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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.

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The authors thank the anonymous referee 1 for carefully reading this large manuscript and giving valuable comments and excellent suggestions regarding the formation of sodium adducts. A further re-measuring of the mass spectra at high resolution proved his suggestions to be correct. This enabled to identify the exact molecular formulas and tentative structures of the oligomers, and thus clarifying several aspects of our manuscript. The referee criticizes the term "Photooxidation". Of course, we meant oxidation by all ways, and we therefore replace the term "photooxidation" by "oxidation". The referee remarks that, in spite of our detailed investigation of the oligomers formed during ozonolysis of the enol ethers and alkenes by ESI(+)/MS and MS/MS techniques, we did not determine or at least suppose their final structure from the underlying measurements. First of all, we would like to note that the elucidation of the detailed structure of the described oligomers was not the main objective of our work. The presented results allow us to unambiguously identify the chain units of the oligomers, which systematically correspond to the main Criegee Intermediate (CI) formed during alkene ozonolysis. Together with the observations from our previous study (Sadezky et al., 2006), they show the formation of oligomers consisting of CI-like chain units during the gas-phase ozonolysis of a variety of small alkenes and enol ethers, representing the main constituents of the formed SOA. While the neutral fragments are clearly identified, the elemental compositions given for the parent and fragment ions are indeed very difficult to convert to chemically meaningful structures, as the referee also remarks. Therefore, we decided to refrain from speculating about the detailed oligomer structures without disposing of any clear facts, and assigned their elucidation to future work. The referee suggests to particularly verify the elemental compositions given for the parent and fragment ions in order to find the true structure of the oligomers. He/she does not agree with our statement, that the good fragmentation spectra obtained for the newly discovered oligomers in our present work generally disagree with Na+-adducts formed in the ESI(+) ion source. Based on this statement, we had assumed ion formation by protonation of the oligomer molecules in the ESI(+) ion source, and therefore, we had taken into account elemental compositions consisting only of the elements C, H, and O for the parent and fragment ions. The referee however points out that a poor fragmentation of Na+ adducts during ESI(+)/MS/MS experiments, although often observed, is not a general phenomenon and depends on the structure of the molecule. The referee then suggests a series of elemental compositions for the parent and fragment ions containing a Na-atom, with mass errors similar to those of the sum formulas consisting only of C, H, and O, which we presented in the Tables 3(a-d) in our work. As mentioned in the experimental part of our work, technical problems in the FTICR at the time of the measurements lead to slightly higher mass errors of about 5 to 7 ppm, which, however, turned out to be not sufficient for a clear distinction of these two sum formulas. The ambiguity of the elemental compositions attributed to the parent and fragment ions does not affect the identity of the neutral fragments determined in our work, as their sum formulas given in the Tables 3(a-d) remain the same when considering the Na+ adducts suggested by the referee. In order to clarify this issue, we repeated the accurate mass measurements on the FTICR mass spectrometer at the University of Giessen, which has been repaired in the meanwhile and now reaches relative mass errors below 2 ppm. Our new measurements clearly identify the elemental compositions of the Na+ adducts suggested by the referee as correct, with the relative mass errors remaining below 1 ppm. Our previously suggested sum formulas based only on the elements C, H, and O, however, show significantly higher relative mass errors between 5 and 15 ppm. In order to experimentally confirm the presence of Na+ in the oligomer parent ions, we performed additional accurate FTICR MS measurements to investigate the eventual ionization of the oligomer molecule by single-charged ions other than Na+ (see new Tables 3a-d). Thus, a series of less intense oligomer parent ions, referred to as type (b) (Table 2), has been identified as the K+ adducts of the same oligomer molecules that constitute also the Na+ adducts. Moreover, FTICR MS experiments with addition of excess Li+ to the analyte solution reveal the formation of oligomer parent ions that are composed of the same oligomer molecule and a Li+ instead of a Na+ (see new Tables 4a-b). These new experiments thus prove that the referee's assumption of Na+ adducts for the parent and fragment ions, as well as his suggested elemental compositions are correct. The new elemental compositions indeed now enabled us to deduce the identities of the oligomer starting and end groups X and Y as well as a possible structure for the entire oligomer molecule. The resulting molecular structures are in very good agreement with the principal structure of the oligomers already suggested in our present work and in our previous study (Sadezky et al., 2006). They indeed correspond to linear saturated oligomeric chains X-[CI]n-Y, whose endings X and Y are reflected by the initially fragmented neutrals and the final fragment ions of the two main fragmentation pathways, as presented in the new Figures

