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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Dependence of particle nucleation and growth on high molecular weight gas phase products during ozonolysis of α-pinene" *by* J. Zhao et al.

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The authors would like to thank the reviewer for valuable comments. The reviewer's comments are addressed point by point below.

1. The ozonolysis of a-pinene was done without OH scavenger. Ozone reacts only with compounds with a C-C double bond. Thus, there is only one generation of products produced by ozonolysis. Later generation of products can only be produced by OH radicals formed during the ozonolysis reaction. Adjust the terminology accordingly, eg. Page 10, line 13.

We agree that later generation products were produced by further reactions of OH radicals during the ozonolysis. We modified the sentence on p. 9328 as "Because no scavenger was added to remove OH radicals, we cannot rule out the possibility that reactions of OH radicals with products from α-pinene ozonolysis contributed to nucleation."

2. This also questions the cleaning procedure of the chamber (Page 8, line 12). Ozone alone reacts only with compounds with a C-C double bond. Without OH radicals this method does not efficiently clean the chamber. Is this the reason for the high background of experiment E1? The criteria given for a clean chamber does not include oxidized organic species. What can you tell about cleanliness with respect to oxidized organic species from PTRMS and CIMS data?

Our routine chamber cleaning procedure involved continuously circulating high levels of ozone (several ppm) through the chamber for at least one day. Before each experiment, we monitored the cleanness of the chamber with the Cluster CIMS. Typically, the signals of the peaks corresponding to category I-III compounds before adding ozone are significantly lower (1-10%) than those upon adding ozone. We believe that when high levels of ozone were introduced, a lower concentration of OH radicals was also introduced into the chamber, limited by the water content of the zero air that was exposed to the UV lamp. The high background of experiment E1 might be due to insufficient OH radicals produced to clean the chamber. The PTRMS only measured limited volatile organic compounds including the precursor α-pinene and it did not have a sufficient sensitivity to measure most of the oxidized compounds. We added several sentences on p. 9326: "The source of those background oxidized VOCs and particles is not known. It is possible that they were formed from the residual products of the prior experiment. However, the amount of aerosol formed after the ozone was added greatly exceeded the amount of aerosol present before the ozone was added (point b in Figure 1b)."

3. Page 13, line 2: Category II products start to increase with addition of ozone and

are therefore not later generation products. Ozonolysis (and OH radical reactions, which also occur to a lesser extent) forms not only products of low volatility, but also of medium and high volatility. My understanding is that category I products are low volatility products which condense first while category II products have a higher volatility and condense later when there is higher particle mass. To distinguish between first and later generation products one would need to perform the experiment with and without OH scavenger. Later generation products will have been formed in the present experimental setup, but the authors do not convincingly demonstrate which products belong to these. Page 13, line 7: It seems to me that category III products also start to increase with addition of ozone indicating that they are not (only) later generation products. My interpretation is that category III products belong to the volatile fraction of ozonolysis and OH reaction products and may be first and eventually higher generation products.

As shown in Fig. 3, there is about one hour delay for reaching the maximum level of category II products compared to that of category I products. We agree that both category II & III products are possibly a mixture of first and later generation products. We modified two sentences on p.9330, "This suggests that these products are later generation products of α-pinene ozonolysis." and "Because their appearance is further delayed in time, we infer that Category III compounds are still later generation products than Category II compounds." as "This suggests that these products are both first of α-pinene ozonolysis and later generation products formed through further OH radical reactions." and "Because they accumulate over time, we infer that Category III compounds are a mixture of first and later generation products that are contributed from both α-pinene ozonolysis and further OH radical reactions."

4. I would also like to see in Figure S6 the time trends of category II and III products.

Figure S6 was modified to show the time trends for all three category products. It should be pointed out that all category products follow similar trends as was observed for the two other experiments. But in general, the spectra measured with acetate dimer

ion are more complicated than those from nitrate dimer ion.

5. Page 20, line 22 ff: The authors claim that high m/z peaks belong to high molecular weight species. Can they confirm that these species are not just clusters (dimmers) of molecules with molecular weights of 200-300 amu.?

