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Atmospheric
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Discussions

Interactive comment on "Reversible and irreversible processing of biogenic olefins on acidic aerosols" *by* J. Liggio and S.-M. Li

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Response to General Comments:

We would like to thank the reviewer for the comments and concerns regarding this manuscript. However, we feel that this reviewer has overlooked the main focus of the paper, by concentrating predominantly on organic reaction mechanisms, which by our own admission may have unnecessarily complicated this manuscript. Although we agree that formulating mechanisms solely from AMS data may be somewhat of an over extension we did not intend this to be the focus of the paper, nor did we intend the proposed mechanisms to be taken as the only possibilities. We have therefore removed some of the mechanistic discussion and figures from the manuscript (see response to specific comments). The important part of this paper remains the fact the significant biogenic VOCs are taken up by acidic aerosols, and that whatever mechanisms are

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at work have resulted in reversible and irreversible products. Furthermore, we believe that the estimation of uptake coefficients and/or mass accommodation coefficients is also a very important aspect of this work, regardless of the mechanistic uncertainties.

The reviewer also has stated that GC-MS or HPLC-MS analysis should be done on reaction products. Although we agree that off-line analysis may solidify the assertion of the formation of high MW products, we do not believe that it is necessary for this paper. We strongly believe that fragments in the mass spectra greater than the parent MW is clear evidence for the existence of heterogeneous reactions (see specific comments below), although we agree that assigning structures and mechanisms may not be prudent based on the mass spectra alone. This however does not mean that heterogeneous reactions have not occurred, and does not diminish any of the quantitative aspects of this paper. Furthermore, AMS derived mass spectra of the pure BVOCs have now been added to the manuscript, which are clearly different than the heterogeneous reaction spectra and further demonstrated the formation of high MW products; which we continue to believe to be polymers and/or esters.

With respect to the off-line methods suggested, GC-MS is certainly not a suitable technique for the separation and detection of polymers/oligomers. The high injection temperatures means that polymers are undoubtedly decomposed resulting in a similar problem to that which is facing the AMS. In the unlikely event that high MW oligomers were to remain intact, they would certainly not be eluted through a typical GC column. On the other hand, HPLC-MS may be more suitable for such analysis. LC-MS spectra of polymers/oligomers have been isolated on several occasions (Kalberer et al., 2006; Samburova et al 2005). However, it is very difficult to assign such a complicated spectra to a specific compound or polymer, and in doing so uncertainties regarding spectral assignments do not disappear. Tandem MS/MS analysis may help identify compounds to some degree; however, we do not have access to an HPLC-MS or a tandem MS system. For these reasons we are not convinced that adding another MS interpretation to this paper will add significantly to it, especially since it was not intended to be the focus of the paper.

Another concern of the reviewer involves the experimental conditions utilized. We agree that the BVOC concentrations are quite high due to experimental limitations. However, we have addressed this issue in the original manuscript and do not believe it to be as important as the reviewer claims. With respect to pH, highly acidic particles, even pure sulphuric acid, are not completely out of the ordinary and likely are present under certain conditions in the ambient atmosphere (see specific comments below and response to reviewer #1).

The reviewer's concern seems to revolve around the fact that no ambient evidence of such oligomers is presented in this paper. Although we agree that our own ambient evidence would be great, this study was intended to be a laboratory study only and not an ambient measurement paper. However, we note that polymers have already been detected in ambient aerosols by others (Kalberer et al., 2006; Zappoli et al.,1999; Denkenberger et al., 2007), but it is not always possible to say what the precursors were. Furthermore, terpene-like polymers have also been detected in ambient surfaces films (Lam et al., 2005) which have been potentially attributed to secondary reactions similar to the ones postulated in the present paper. The results of this paper corroborate those ambient observations. The difficulties are in separating the specific polymers from the rest. It is unclear in any event, how one would go about detecting such specific polymers as seen in the present study in ambient aerosols, particularly since levels are probably low, and BVOC polymers may not look any different than other polymers in a mass spectrometer.

As a result of all the above arguments, we strongly disagree with the reviewer in stating that a major revision is required and that it is not suitable for publication in ACP. We do believe that the reviewer has made some important comments which are addressed below.

Response to Specific Comments:

Page 11975, line 15-29:

We have modified the manuscript to cite the appropriate authors

Table 1:

We agree that the pH must be calculated with H3O+ activities. We have done so, and changed the appropriate columns in Table 1. This does have a significant effect for some experiments however; the revised pH values still support the explanation for higher organic mass yields at lower RH. Some experiments are highly acidic, but this does not negate their relevance (see response to reviewer #1).

