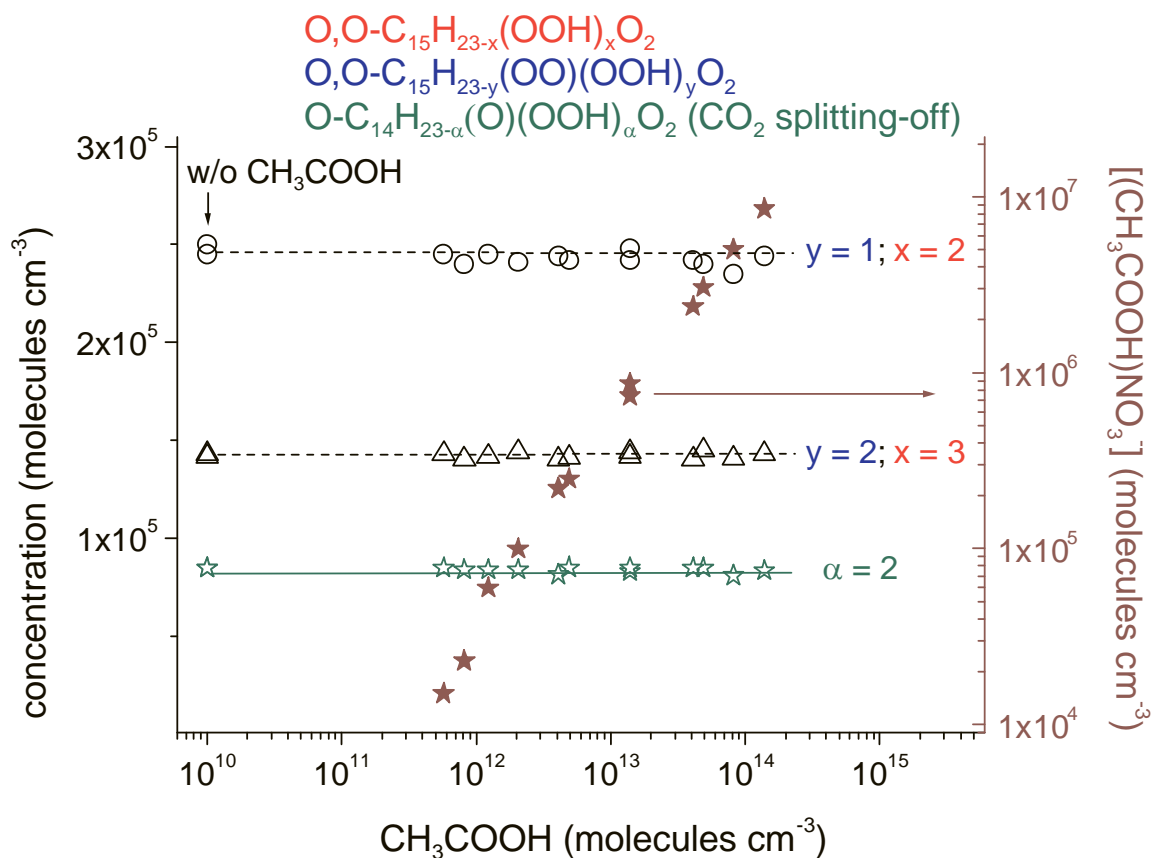


**Figure 76.** Further reaction steps of the alkyl radical 4b. Oxygen atoms arising from the attacking ozone are highlighted in blue, alkyl radical functional groups with a shaded oval and  $RO_2$  radical functional groups with a shaded rectangle. Detected species are surrounded by a solid rectangle. The stated position, where the internal H-transfer takes place  $5 \rightarrow 6$ , represents an examples only.