We assigned the observed high m/z peaks as ions containing an NO3- (at even masses) or an NO3-HNO3 (at odd masses) (p. 9331). If we assume that the dimers are formed either by hydrogen bonding or by covalent bonding that loses one water molecule, then we can find the corresponding possible monomer for most of the high m/z peaks. For example, m/z 494 peak (group 8 in Fig. 4c) is related to monomer peaks at m/z 278 (with an NO3-, Category III) or 341 (with an NO3-HNO3, Category II) or 287 (with an NO3-, Category II); m/z 558 peak (group 12 in Fig. 4c) corresponds to monomer peaks at m/z 310 (with an NO3-, Category II) or 373 (with an NO3-HNO3, Category I). Other pathways for the dimer formation are also possible. It is also possible that some of the high m/z peaks are high molecular weight species rather than dimers of lower molecular weight compounds. Without high mass resolution, it is not possible for the Cluster CIMS to definitely identify the molecular composition of those high m/z peaks. Elucidation of the molecular composition and structures of those high m/z peaks is a subject of future studies.

We added several sentences on p.9335 after "... predominantly in the 430–560 amu range.": "Some of Category I products are possible dimers of products in a lower mass range (100-300 amu), forming via hydrogen bonding or covalent bonding that loses one water molecule, or other possible formation pathways, while some of them are high molecular weight compounds rather than dimers (Fig. S6). However, high mass resolution is needed to confirm the above statement. The current unit mass resolution of the Cluster CIMS cannot definitely identify the molecular composition of those compounds". We added Table S6 to the supplementary information.

6. The authors mention that the nitrate ion has a high selectivity for ionization. Indeed,

it is puzzling that the category I species show the highest concentrations. It is not expected that the species with lowest volatility are the most abundant, higher than the semi-volatile and volatile species. Could you comment on that? This should also be considered for the estimation of growth rates (page 18/19).

It is likely that category I species have lower proton affinities for the corresponding anions so that they have higher detection sensitivities than other category species. That is the reason why measured concentrations of category I compounds were higher during the event period than other category species. It does not mean that they are the most abundant species. In fact, the exploratory experiments with acetate dimer ion as the reagent ion show much higher concentrations of category II and III species. We modified a sentence on p. 9336, “Oxidation products with less electronegativity might not be measured by the Cluster CIMS with the nitrate dimer ion.” as “Oxidation products with less electronegativity might not be measured or might be detected with a lower sensitivity (e.g., category II and III) when the nitrate dimer ion is used as the reagent ion.”

7. Page 5, line 16: Ehn et al. 2011: the reference is 2012. Check also other citations of Ehn et al.

All citations and references were corrected.

8. Page 13, line 11: fig 1c not 1b

Corrected.

9. Page 15, line 2: peak at 308 is not in Table 1.

Peak at m/z 308 belongs to category II species and it is in Table 2.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 9319, 2013.

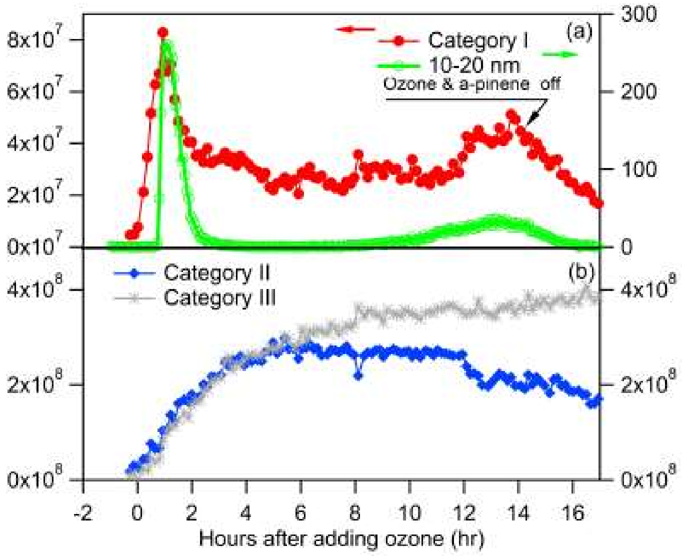

Fig. S6. Time-dependent total concentrations of the category I-III products measured with the Cluster CIMS, along with the total concentrations of 10-20 nm particles measured with the SMPS for *E3*. (a) Category I products and 10-20 nm particles; (b) Category II and III products.