Page 11977, line 9-10:

We agree that varying one parameter at a time would simplify the interpretation significantly. However, currently doing so is an experimental challenge. Precisely controlling the concentration of BVOC in the chamber was usually not possible, since the amount volatilized was somewhat variable, as was the volume of the expandable Teflon chamber. The same can be said for the initial aerosol concentration, which has the added variability of the atomization process. With respect to the comparison with neutral particles, we have observed previously that no uptake occurs on such neutral aerosols for a similar biogenic compound (Liggio and Li, 2006). Furthermore, we do not believe it is necessary to perform neutral aerosol experiments for every compound studied, when it is clear that it would not occur. As stated above, AMS derived mass spectra of the pure BVOCs are very different than the spectra reported here. There is no doubt that heterogeneous reactions have occurred which would not otherwise occur as a result of some physical process (ie: absorption/adsorption). Indeed, it is highly unlikely that solubility or adsorption/absorption on neutral aerosols without reaction can account for the amount of uptake which is observed. We have stated these facts in the revised paper.

Page 11977, line 10-11:

The seed particle diameter is referring to the vacuum aerodynamic diameter not the mobility diameter. The mobility diameter is closer to 300 nm. This size of particle was chosen to take advantage the single particle detection capabilities of the AMS which is most efficient in this range. This has already been stated in the manuscript (pg 11978, line 28).

We agree that highly acidic particles are more likely in nano-particles. In separate field studies, we ourselves have often observed that newly nucleated nano-particles would grow into submicron size range of a few hundred nanometers, either through coagulation or condensation, over forested areas and these events were associated with sulphuric acid. However there is currently no such instrument capable of measuring the organic composition of nano-particles. We may have been able to use slightly smaller particles but nowhere close to nano-particles. We have added text to the manuscript to clarify this point.

Page 11977, line 24:

We have included PTR-MS data in the supplemental information and a reference to it.

Page 11978, line 15:

The AMS operating conditions have now been included in the experimental section. We have thought about utilizing lower EV and temperatures, however this would interfere with the quantification of the inorganic mass, and in practice the interpretability is only slightly enhanced. The best method may be with a different ion source completely, such as a UV source etc.

Page 11979, line 3:

We have made the appropriate change.

Page 11979, line 14:

The time profiles of other experiments look very similar, and there are indeed significant wall losses. However, as we have explained in the manuscript (pg 11979 line 17-22), the wall losses are corrected for by normalizing the mass by the particle number. The result is the mass on a per particle basis, which does not depend on wall losses. For this reason we feel that adding more time profiles to the supplemental section would not add any important information.

Page 11980, line 20:

We agree and have made the requested change

Page 11980, line 22-23:

We have adjusted the pH values (see above). However, as far as we know there is no solubility data available for these specific compounds in acidic media. Nonetheless, it is generally known that olefins are more soluble in acidic solution. Given the new pH values this may be even more relevant.

Page 11981, line 25-26:

We have indeed observed an increase in the PTR-MS signal upon increasing the RH. However, it is not clear whether this was a result of the off-gassing of BVOC from aerosols or a change in the response of the PTR-MS at higher RH which may occur. Regardless, it is doubtful that the instrument is sensitive enough to measure such a small change due to aerosol off-gassing in a large background. We have added text to the revised version explaining this point.

Page 11982, line 8-9:

We disagree with the reviewer. On the contrary, we believe there is significant evidence of heterogeneous reactions. The fact of the matter is that there is significantly more mass taken up than any physical process could possibly account for especially for such high vapor pressure species. In addition, one cannot ignore the fact that many fragments are observed beyond the parent m/z. These must have arisen from some sort of reaction, regardless of the mechanism. Unfortunately, the mass range of this

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particular version of the AMS is limited to 300 amu, and the sensitivity is lower than that of current TOF AMS models. Moreover, the intense heating and ionization results in numerous small fragments and less larger ones. Therefore, one cannot infer that the relative importance of polymers is small based on the low intensities of larger fragments or the fact that they are all less than m/z 300. The fact that they are there at all must imply that they have formed and is in itself clear evidence to support the sentence in question. Moreover, AMS spectra of the pure compounds are very different than the spectra presented here; they do not have any fragments larger the parent MW and are different in the low mass range as well. Given this evidence, the formation of heterogeneous products is in our opinion not disputable.

Page 11982, line 21-24:

(see above response)

As noted above, the m/z signals must be less than 300 since that is the limit of the instrument. Although their intensities are low, sesquiterpenes also have fragments greater than the parent compound up to the limit of the AMS. They do not clearly show up in the figures as presented but they are certainly above the detection limits of the instrument. Considering that the MW of the terpenes is 136, 154, or 204, Figure 4 does indeed show that there are many fragments greater than the MW, although we agree that their intensities are low primarily as a result of the detection process itself (see above). This does not mean that they do not exist. We cannot however state with certainty how large the polymer is because of the stated instrumental limitations.

Page 11982-11985, Section 3.2. and 3.3., Figure 5 and Figure 3 of Supplemental Information:

We agree that there may be some issues with the mechanisms, and we have removed some of them from the paper as they were never intended to be the focal point. In any case, we did not state that the proposed structures were the only possibilities nor did we state the mechanisms were the only possible pathways. In fact we realize that there are likely many other reaction pathways, some of which may be more energetically favorable than what was presented. We merely meant to show some of the potential mechanisms/products. However, because of the larger m/z fragments, and the fact that they are olefins to start with, we are certain that a cationic polymerization must have occurred to some extent, the exact mechanisms we agree are not clear. To remove the confusion surrounding mechanisms, Figure 3 and Figure 4 of the supplemental information have been removed.