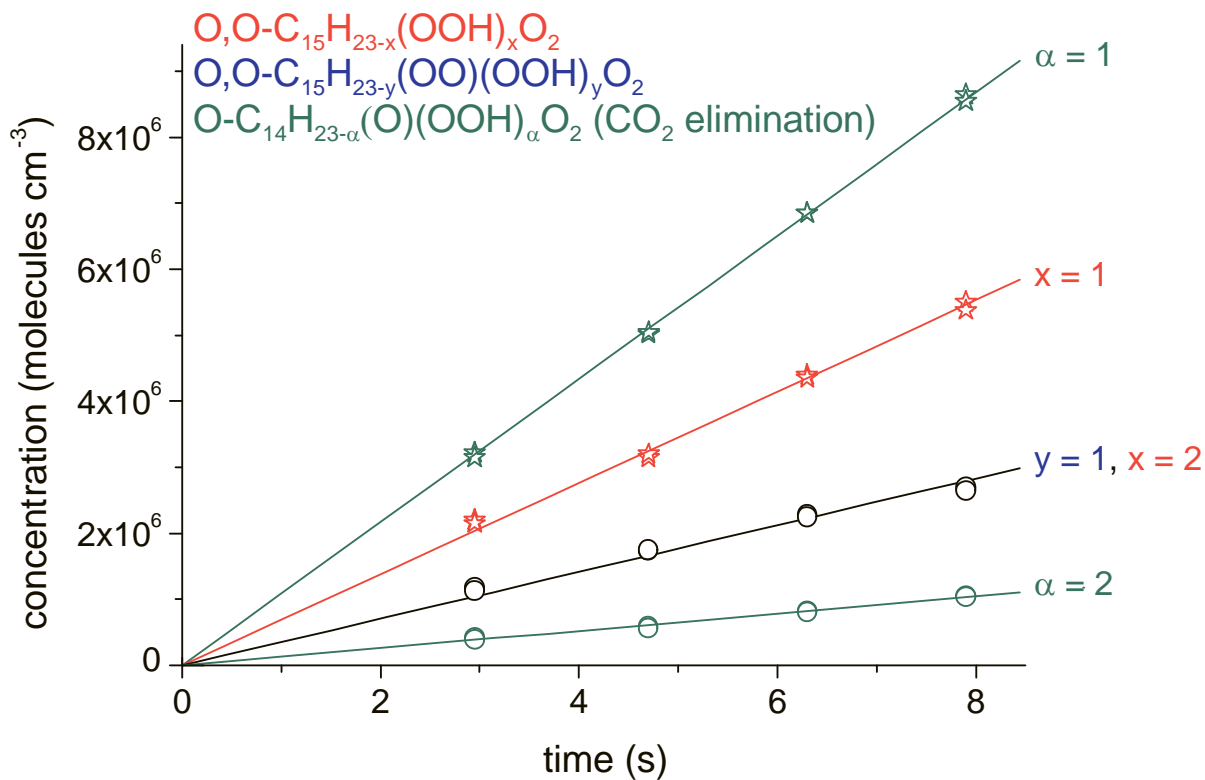




**Figure 87.** Further reaction steps of the RO<sub>2</sub> radical (7). Oxygen atoms arising from the attacking ozone are highlighted in blue, alkyl radical functions with a shaded oval and RO<sub>2</sub> radical functional groups with a shaded rectangle. Detected species are surrounded by a solid rectangle. The stated position, where the internal H-transfer takes place 7 → 10a, represent an example only. The dashed arrows indicate that the stated reaction pathway remains uncertain.



**Figure 98:** Highly oxidized RO<sub>2</sub> radicals from the ozonolysis of β-caryophyllene from the three product groups “norm. AutOx.” with O,O-C<sub>15</sub>H<sub>23-x</sub>(OOH)<sub>x</sub>O<sub>2</sub>, x = 2 and 3, “ext. AutOx.” with O,O-C<sub>15</sub>H<sub>23-y</sub>(OO)(OOH)<sub>y</sub>O<sub>2</sub>, y = 1 and 2, and “ext. AutOx. -CO<sub>2</sub>” with O-C<sub>14</sub>H<sub>23-α</sub>(O)(OOH)<sub>α</sub>O<sub>2</sub>, α = 2 as a function of the CH<sub>3</sub>COOH concentration. CH<sub>3</sub>COOH acts as a sCI scavenger. The black colored data points stand for the RO<sub>2</sub> radicals from the “norm. AutOx” group and from the “ext. AutOx” group with x = 2 and y = 1 (circle) as well as with x = 3 and y = 2 (triangle). The adduct (CH<sub>3</sub>COOH)NO<sub>3</sub><sup>-</sup> was detected with lower-limit concentrations which are a factor of 2 × 10<sup>7</sup> lower than the acetic acid concentration in the tube. [β-caryophyllene] = 8.3 × 10<sup>10</sup>; [O<sub>3</sub>] = 4.7 × 10<sup>10</sup>; [CH<sub>3</sub>COOH] = (0-1.4) × 10<sup>14</sup> molecules cm<sup>-3</sup>; reaction time: 7.9 s.



**Figure 109.** Time dependence of highly oxidized  $RO_2$  radical formation from the ozonolysis of  $\beta$ -caryophyllene using acetate ionization, data from the “norm. AutOx.” group with  $O,O-C_{15}H_{23-x}(OOH)_xO_2$  with  $x = 1$  and 2 (in red), from “ext. AutOx.” with  $O,O-C_{15}H_{23-y}(OO)(OOH)_yO_2$  with  $y = 1$  (in blue) and from “ext. AutOx.  $-CO_2$ ” with  $O-C_{14}H_{23-\alpha}(O)(OOH)_\alpha O_2$  with  $\alpha = 1$  and 2 (in green). The black colored data points (open circles) stand for the sum of the  $RO_2$  radical from the “norm. AutOx” group,  $O,O-C_{15}H_{23-x}(OOH)_xO_2$  with  $x = 2$  and from the “ext. AutOx” group,  $O,O-C_{15}H_{23-y}(OO)(OOH)_yO_2$  with  $y = 1$ .  $[\beta\text{-caryophyllene}] = 8.6 \times 10^{10}$ ;  $[O_3] = 3.1 \times 10^{11}$  molecules  $cm^{-3}$ ; reaction time: 3.0-7.9 s.