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Atmospheric
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Interactive comment on "Formation of secondary organic aerosol and oligomers from the ozonolysis of enol ethers" *by* A. Sadezky et al.

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The referee does not agree with our suggestion that the oligomers, which we newly described in our study as reaction products from the enol ether ozonolysis, might be formed from gas-phase reactions and subsequently initiate the observed new aerosol particle formation by homogeneous nucleation. First, we have to mention here that a fundamental discussion about the ability of low-volatile organic compounds (with saturation vapor pressures of about 10^{-7} Torr or lower, see below) to be able or not to form aerosol by homogeneous nucleation under the given conditions and about other nucleation processes eventually involved are not the focus of our publication.

The main aim of our work is to report the discovery of so far unknown, high-molecular oligomers containing Criegee Intermediate-like chain units as main constituents of the SOA formed from gas-phase ozonolysis of enol ethers. However, although this is not

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the intention of our publication, we will explain in the following the aspects that led us to our suggestion of SOA formation by homogeneous nucleation of these oligomers in order to reply to the referee's comments.

In section 3.2.1 (page 5635), in which we report the formation of new particles observed during enol ether ozonolysis and describe the time-dependent development of aerosol number size distributions (Figure 3), we also suggest that the observed SOA formation occurs by homogeneous nucleation of low-volatile reaction products (page 5635, lines 22 to 25). This suggestion is based on a previous publication of the referee (Bonn et al., 2002) in which they describe SOA formation from gas-phase ozonolysis experiments of monoterpenes. The experiments of Bonn et al. (2002) have been performed in the same atmospheric reaction chamber at the Max-Planck Institute of Chemistry (Mainz, Germany) and under similar experimental conditions as those of our present work. In particular, in both experimental setups, seed aerosol has not been used. The time-dependent evolution of the SOA particle number size distributions, which we report for the enol ether ozonolysis in section 3.2.1 (page 5635, see Figure 3) of our work, is similar to that described by the referee for the monoterpene-ozone reactions (Bonn et al., 2002). According to Bonn et al. (2002), the observed features are characteristic of a nucleation event: strong new particle formation occurs within a few minutes after the start of the ozonolysis reaction and is characterized by the appearance of particle number size distributions with their maxima at very small diameters (< 10 nm) and with their maximum particle number densities rapidly increasing to up to 10^6 particle/(cm^3 nm). Later, these initial particles grow by condensation of semivolatile material on the particle surface and by coagulation, leading to a broadening and a shift to larger diameters of the size distributions and, simultaneously, to a decrease in their maximum particle number densities. Bonn et al. (2002) attribute the observed nucleation event to homogeneous nucleation initiated at the time when enough very low-volatile substances are produced from the monoterpene-ozone reaction and their saturation vapor pressure is exceeded several times in order to meet the requirements emerging from the Kelvin effect. As nucleating compounds, Bonn et al. (2002) suggest large secondary ozonides from reactions of stabilized CI with carbonyl conpounds, such as the so-called SOZ-C18 (molar mass 292 g/mol) from β-pinene ozonolysis, for which the authors assume a saturation vapour pressure of 10^{-15} Torr, thus far below the upper limit of 10^{-7} Torr for homogeneous nucleation reported by Koch et al. (2000). (The saturation vapor pressures of organic compounds suggested to be involved in SOA formation are discussed in detail below.)

