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Atmospheric
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Discussions

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 first point raised by the referee concerns the ozonolysis experiments of IBVE in the presence and absence of excess cyclohexane as an OH scavenger (Table 1). We reported a strong decrease of the SOA yield in the presence of excess cyclohexane. The referee asks if a similar decrease in the SOA yield eventually applies to all vinyl ethers studied in our work. The authors state that this is indeed the case. Experiments with low initial ether and ozone mixing ratios as described in Table 1 have been performed in the presence of an excess of cyclohexane for only one vinyl ether, IBVE. A similar decrease of the SOA mass in the presence of excess cyclohexane is described on pages 5641 to 5642 of our publication for another vinyl ether, EVE, during experiments with high initial reactant mixing ratios used for mass spectrometric analysis of SOA. Also separate experiments (Sadezky, 2005, and a publication in preparation en-

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titled “Ozonolysis of enol ethers: gas phase products and reaction mechanisms” by Sadezky, A., Winterhalter, R., Mellouki, A., Thiault, G. Moortgat, G. K. and Le Bras, G.) conducted for all vinyl ethers with and without excess of cyclohexane at moderate initial reactants mixing ratios show similar tendencies of SOA yields for all vinyl ethers. We will therefore add the following sentence “A similar and systematic decrease of SOA yields in the presence of an excess of cyclohexane has been observed in separate experiments for all five alkyl vinyl ethers studied (Sadezky, 2005)” to our statement about the observed decrease in SOA yields during IBVE ozonolysis in the presence of cyclohexane as OH scavenger on page 5637, line 17, of our manuscript.

Furthermore, the referee asks for a comparison of our observations to the effects of OH scavengers on SOA yields described by Keywood et al. (2004) and Docherty and Ziemann (2003) for cyclohexene and β-pinene ozonolysis, as well as for an eventual central role of acylperoxy radicals in SOA formation, as suggested by Keywood et al. (2004). We note that the SOA yields from vinyl ether ozonolysis described in our work show a similar tendency as the SOA yields from cyclohexene ozonolysis measured by Keywood et al. (2004), that is, they decrease in the presence of cyclohexane as OH scavenger. Docherty and Ziemann (2003) show that SOA yields from β-pinene ozonolysis follow the opposite trend. Keywood et al., (2004) and Docherty and Ziemann (2003) explain these observations by a decrease of the ratio [hydroperoxy radicals]/[organic peroxyradicals] in the presence of cyclohexane, which affects the subsequent radical chemistry of the reaction system. Keywood et al. (2004) suggested that this ratio especially affects the production and chemistry of acylperoxy radicals, now widely suggested as key radicals for the formation of low-volatile products (acids, diacids and peracids, see also Koch et al., 2000), and explained the opposite trends observed for SOA yields from β-pinene and cyclohexene ozonolysis by the contribution of different pathways to acyl radical production. All contributing pathways, however, involve decomposition reactions of the excited CI formed from the initial primary ozonide via the hydroperoxide channel or the “hot acid” channel. The excited CIs formed during vinyl ether ozonolysis, C_1-CI (CH_2O_2) and alkoxy CI ($ROCO_2$) do not carry H atoms in their α-positions, and therefore, if they are not stabilized, decompose via the "hot acid" channel only, implying the measured low OH yields of about 14 % (Klotz et al., 2004). While in the case of cyclohexene ozonolysis, the "hot acid" decomposition channel of the excited CI has been identified as the main formation pathway of a long-chain (C6) acylperoxy radical that can further react to form low-volatile acids, peracids, diacids etc. (Keywood et al., 2004), the same pathway, for vinyl ether ozonolysis, only leads to formation of HCO and ROCO radicals, which are expected to be unstable and to decompose by reaction with O_2. As these radicals should not contribute to the formation of high-molecular reaction products, a reaction mechanism different from that suggested by Keywood et al. (2004) for cyclohexene ozonolysis should be responsible for the observed effect of cyclohexane on the SOA yields from vinyl ether ozonolysis. We will add a new paragraphe resuming these remarks to the discussion (section 4) on page 5649 of our publication.

In this context, we state that the gas-phase reaction mechanisms involved in SOA and oligomer formation during vinyl ether ozonolysis are actually unknown. Therefore, the aim of our work was mainly to report the - unexpected - presence of oligomeric compounds containing CI-like repeated chain units as main constituents of the SOA formed from enol ether ozonolysis. Formation of these oligomeric products, as well as the influence of cyclohexane on SOA yields, cannot be explained by any classical mechanism established so far and, as also stated by the referee, must involve some new chemistry, eventually based on radical-radical or CI-radical reactions which are so far unknown. Therefore, any discussions about the mechanisms eventually leading to formation of the observed oligomers and SOA are purely speculative at this stage and will require, as noted by the referee, detailed modelling studies that take into consideration diverse classical as well as new gas-phase mechanisms. Such a modelling study would however be beyond the scope of this publication.

