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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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General:

The paper investigates the formation of secondary organic aerosol mass and the production of oligomeres in the gas phase ozonolysis of enol ethers. It describes the amount of secondary organic aerosol yield formed during the gas-phase reaction and aims to estimate the nucleation compounds saturation vapour pressure. The most interesting point however is the description of the oligomeres detected in the aerosol samples collected, describing a stepwise increase in molar mass by 46 g/mol.
The topics studied and described are certainly of relevance especially when consider-

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ing the increased used of these types of solvents and their release to the atmosphere. I am sure that the study of the formed oligomeres and their production mechanism are among the key issues in understanding the complexity of secondary aerosol formation from reactive gas-phase precursors. Hence, the detected oligomeres and their relation, i.e. masses increase by 48 g/mol each step are very interesting results. The experimental approach is certainly valid and the results interesting. However, there are some aspects I would like to raise and some of the conclusions don't seem take into account both physical and chemical properties, which might lead to a different interpretation.

Technical comments:

Within the abstract and at various locations in the paper the term 'Criegee intermediates' is used solely, which might lead to a confusion by any reader. For example the sentence 'The main stable gas-phase . . . formed with yield of 60 to 80 %, implying that similar yields of the corresponding Criegee Intermediates (CI) CH_2O_2 and CH_3CHO_2 for EPE are generated." implies that the yield of the Criegee intermediate varies between compounds, which is not the case. The Criegee Intermediate is the direct decomposition product of the primary ozonide in its excited form ([Finlayson-Pitts and Pitts (2000)])! I am sure that the authors refer to the *stabilized* form, which is definitely varying. In this case I would like to ask the authors to address it correctly in the text to prevent misunderstanding. Otherwise we would have a possibility to either find an unknown reaction pathway for primary ozonides or we could directly observe these.
The expression 'atmospheric temperature' within the abstract needs to be used more carefully too. The temperature of 296 K is certainly a temperature to be found in the atmosphere, but e.g. 230 K as well. The term refers to room temperature.

Specific comments - major issues:

I entirely disagree with the term homogeneous nucleation in this paper and the related (used) approach for secondary organic aerosols. Please use the physico-chemical properties and description to see that especially for secondary organics homogeneous nucleation cannot be applied. For doing so take into account the Kelvin effect (e.g. [Seinfeld and Pandis(1994)]). For tiny aerosol particles at their nucleation state, the saturation vapour pressure above a ‘molecule’ or ‘cluster’ of molecules is given by:

$$p_{sat}^{nuclei} = p_{sat}^{flat} \cdot exp\left(\frac{2\sigma \cdot v_m}{r_p kT}\right) \tag{1}$$

Therein, the exponential or Kelvin term can be calculated by taking into account the present temperature T (296 K), the Boltzmann constant k (1.38×10^{-23} J K^{-1}), a reasonable surface tension for organics s (0.030 N m^{-2}) and the calculated molecular volume v_m and the radius of the nuclei r_p. Assuming e.g. one of the most important non-volatile compounds in alkene ozonolysis pinic acid (molar mass M of 186 g/mol) to be a homogeneous nucleating component, the molar volume becomes

$$v_m = \frac{M}{\rho \cdot N_A} \tag{2}$$

Avogadros constant N_A is given by 6.022×10^{23} molecules mol^{-1} and a reasonable density ρ of 1400 kg m^{-3} can be applied. The latter is found for secondary organic aerosol from toluene oxidation ([OSOA final report (2002)]), which has a similar size of the parent hydrocarbon. This gives a molecular volume of 2.2e-28 m^3 and a spherical radius of 0.375 nm. The Kelvin effect is thus 5683, expressing that for pure homogeneous nucleation the saturation concentration needs to be exceeded 5683 times to cross the nucleation barrier. For the best studied pinic acid, which I guess is even less volatile than the products formed in this study, the saturation vapour pressure of [Bilde and Pandis(2001)] can be used resulting in a necessary volume mixing ratio to allow homogeneous nucleation of 1.85 ppmv! Taking into account the given aerosol yields between 3.5 and 4.7 mol% this requires nearly pure enol ether ozone reactions. Consequently, I doubt if one can apply the approach used herein to obtain the saturation vapour pressure of the (idealized) major aerosol constituent. By contrast, I am sure that the process is of heterogeneous nature as e.g. formulated e.g. in [Tolocka *et al.*(2006)], a paper, which should be included in this context as well. Therefore, I would like to ask the authors to rework the first part on the homogeneous nucleation.

Second, it was interesting to see that a single compound aerosol yield [Pankow (1994)] is sufficient to describe the aerosol mass formed. [Odum *et al.*(1996)] claimed to have a need for two, i.e. a non- and a semi-volatile one. Since semi-volatiles are present in anyway and will contribute, I would conclude that the aerosol formation is due to heterogeneous reactions of semi-volatile products at the nuclei or particle surface rather than a non-volatile compound formation in the gas-phase. These results are really important and make this study quite valuable.

An interesting point mentioned is the OH effect. It is correctly stated that earlier studies have found a smaller contribution of OH reactions to the aerosol yield. But why is the aerosol yield going down when adding an OH-scavenger (cyclohexane)? If any products of cyclohexane + OH influence the aerosol production they should be similar of size or even larger and enhance aerosol formation, but not reduce. It seems that at least one product of the enol ether OH reaction is required to cause aerosol mass production.

Finally, I am suspicious about the actual formation of oligomeres in the gas-phase ([Tolocka *et al.*(2004)], Tolocka *et al.*(2006)]). They might also be formed in liquid-like

phase aerosol reactions, either directly or during sampling. Any unstable previous products will certainly get destroyed latest during the analytical process.
To conclude, the Kelvin effect of the saturation vapour pressure should be treated when considering the possible saturation vapour pressure of nucleating compounds and the outcome should be treated in a broader physico-chemical sense. However, let me thank the authors for their certainly relevant contributions regarding the aerosol product formation of enol ethers, a topic to be studied further.

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