Mainly due to the absence of preexisting aerosol, we have considered plausible the conclusion of Bonn et al. (2002), that the observed nucleation event is caused by homogeneous nucleation of low-volatile ozonolysis reaction products. The proposition of Bonn et al. (2002) should therefore apply to the experiments of our work as well, as the use of the same experimental setup under similar conditions, especially in the absence of seed aerosol, leads to the observation of new aerosol particle formation with similar features. Background concentrations of detectable (> 3 nm) particles in the reaction chamber were measured in our work to be less than 200 particle/cm^3 (page 5635, lines 22 to 25), which is in agreement with the blank measurements of Bonn et al. (2002) taken before the reaction start, showing very low concentrations of preexisting aerosol particles. Therefore, concentrations as high as 10^6 particle/cm^3 of preexisting aerosol particles, all of them with diameters smaller than 3 nm – thus undetectable by our analytical devices – would be needed in the reaction chamber in order to explain the observed nucleation events by the classical heterogeneous nucleation. We have considered this scenario less likely than the suggestion of Bonn et al. (2002), that new particle formation takes place through homogeneous nucleation initiated by low-volatile ozonolysis reaction products. As secondary ozonides as well as diacids and multifunctional acids are excluded as low-volatile nucleating reaction products by the gas-phase reaction mechanism of the enol ether ozonolysis, we have suggested in the conclusion of our publication (page 5651, line 24 to 25), that the high-molecular oligomers newly discovered in our work might initiate homogeneous nucleation, thus leading to new SOA particle formation.

If, in the meanwhile, new insights into nucleation mechanisms involved in SOA formation have shown that, as the referee stated in his review, homogeneous nucleation cannot be applied to secondary organics, therefore signifying that the referee today revises his own previous work (Bonn et al., 2002), we have not been aware of it. We will be grateful to learn about new theories which emerge beside the classical approaches of homogeneous and heterogeneous nucleation, and which could lead to new links between reaction chemistry and microphysics and therefore to a more coherent understanding of SOA formation.

However, as stated above, the aim of our publication is not to suggest a specific, either classical (homogeneous or heterogeneous) or new nucleation mechanism for the SOA formation from enol ether ozonolysis, as our experiments do not allow to deduce explicit proofs for any nucleation theory. Therefore, discussions in this regard will be entirely speculative and are beyond the scope of this publication. We will consequently refrain from referring to any nucleation theory eventually playing a role in the observed SOA formation and reformulate the relevant paragraphs in the section 3.2.1. (page 5635, lines 22 to 25) and in the conclusion (page 5651, lines 24 to 25) in a more general way. We will limit the text on page 5635, lines 22 to 25, to the mention of the measured low particle background concentrations and the absence of seed aerosol, and delete the subsequent text passage, in which SOA formation by homogeneous nucleation is suggested in consequence. In the conclusion, on page 5651, lines 24 to 25, we will simply mention that oligoperoxides “might initiate nucleation” instead of suggesting that they “lead to new SOA particle formation by homogeneous nucleation”.

The referee states that to his opinion, the SOA and oligomer formation process in our work is of heterogeneous nature, as formulated by Tolocka et al. (2004) and Tolocka et al. (2006). However, the work of Tolocka et al. (2006), which the referee asks to include in this context, does not deal with heterogeneous processes involved in SOA and oligomer formation. We contacted the referee about this issue, who apologized for providing us the wrong reference. Interestingly, the work of Tolocka et al. (2006) instead provides other evidence for gas-phase reaction mechanisms leading to the formation of high-molecular SOA constituents during ozonolysis experiments in the absence of seed aerosol. We discuss the results of Tolocka et al. (2006) below.

Therefore, in the following, we refer only to the work of Tolocka et al. (2004), which we already mentioned among similar studies (e. g. Gao et al., 2004) in the discussion (section 4) on page 5650 of our publication. In their publications, the heterogeneous processes suggested are liquid-phase chemical reactions, in particular aldol condensation and gem-diol formation, of carbonyl-containing products formed by the ozonolysis reaction, such as pinonaldehyde formed in the α-pinene ozonolysis (Tolocka et al., 2004). These reactions supposedly take place on the particle surface or inside the aerosol particles, and are therefore referred to as heterogeneous or multiphase reactions. They are suggested to transform the relatively high-volatile carbonyl compounds adsorbed onto the particle surface into low-volatile oligomeric species, therefore shifting their partitioning equilibrium towards the particle phase and contributing to the formation of new SOA matter. The mechanisms of these reactions are well known from classical liquid-phase carbonyl chemistry and require acid catalysis. In the cited studies of Tolocka et al. (2004) and Gao et al. (2004), most ozonolysis experiments have therefore been performed in the presence of acid seed aerosol (acid seed aerosol consists of solid ammonium or magnesium sulfate acidified by an excess of sulfuric acid). In both studies, a strong decrease of SOA and oligomer formation is observed in the absence of acid seed aerosol, which, according to the authors, demonstrates the need for acid catalysis. On the other hand, Barsanti and Pankow (2004) argue in their theoretical study that acid-catalysed liquid-phase reactions of simple carbonyl compounds are not thermodynamically favoured, even in the presence of acid seed aerosol.

