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Atmospheric
Chemistry
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Discussions

Interactive comment on “Temperature dependence of yields of secondary organic aerosols from the ozonolysis of α-pinene and limonene” *by* H. Saathoff et al.

Anonymous Referee #1

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This paper presents measurements of the secondary organic aerosol (SOA) yield from the ozonolysis of alpha-pinene and limonene at different temperatures and relative humidities (RH). The data are evaluated using the dynamic COSIMA-SOA model with a two-product approach. As expected, SOA yields increases at low temperature. The effect of RH on SOA yield is noticeable for limonene at low temperature, but not near room temperature. The parameters derived from the data for the two effective SOA proxies can reproduce the observed time evolution of SOA mass, particle size, mass, and number distribution.

This paper is generally well written and provides parameters that can be used to pre-

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dict SOA formation by the ozonolysis of these two important terpenes under typical tropospheric conditions. The data presented in this work are also valuable for understanding the SOA formation. After appropriate attention to the items below, this paper can be published in Atmospheric Chemistry and Physics.

Major comments

1. Parameterization of the two effective SOA proxies (products)

The authors demonstrate that the COSIMA-SOA model with the two product-approach can be used for predicting the time evolution of the SOA formation and for parameterizing the SOA formation. There are questions related to the parameterization of two effective SOA proxies. In section 4.1.1, the authors discuss the wall loss rate coefficient of the two effective SOA proxies. Figures 2 and 10 show the time dependent particle and gas mass lost to the walls in the ozonolysis of alpha-pinene and limonene, respectively. A considerable amount of products are lost to the wall. The authors need to elaborate how they determined the wall loss rate coefficient of the two effective SOA proxies in the gas and particle phase.

In section 4.1.3, using the COSIMA-SOA model with the two-product approach, the authors determine the parameters (K, p, alpha) of the two effective SOA proxies by fitting with the experimental data. Do the authors fit the K,i and alpha,i values or po,i and alpha,i values with the experimental data? Is a constant <MWo> value assumed for calculating the K values using Eqn. 3 in ozonolysis of alpha-pinene and limonene?

In section 4.2.2, for the ozonolysis of limonene, the same values as for the experiments with alpha-pinene are used for surface tension, diffusion coefficients and molecular mass of the two effective SOA proxies. Is there any reason for this assumption? Are the SOA products formed from the ozonolysis of limonene similar to those formed from the ozonolysis of alpha-pinene? The same question applies to the effective evaporation enthalpy of the volatile SOA product (page 15624, line 11).

2. RH dependence on SOA formation

In section 4.1.5 (Page 15619), "During this work a substantial impact of the humidity on the SOA yields from alpha-pinene ozonolysis was only observed for the lowest temperatures investigated. The SOA yields for experiments under very dry conditions at 253 K are significantly lower than corresponding humid experiments (Fig. 7)." As shown in Figure 7, the SOA yields under dry and humid conditions at 253K (blue solid and open square) and at 243K (blue solid and open cycle) lie within the uncertainty of the data. The data do not appear to be able to clearly demonstrate the effect of RH on SOA yield of ozonolysis of alpha-pinene at low temperature.

Page 15619, last line, "The present result of an insignificant water effect at 303 K is in contrast to the pronounced positive water effect observed using a flow reactor (Jonsson et al., 2006). The two systems are, however, rather different where the flow reactor study is done at low concentrations, using 2-butanol as OH scavenger and a much shorter residence time (270 s). In addition, results from a smog chamber study done at room temperature showed a positive effect of water at low reactant concentrations while an insignificant water dependence was observed at high reactant concentrations (Bonn et al., 2002). The effect of water observed at low temperatures is in line with observations in a flow reactor where a positive effect has been observed (Jonsson et al., 2008b)." All the authors have done is to state that the data show. Without a fundamental mechanistic explanation of the differences in these experiments, the current data are of little use. These experiments were presumably carried out to provide data that can be used to evaluate ones' fundamental understanding of the RH effect. Lack of this is the greatest weakness of the present paper.

3. Product distribution in particle phase

As shown in Figures 2b and 10b, the amount of more volatile product (Product 2) looks always larger than that of the less volatile product (Product 1) at low temperature. Also, the amount of more volatile product is always larger than that of less volatile product,

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even at low organic mass loading. On the other hand, the amount of more volatile product always smaller than that of the less volatile product at high temperature (Figure 2a and 10a). This is opposite to what one would expect. Do the authors have any explanation?

Other comments

Page 15598, line 6, "There has been a considerable amount of work on aerosol yields from the ozonolyis of alpha-pinene or limonene near room temperature (290-303 K)". ozonolyis changes to ozonolysis.

Page 15599, line 10, "The AIDA aerosol and cloud chamber of Forschungszentrum Karlsruhe (Saathoff etal., 2003) was used to investigate the formation of secondary organic aerosol (SOA)." SOA has been defined.

Page 15599, line 15, "Secondary organic aerosol (SOA) particles were generated by reacting (1S)-(-)-alpha-pinene." SOA has been defined.

Page 15601, line 7, "During the campaigns in 2005 and 2006 alpha-pinene, limonene, pinonaldehyde, and cyclohexanone were measured with a proton transfer mass spectrometer (PTR-MS, Ionicon)." Proton Transfer Reaction Mass Spectrometer.

Page 15607, line 7, it is stated that "At and above 303 K the initial growth rate of the SOA mass is comparable to the decay rate of the alpha-pinene mass. Hence, the ozonolysis is the rate limiting step for the SOA formation under these conditions. With decreasing temperature, however, the initial rate of SOA mass formation gradually slows down compared to the decay of the precursor mass concentration. At 243K the degradation of alpha-pinene proceeds approximately two times faster than the creation of condensed material." This observation is not clearly evident in Figure 2.

Figures 8 and 15 show the temperature dependence of SOA yields from alpha-pinene ozonolysis and limonene ozonolysis for organic mass loading, Mo at 10 μg/m3, respectively. However, no SOA yield data below Mo= 10 μg/m3 are listed in Tables 1 and 2.

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Below Mo= 10 μg/m3 a few SOA yield data are shown in Figure 7 (alpha-pinene) and no data point are shown in Figure 14 (limonene).

Figure

Page 15650, Figure 6a, alpha,1 and alpha,2 is missing in the figure.

Page 15661, Figure 13a, alpha,1 and alpha,2 is missing in the figure.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 15595, 2008.