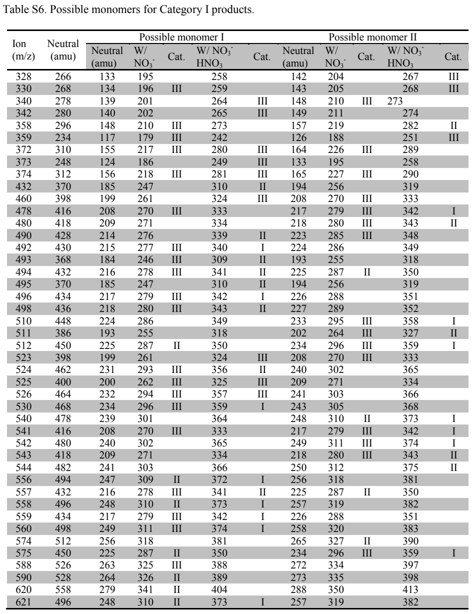

Table S6. Possible monomers for Category I products.

Ion (m/z)	Neutral (amu)	Possible monomer I					Possible monomer II				
		Neutral (amu)	W/ NO_3^-	Cat.	W/ NO_3^- HNO_3	Cat.	Neutral (amu)	W/ NO_3^-	Cat.	W/ NO_3^- HNO_3	Cat.
328	266	133	195		258		142	204		267	III
330	268	134	196	III	259		143	205		268	III
340	278	139	201		264	III	148	210	III	273	
342	280	140	202		265	III	149	211		274	
358	296	148	210	III	273		157	219		282	II
359	234	117	179	III	242		126	188		251	III
372	310	155	217	III	280	III	164	226	III	289	
373	248	124	186		249	III	133	195		258	
374	312	156	218	III	281	III	165	227	III	290	
432	370	185	247		310	II	194	256		319	
460	398	199	261		324	III	208	270	III	333	
478	416	208	270	III	333		217	279	III	342	I
480	418	209	271		334		218	280	III	343	II
490	428	214	276		339	II	223	285	III	348	
492	430	215	277	III	340	I	224	286		349	
493	368	184	246	III	309	II	193	255		318	
494	432	216	278	III	341	II	225	287	II	350	
495	370	185	247		310	II	194	256		319	
496	434	217	279	III	342	I	226	288		351	
498	436	218	280	III	343	II	227	289		352	
510	448	224	286		349		233	295	III	358	I
511	386	193	255		318		202	264	III	327	II
512	450	225	287	II	350		234	296	III	359	I
523	398	199	261		324	III	208	270	III	333	
524	462	231	293	III	356	II	240	302		365	
525	400	200	262	III	325	III	209	271		334	
526	464	232	294	III	357	III	241	303		366	
530	468	234	296	III	359	I	243	305		368	
540	478	239	301		364		248	310	II	373	I
541	416	208	270	III	333		217	279	III	342	I
542	480	240	302		365		249	311	III	374	I
543	418	209	271		334		218	280	III	343	II
544	482	241	303		366		250	312		375	II
556	494	247	309	II	372	I	256	318		381	
557	432	216	278	III	341	II	225	287	II	350	
558	496	248	310	II	373	I	257	319		382	
559	434	217	279	III	342	I	226	288		351	
560	498	249	311	III	374	I	258	320		383	
574	512	256	318		381		265	327	II	390	
575	450	225	287	II	350		234	296	III	359	I
588	526	263	325	III	388		272	334		397	
590	528	264	326	II	389		273	335		398	
620	558	279	341	II	404		288	350		413	
621	496	248	310	II	373	I	257	319		382	

Fig. 2. Table S6. Possible monomers for Category I products.