5 and 6. For the given molecular structures, we assume the peroxidic oligomer chain units -[CHR'-O-O]n- suggested before in our work. The new formulas presented in Figures 7(b-d) also demonstrate that oligomers formed through gas-phase ozonolysis of different alkenes and enol ethers indeed have a common basic structure and differ among each other only by the substituents originating from the initial alkene, thus indicating a common formation mechanism. The referee expresses his surprise about the fact that the initially fragmented neutrals of both fragmentation pathways have considerably higher masses, different numbers of carbon atoms and lower oxygen contents in comparison with the CI-like chain units. The fragmentation mechanisms given for the new molecular structures in Figure 7d explain this observation by migration of R' groups among adjacent chain units during the fragmentation. In view of the additional experiments, we have included the new results and consequently rewritten most of section 3.3.2. "Oligomer ion fragmentations and elemental compositions"; (new section title). This section was now restructured into 3 subdivisions as: 1. Elemental compositions; 2. Principle structure of type (a) oligomers; 3. Isomers. We have replaced the Tables 3(a-d), where we present now parent ions, fragment ions and fragmented neutral molecules using MS/MS-FTICR for the fragmentation pathways of the same oligomer ions. These new data were obtained with the improved accuracy (below 1 ppm) of the FTICR, compared to the data presented previously obtained with much lower accuracy. Only the composition of [X-[CI]n-Y + Na]+ ions were compared with the ions [X-[CI]n-Y + H]+ having the lowest relative mass error based on C, H and O only. All other possible formulas [X-[CI]n-Y + H]+ with higher relative mass errors were deleted. Moreover new Tables 4a-d were added showing the MS/MS-FTICR measurements of the elemental compositions of type (a) and type (b) parent ions, which represent the Na+ and K+ adducts, respectively, of the same oligomers. Also shown are the Li+ adducts, which were formed after adding excess Li+ to the analyte solution, supporting thus exchange of Na+ by Li+ ions. Figures 5 and 6 were exchanged with new figures demonstrating new structural principle and fragmentation pathways for the enol ethers and symmetric alkenes. The suggestions of the referee lead to the identification of the X and Y end

groups and of the general chemical structure of the oligomers, as presented in Figures 7(a-c). Fragmentation mechanisms for the oligomer molecules are exemplarily shown in Figures 7(d-e), whereas a tentative oligomer formation mechanism is suggested in the new Figure 8, involving the repeated addition of stabilized Criegee Intermediates to organic peroxy radicals. For a detailed analysis of the oligomer structure and fragmentation mechanisms, real structural proof would involve multiple MS and NMR analysis and must be assigned to future work. The new elemental compositions allowed us to suggest a tentative structure. A real structural elucidation, however, should be proven by additional MS3 experiments. The referee furthermore notices that the different oligomer ion series identified in the MS spectra, which we marked by b, B, C, D, E, F could correspond to a mass difference in relation to ion (a) of + 16, -42,-14, +14, +30 and +68, as we suggested, but might as well represent other mass differences related to the (n+1)- or (n-1)-ion (a). We notice here that these ions have not been identified except the ion (b), which has been shown in our new experiments to correspond to the K+ adduct of the ion (a). We used this classification for illustrating the presence and regularity of several ion series with similar chain units rather than for deducing precise structural implications. The technical errors mentioned by the referee have been corrected.

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