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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Oligomer formation during gas-phase ozonolysis of small alkenes and enol ethers: new evidence for the central role of the Criegee Intermediate as oligomer chain unit" *by* A. Sadezky et al.

Anonymous Referee #1

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General comments

The paper describes the identification of oligomers in secondary organic aerosols derived from the ozonolysis of different small alkenes and one enol-ether. Detailed mass spectrometric analysis was used to identify structures or at least the chain carriers of the oligomers. QTOF-MS/MS analyses deliver fragmentation pathways and FT-ICR-MS and MS/MS were used to measure the elemental composition of oligomers and fragments. Results of the measurements were discussed very detailed and often compared to a previous paper of the authors. The authors conclude that stabilized Crigee

Intermediates are responsible for the build up of the oligomers and as a result oligoperoxides were proposed as a likely structure. This structure is the first time observed in secondary aerosols. A detailed literature comparison of peroxides in SOA is given. Appropriate literature is cited in this paper. The used scientific methods are generally adequate. Conclusions are described explicit and can be understood.

The paper deals with an up to date topic. Formation mechanisms of atmospherically relevant and experimentally observed oligomers are still unclear and urgently need to be understood to proceed in the topic of SOA formation. The present work might be a step to a better understanding of SOA formation processes. However, the authors themselves point to the restriction that the experiments were performed far from atmospherically relevant conditions. Water (and other species) might suppress the oligomer formation in the atmosphere by this mechanism acting as a main reactant for the stabilized CIs. Furthermore, concentrations of alkenes and ozone in the experiments are orders of magnitude higher than in the atmosphere.

I have the impression that this paper is unfortunately very long and (maybe therefore) very hard to read. Some discussions and explanations seem to be repeated in the paper resulting in unnecessary extension of the text. Maybe the structure could be improved to get a shorter text and a better readability.

Despite this and some other things described later the underlying work is very valuable and should be published in ACP. However, a few revisions might improve this paper.

Specific comments

Introduction, first paragraph:

SOA is also formed by reactions which are not photooxidation like ozonolysis (used by the authors!) and reaction by NO3 radicals. That should be changed.

Topic: Structure of oligomers Although detailed measurements were carried out the final structure of the oligomers was not determined or at least supposed from the un-

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derlying measurements. This was assigned to future work. On the one hand it is very nice that no ambiguous structures were supposed because a lot of these supposed and ambiguous structures already can be found in the literature. On the other hand it is interesting that initially fragmenting neutrals mostly have a considerably higher mass than the chain units and therefore as the CIs. Elemental compositions from exact mass measurements are not easy to be converted to structures which make sense in respect to involved reactants. The carbon number of the initially fragmented neutrals is different to the CI carbon number or a multiple of it. In the same time the oxygen content seem to be very low for some initially fragmented neutrals. This makes it difficult to find a reaction pathway even if small products like formaldehyde, acetaldehyde, etc. are taken into account. To find a likely structure for the beginning and terminating groups of the oligomers would be nice particularly to verify the proposed oligomeric structure itself.

Topic: Oligomer series, Table 2, Fig. 2(a-d), section 3.3.1

Different observed ion series are marked by a, b, B, C, D, E, F what corresponds to a difference of the molecular weight in relation to ion (a) of +16, -42, -14, +14, +30 and +68, respectively. It might also be true, that B and C correspond to +18 and +46 of the (n-1)-ion and b, D and E correspond to -58, -46 and -30 of the (n+1)-ion, respectively.

Topic elemental compositions, Section 3.3.2.2., Table 3 (a-d)

It is true, that Na+ adducts often lead to an unclear or no fragmentation. However, this is dependent on the structure of the molecule! If e.g. polyethylene glycol is ionized by ESI sodium adducts are easily formed. These ions can be fragmented showing a nice spectrum. If enough oxygen atoms remain as electron pair donors in the fragment ion it is possible to observe a MS/MS spectrum of sodium adducts. Here, only one sentence as explanation for the exclusion of the possibility of sodium adducts does not seem to be appropriate. Furthermore, sometimes sodium adducts fit better or are equal to measured accurate masses than other elemental compositions. This is not true for the

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neutrals. In detail:

Tab. 3a:

measured accurate mass / elemental composition / relative mass error (ppm)

379.19565 / C17H31O9 / -1.6071

379.19565 / C15H32O9Na / +4.736

233.06445 / C9H13O7 / -4.8459

233.06445 / C7H14O7Na / +5.67

159.02772 / C6H7O5 / -6.7906

159.02772 / C4H8O5Na / +8.3318

84.9936 / C3HO3 / +18.585

84.9936 / CH2O3Na / +47.4

Tab. 3b:

395.19255 / C17H31O10 / +3.4816

395.19255 / C15H32O10Na / -9.69

275.11061 / C12H19O7 / -6.9777

275.11061 / C10H20O7Na / +1.9

201.07450 / C9H13O5 / -6.2172

201.07450 / C7H14O5Na / +5.96

For Tab. 3c+3d it is similar. It is clear, that a sodium atom in a fragment is nonsense if it is not present in the parent ion. However, the accuracy of the FTMS is lower than usual (10ppm) as it is written in the experimental section. It might be necessary to think

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about adduct formation to find the true structure of the oligomers.

Technical comments

3.2., third paragraph: Change <Docherty et Ziemann> to <Docherty and Ziemann>

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