In any case, the experimental conditions of our work are very different from those of Tolocka et al. (2004) and Gao et al. (2004) by the fact that we do not use any seed aerosol. In contrast to the studies of Tolocka et al. (2004) and Gao et al. (2004), we observe well-detectable quantities of oligomers in the SOA formed from enol ether ozonolysis in spite of the absence of an initial particle surface and an acid catalyst.

According to the referee's opinion, heterogeneous chemical reactions similar to those suggested by Tolocka et al. (2004) should account for the observed SOA and oligomer formation in our experiments. However, such reactions cannot explain the origin of the nucleation events described above, which are characterized by intense new particle formation within a few minutes after the start of the ozonolysis reaction. The heterogeneous processes described by Tolocka et al. (2004) are liquid-phase chemical reactions occurring on particle surfaces and are very different from the entirely microphysical phenomenon of nucleation, such as the heterogeneous nucleation of organic compounds on preexisting sulfate clusters suggested by Kulmala et al. (2004).

Supposing that heterogeneous chemical reactions on particle surfaces were indeed able to significantly contribute to SOA particle growth, then a different, so far entirely unknown mechanism involving unknown molecular constituents would cause the observed nucleation event. The initial aerosol formed in this way would then provide the necessary particle surface and the eventual acid catalysts for heterogeneous chemical reactions according to Tolocka et al. (2004) to take place, by which the oligomers described in our work, and thereby the major part of the SOA matter, would be produced. As the nucleation event occurs shortly after the beginning of the enol ether-ozone reaction, the unknown compounds, which would initiate nucleation and cause the initial particle growth, would also be related to reaction products of the ozonolysis reaction. However, the main and only constituents identified in the SOA by use of the very sensitive ESI(+)/MS technique are the described oligomers, whose molecular weights and oxygen content moreover suggest that they are very low-volatile. We consider very unlikely the existence of another, different class of similar low-volatile reaction products from the same enol ether-ozone reaction, which would instead initiate the observed nucleation event and generate the particle surface needed for the subsequent formation of the described oligomers by heterogeneous chemical reactions.

Therefore, we are convinced that the oligomers identified in our work are most likely

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formed by reactions in the gas-phase following the initial enol ether – ozone reaction, and might then initiate nucleation, thus leading to the observed nucleation event. Further conclusions on the detailed nucleation mechanism cannot be drawn from our experiments, as stated above.

An eventual formation of the oligomers in the liquid phase during the aerosol filter sampling procedure, as considered by the referee, can be largely excluded by the blank experiments presented in the section 3.3.2. (pages 5641 to 5642) of our publication.

In the following, we would like to comment on the publication of Tolocka et al. (2006) suggested by the referee. Tolocka et al. (2006) study the chemical composition of SOA particles with sizes up to 50 nm produced within the first few seconds of α-pinene ozonolysis in the absence of seed aerosol. By use of photoionization aerosol mass spectrometry (PIAMS), the authors newly identify SOA constituents between m/z 300 and 400 and attribute them to products of gas-phase addition reactions of the stabilized CI (SCI) with a variety of species. Their observations indicate that products of SCI reactions might play a key role in the formation of SOA constituents. This suggestion is also made in our work based on the observed reduction of SOA formation during enol ether ozonolysis experiments in the presence of SCI scavengers (section 3.3.2., page 5541, and section 4, pages 5648 to 5649).