The only mechanistic clue is so far given by the observed simultaneous suppression of oligomer and SOA formation in the presence of HCOOH as CI scavenger: it shows that the reaction of the CI with HCOOH, which is generally accepted to involve the stabilized form of the CI (SCI) (Calvert et al., 2000), is in direct concurrence with the reactions leading to SOA and oligomer formation, and therefore points towards a direct implication of the SCI in these reactions. The referee asks for rate constants of this and other known reactions between SCI and CI scavengers. Relative rate constants have been measured for a number of SCI-molecule reactions (e. g. Calvert et al., 2000). For reactions of the stabilized C_1-CI (CH_2O_2) with H_2O, HCHO and HCOOH, relative rate constants $k_{(SCI+H2O)} : k_{(SCI+HCHO)} : k_{(SCI+HCOOH)}$ have been determined to 1 : 700 : 14000 (Calvert et al., 2000; Neeb et al., 1998; Neeb et al., 1997), thus identifying HCOOH as a very effective CI scavenger. Relative rate constants for similar reactions of the stabilized C_{13}-CI ($CH_3(CH_2)_{11}CHO_2$) determined by Tobias and Ziemann (2001) show similar tendencies. From the measured relative rate constants, an absolute rate constant of 5.2×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for the reaction of the stabilized C_1-CI (CH_2O_2) with HCOOH has been estimated (Calvert et al., 2000). Based on these values, monitoring of the SOA formation as a function of the HCOOH concentration, as suggested by the referee, should indeed allow to gain an estimate of the rate constants of the main reaction leading to SOA formation and will be an interesting issue for further studies.

Considering the observations of Keywood et al. (2004) and Docherty and Ziemann (2003), the observed influence of cyclohexane on SOA yields from vinyl ether ozonolysis, although so far unexplained, might indeed point towards an involvement in particular of peroxy radical chemistry, in addition to the chemistry of the SCI. Under these aspects, the suggestion of the referee, that peroxy radical-CI biradical reactions might be involved into oligomer formation, seems very interesting. To our knowledge, no literature about peroxy CI reactions has been published so far. The overall reaction rate of such a reaction in the vinyl ether-ozone reaction system should be slower than that of the SCI-HCOOH reaction (depending on the HCOOH concentration), but must significantly exceed those of chain-terminating peroxy-peroxy radical (RO_2 and HO_2) reactions. The referee's proposition is an interesting starting point for future modelling studies taking into account these aspects.

The referee furthermore asks if there exists evidence for the inclusion of the minor CI, alkoxy-CI ($ROCHO_2$), formed from decomposition of the primary ozonide during enol ether ozonolysis. We have identified the oligomer chain units that correspond to the major C_1-CI (CH_2O_2) and C_2-CI ($C_2H_4O_2$) in the oligomer fragmentation spectra (ESI(+)/MS/MS experiments) through systematic and repeated losses of neutrals with similar chemical compositions. Analogous direct losses of entities with the chemical composition of the alkoxy-CI ($ROCHO_2$) have not been observed in this work. There still exists the possibility that an alkoxy-CI-like unit might be comprised into the starting or the end group of the oligomer. We have shown by comparison of ESI(+)/MS and ESI(+)/MS/MS spectra of oligomers from different vinyl ethers the systematic presence of one RO group in the starting group “X”, however, the inclusion of a different CI, such as RCHOO, as a chain unit into the oligomer molecule would rather be expected to occur in a statistical manner.

In this context, the referee generally asks if ozonolysis experiments with mixtures of different alkenes producing similar CI (alkyl vinyl ether – ethene mixtures for C_1-CI or ethyl propenyl ether – 2-butene mixtures for C_2-CI) would lead to oligomer chain length enhancement. The referee also suggests ozonolysis experiments of alkene mixtures producing different major CI, such as alkyl vinyl ether – ethyl propenyl ether mixtures, in order to investigate the eventual formation of oligomer chains composed of mixed CI-like chain units. Both kinds of experiments would give evidence for the incorporation of CI simultaneously produced from different alkene-ozone reactions into the same oligomer molecule. While we have not performed any experiments of the first type (ozonolysis of alkene mixtures producing the same CI), experiments of the second type (ozonolysis of alkene mixtures leading to formation of different CI) have recently shown formation of oligomers with mixed CI-like chain units. We will publish these results very soon.

The referee notes that attribution of a structure to the final fragment ions is difficult. We remark that the results of this work have allowed us to prove the oligomeric structure of the newly discovered compounds and to determine the identity of the chain units. However, we could not to clearly determine the identity of the starting and end groups X and Y of the oligomers, which we suggest to be represented by the final fragment ions, and therefore, the entire oligomer structure is not clear so far. The simultaneous presence of at least four isomers of the parent ion in the oligomer fragmentation spectra particularly complicates this task.

The referee asks if we could completely exclude that the oligomer formation process eventually occurs on the aerosol, thus by heterogeneous processes such as those suggested in the studies of Tolocka et al. (2004) and Gao et al. (2004). We are convinced that the formation of the oligomers described in our work most likely occurs by gas-phase reactions following the initial enol ether – ozone reaction mainly due to the fact that, in contrast to Tolocka et al. (2004) and Gao et al. (2004), we do not use any seed aerosol in our experiments. The mechanisms suggested in the cited studies of Tolocka et al. (2004) and Gao et al. (2004), however, are reported to be strongly dependent on the presence of acid seed aerosol. Moreover, a nucleation event is observed to occur in all our experiments, leading to intense new particle formation within the first few minutes of the enol ether-ozone reaction (section 3.2.1. and Figure 3), which cannot originate from products formed by heterogeneous reactions on particle surfaces. Oligomers previously formed by gas-phase reactions, however, might also play a role in nucleation and therefore in the observed new SOA particle formation. We discuss these issues in detail in our answer to the first referee (B. Bonn).

Finally, the referee asks if the described oligomer formation might be a peculiarity of vinyl ethers or a general feature of all alkene ozonolysis reactions. We have performed ozonolysis experiments for short-chain hydrocarbon alkenes, which have shown that this phenomenon is not limited to enol ethers. A publication about the new experiments will soon be submitted.

The authors would like to thank to the referee for the interesting and constructive re-

view.

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