Figure 3 of Supplemental Information:

We have shown both tertiary and secondary carbocations in this figure and several positions. We agree that tertiary carbocations are generally more stable, but that doesn't mean that it does not occur. We agree that ring opening may not be the first step, and we cannot be sure what the first step might be. As noted previously, there are likely many pathways involving ring opening, tertiarty carbocations etc... We cannot show them all nor be certain which ones are most important and therefore have removed this figure completely. We also agree that assigning fragments to partial structures may not be entirely useful at this point and thus have also removed this from any figures. Furthermore, we agree that similar fragmentation patterns may not mean similar mechanisms, only similar products.

Figure 5:

We agree with the reviewer that tertiary carbocations may be less likely in this case, but as noted above we did not intend the mechanisms to be the focal point of the paper or the only possibilities. Assuming secondary carbocations does not change the outcome of the paper. We have however adjusted the manuscript to emphasize that the mechanisms in this figure are only some of the potential mechanisms and perhaps not the most favorable.

We agree that sulfate under most conditions may not be a good nucleophile. However, in some cases, particularily where other nucleophiles are less prevalent, this may re-

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main possible. This may be the case in the highly acidic experiments at low RH. We have stated such in the revised manuscript.

Sulfuric acid is indeed a good dehydrating agent, which may influence the uptake of hydroxy-monoterpenes. At this point we cannot be certain what the effect would be, mainly because hydroxy-monoterpenes and other terpenes are both taken up significantly under high acidity conditions. However, it does appear that the uptake is somewhat higher for hydroxyl compounds, although it is not clear why.

The position of a double bond likely does affect the reactivity and the formation of carbocations, however it is difficult to see significant changes in the uptake for monoterpenes based on this fact. It does not seem to make much of a difference in terms of the uptake. In any event this was not intended to be a mechanistic study.

Section 3.2. and 3.3:

Since the MW is 204 amu, a large abundance of m/z 205 would imply that an olefin has been protonated at some point resulting in a carbocation. This would undoubtedly result in the addition of another molecule of some kind. This is supported by the even larger m/z fragments. Normally the M+1 peak in mass spectrometry is quite low. There is no reason to think that the M+1 peak in an AMS spectrum of b-caryophylene should be any bigger than the M+1 of a NIST spectrum. The observation of any M+1 fragment in mass spectrometry is related to the detection pressure. Under the low pressure conditions of the AMS there is no reason to believe that the M+1 peak should be enhanced. If fact, the relative proportion of m/z 205 in our spectra is at least an order of magnitude greater than in the NIST spectra. Since such a large M+1 peak is very unlikely under these conditions it must have arisen from a larger molecule. Furthermore, what is observed here is significantly higher than what is observed in the AMS spectrum of pure b-caryophyllene. The AMS derived spectra of many of the pure starting materials have been appended to this paper to show that they are significantly different than the end products, and do not contain fragments greater than the parent m/z thus providing

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even more evidence for heterogeneous reactions.

We agree that a decrease in the sulfate signal alone is not the best evidence for organosulfate formation, but it is some indication. Since the sulfate mass is on a per particle basis, this is an indication of a SO4 conversion. We can see how the reviewer might have had issues with this if a decrease in the non-normalized sulfate signal was used. This however is not the case (see comment for Page 11979, line 14). We do think that we may have over-extended our interpretation somewhat and thus have removed Table 3, but this does not mean that organosulfates have not formed, only that the quantification is uncertain. Indeed organosulfates have been observed recently in ambient and lab studies as stated in the paper.

Equilibrium constants for the hydration of these particular species under different aqueous conditions are not available. However, there is a clear decrease in the amount of organic mass (per particle) after increasing the RH. This means that mass was lost. If equilibrium were shifted towards hydration instead one would expect the organic mass to increase not decrease. This is not what was experimentally observed. The only reasonable way to lose material is via volatilization, which must imply that equilibrium shifted to the gas phase.

Low RH - high RH means subtraction of the spectra of the low RH portion of experiment #9 from the high RH portion of the same experiment (#9). In doing this we are able to see what the spectra of the evolved material might look like. This is clarified in the revised manuscript.

Page 11987, line 2:

An SMPS was not connected to the chamber, as its input flow would deplete the volume of the bag too quickly. Since the mass was normalized per particle, collection efficiency issues associated with the AMS are not important. The reliability of the mass is then mostly dependent upon the ionization efficiency calibration, which was done often during these experiments. We anticipate the AMS derived mass is rather accurate and unlikely to be more than 20% uncertain.

Page 11991-11995, Atmospheric Significance:

We agree that this section may be somewhat long and confusing. We have modified it in the revised version (see response to reviewer #1).

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