Most of the mass peaks newly observed in their work are assigned by Tolocka et al. (2006) to products of well-known SCI-addition reactions, in particular to secondary ozonides formed by SCI-aldehyde addition (e. g. pinonaldehyde). Similar high-molecular secondary ozonides such as the so-called SOZ-C18 have been suggested in the referee's previous work (Bonn et al., 2002) as reaction products nucleating homogeneously, thus leading to SOA formation during monoterpene ozonolysis (see above).

Tolocka et al. (2006) moreover take into consideration the self-reaction of the SCI combined with the addition of a water molecule, eventually leading to a linear peroxidic species with a basic structure similar to that, which we attribute to the newly identified

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oligomers in our work (section 4, page 5648, and Figure 9). We suggest in section 4 (pages 5648 to 5649) of our publication, that SCI are involved in oligoperoxide formation from enol ether ozonolysis. At that time, we were not aware of the work of Tolocka et al. (2006), whose publication in 2006 apparently crossed with our present study.

Tolocka et al. (2006) also discuss addition/elimination reactions of small oxygenated molecules, such as H_2O, H_2O_2 and HCHO, from or to the SCI-addition products in order to explain small mass differences between ions. Some of the elimination reactions might, according to the authors, occur as molecular decompositions – not as heterogeneous reactions – in the high-pressure environments of the aerosol phase or the desorption step of the PIAMS analysis.

Moreover, Tolocka et al. (2006) conclude from measurements of the elemental compositions of the SOA at different formation stages, that small, highly oxygenated and therefore polar oligomers might induce new particle formation. This is consistent with the high oxygen content of the oligomers (section 3.3.6., pages 5646 to 5648; and Tables 4a and b) described in our work and with our suggestion that they might already participate in the initial stage of SOA formation during enol ether ozonolysis.

Tolocka et al. (2006) do not give any precisions about the nucleation mechanism leading to SOA particle formation in their experiments.

We would like to state that even though our assumption that SOA formation in our experiments occurs through homogeneous nucleation of low-volatile products formed from enol ether ozonolysis might not be correct, this will not affect at all our approach to assess SOA formation and growth in the section 3.2.2. (pages 5636 to 5638). In fact, the approach of Odum et al. (1996) is solely based on the absorption-partitioning processes established by Pankow (1994) and is not related to any specific nucleation mechanism, such as homogeneous or heterogeneous nucleation. It is a general method for the representation of laboratory data on SOA formation and growth and has been successfully applied in the past to experiments of α-pinene ozonolysis and

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OH-initiated photooxidation of aromatics in the presence of ammonium sulfate seed aerosol (Kroll and Seinfeld, 2005; Odum et al., 1996), thus to experimental conditions under which homogeneous nucleation definitely does not take place.

Furthermore, Kroll and Seinfeld (2005) mathematically extend the expression of Odum et al. (1996), thus showing that the two approaches, which we use in the section 3.2.2. (pages 5636 to 5638) to assess the SOA formation and growth, are formally compatible. Our first approach, defined by Eq. 1 (page 5636), yields the SOA yield a and the SOA formation threshold ΔAVE_{thresh}, and our second approach, defined by Eq. 4 (page 5637) and corresponding to the one-component model according to Odum et al. (1996) yields the yield α_i and the partitioning coefficient K_i of a hypothetical semi-volatile SOA constituent i (see Table 1 in our publication). Both approaches have also been used by Klotz et al. (2004) in order to assess SOA formation from the ozonolysis of methyl vinyl ether (MVE) without seed aerosol (see Table 1 in our publication).

The referee expresses his surprise about the fact that, upon application of the model of Odum et al. (1996) in our work, a single hypothetical compound partitioning between the gas- and the particle-phase is sufficient to describe the observed SOA formation and growth. Odum et al. (1996) themselves claim to have a need for two such compounds, i. e. a non- and a semi-volatile one. The referee concludes that the single partitioning compound in our approach corresponds to semi-volatile organics always present and contributing to SOA formation. According to the referee, the absence of a second, therefore non-volatile compound indicates that such a compound is not formed in the gas phase, but that instead heterogeneous reactions of semi-volatile products at the nuclei or particle surface cause the main part of SOA formation.

A different interpretation of the one-component model according to Odum et al. (1996) is given in the work of Kroll and Seinfeld (2005). According to Kroll and Seinfeld (2005), the one-component model of Odum et al. (1996) represents a reasonable approximation to the two-component model when assuming that the second, non-volatile compound entirely partitions in the aerosol phase and constitutes the bulk absorbing organic matter M_0.

An eventual contribution of heterogeneous reactions such as those suggested by Tolocka et al. (2004) is, although not excluded, however critically assessed by Kroll and Seinfeld (2005). The formation of low-volatile oligomeric species from relatively high-volatile organic compounds by heterogeneous reactions, as described above, is expected to assist the partitioning of those compounds into the particle phase, thus eventually increasing the partitioning coefficient K_i. Kroll and Seinfeld (2005), however, doubt that those heterogeneous reactions might indeed significantly influence K_i, because they are based on acid catalysis, thus on a kinetic phenomenon, and cannot entirely explain a long-term enhancement of total SOA growth in the presence of acid seed aerosol as observed by Tolocka et al. (2004) and Gao et al. (2004).

The referee criticizes the approach that we used to estimate the saturation vapor pressure of the (idealized) major aerosol constituent yielding values between 1×10^{-7} and 18×10^{-7} Torr. The referee points out that in order to conclude on new particle formation by homogeneous nucleation of organic compounds, the Kelvin effect must be taken into account, which, according to the referee's calculations, leads to a necessary supersaturation of 5683 times the actual saturation vapor pressure of the organic compound for aerosol particles at nucleation size. The calculations of the referee are certainly correct, however, at this point, we have to clear some confusion about the kind of saturation vapor pressures which we discuss: we did not directly estimate the specific saturation vapor pressure of the newly discovered oligomers by the approach used in our work.

Our estimated values for saturation vapor pressures of 1×10^{-7} to 18×10^{-7} Torr have been formally derived in this work from the measured SOA formation and growth evaluated by the Eq. 1 (page 5636) and 4 (page 5637). As both methods are independent of the specific nucleation mechanism and take only absorption/partitioning processes into account, as detailed above, this is also valid for the values for the saturation vapor pressures of the SOA constituents derived from these two approaches by Eq. 5 and

6. The first approach is based on the partitioning coefficient K_i (Eq. 5, page 5637; Pankow, 1994), which is characteristic of a single hypothetical semi-volatile compound i responsible for the measured aerosol growth (Odum et al., 1996) and is obtained by application of the one-component model according to Odum et al. (1996) (Eq. 4, page 5637). In the second approach, which is also applied by Koch et al. (2000) to aerosol formation from monoterpene ozonolysis, the minimum concentration of the hypothetical nucleating compound necessary to initiate new particle formation is determined from the SOA yield a and the SOA formation threshold ΔAVE_{thresh} (Eq. 1, page 5636), and its saturation vapor pressure is derived by Eq. 6 (page 5638). In both methods, the variables K_i, a and ΔAVE_{thresh}, which lead to the saturation vapor pressure by Eq. 5 and 6, are determined from the experimentally observed aerosol formation and growth, which implies that for the involved SOA constituents, the Kelvin barrier has necessarily been overcome. As Eq. 5 and 6 are, however, based on flat liquid surfaces, the obtained values for the saturation vapor pressures therefore have to be treated as upper limits, and the real values, taking into account the Kelvin effect, must be considerably lower. This fact was mentioned in the section 3.2.2. (page 5638, line 13 to 18) of our publication. The values for the upper-limit saturation vapor pressures of 1 $\times$ 10^{-7} to 18 $\times$ 10^{-7} Torr yielded by the equations 5 and 6 in our work reasonably agree with those determined for monoterpene ozonolysis by Koch et al. (2000), which are of 1.7 $\times$ 10^{-7} Torr and 0.56 $\times$ 10^{-7} Torr.

The described approaches to estimate the saturation vapor pressures of compounds participating in SOA formation are based on the observed aerosol formation and growth only and do not allow to draw direct conclusions on the chemical nature of the compounds involved. It has been suggested (Koch et al., 2000) that the compounds initiating nucleation in the aerosol formation from monoterpene ozonolysis might be diacids, such as pinic acid. This suggestion is based on the fact that diacids are the lowest-volatile reaction products known to be formed from monoterpene ozonolysis, and that their vapor pressures are in the range of the upper limit measured by Koch et al. (2000) for the nucleating compound, that is, about 10^{-7} Torr (Capouet and Müller, 2006; Bilde and Pandis, 2001; Saxena and Hildemann, 1996). The referee also accepts this upper-limit of 10^{-7} Torr in his work (Bonn et al., 2002) in order to support his suggestion of large secondary ozonides (SOZ-C18) with an estimated saturation vapor pressure of 10^{-15} Torr as key compounds initiating homogeneous nucleation. Argumenting in a similar way, we suggest that the oligomers newly described in our work, which should be by far the lowest-volatile known compounds formed during enol ether ozonolysis, might initiate the nucleation that leads to the observed aerosol formation.

The referee argues that, based on his calculations of the Kelvin effect for particles at nucleation sizes and on the saturation vapor pressure of pinic acid published by Bilde and Pandis (2001) of 3.2×10^{-7} Pa (2.4×10^{-7} Torr), a volume mixing ratio of 1.85 ppmv of pinic acid is necessary to allow homogeneous nuclation. The referee concludes from this calculation that when taking into account the measured low aerosol yields of up to 4.7 %, similar high concentrations of a nucleating compound cannot occur in our reaction system, especially not of the oligomers with molecular masses up to 400 u, which we identified in our work as main aerosol constituents and for which the referee estimates a higher saturation vapor pressure than for pinic acid. We state here that we cannot provide a direct estimation of the specific saturation vapor pressure of these oligomers, because their exact structures are so far unknown. At present, any such estimation is largely speculative. Nonetheless, regarding the main molar masses of 300 to 400 g/mol and the apparent high content in oxygen of the oligomers newly described in our work, we rather doubt that their specific saturation vapor pressure will actually be higher than that of pinic acid (molar mass 186 g/mol), as assumed by the referee.

In view of the fact that the detailed nucleation mechanism, the main issue raised by the referee, is irrelevant for the methods which we use in the section 3.2.2. (pages 5636 to 5638) including our estimation of the upper-limit saturation vapour pressures of compounds participating in SOA formation, we do not see any need for changes in this section.

Finally, the referee comments on the observed decrease of SOA yields during vinyl ether ozonolysis in the presence of excess cyclohexane as an OH scavenger. The referee states that if any products from the cyclohexane-OH reaction eventually influence the SOA production, they should be of rather large sizes and therefore enhance SOA formation instead of reducing it. He concludes that at least one product of the enol ether-OH reaction is consequently required to cause aerosol mass production.

In the introduction of our publication (page 5631, line 12 to 17), we mention the work of Klotz et al. (2004), who studied the gas-phase reactions of methyl vinyl ether (MVE) with ozone, OH and NO_3, and clearly state that only the MVE-ozone reaction leads to significant SOA formation, but not the MVE-OH nor the MVE-NO_3 reaction.

SOA yields have been reported to decrease in the presence of cyclohexane as an OH scavenger also for the ozonolysis of larger alkenes, such as cyclohexene (Keywood et al., 2004). Keywood et al. (2004) conclude in their work that tendencies of SOA yields both to decrease or to increase in the presence of excess cyclohexane could occur and depend on the specific alkene. The authors attribute these effects to changes in the radical chemistry of the reaction system induced by the OH-scavenger reactions. We discuss the work of Keywood et al. (2004) and its significance for our observations in detail in our answer to the second referee.

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