A Chamber Study of Aging of Secondary Organic Aerosol Formed by photo-oxidation of β-pinene

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Introduction

The chemical aging processes can influence both the chemical and physical properties of secondary organic aerosols (SOA) and subsequently their effects on climate change and human health. Further oxidation of primary oxidation products with oxidants such as the hydroxyl radical (OH) and ozone (O_3) can result in either less volatile products which contribute to SOA mass or form higher volatility products which do not. However, little is known about the effects of aging on SOA. The objective of this study was to investigate the chemical aging processes of oxidation products generated from the OH initiated oxidation of β-pinene to examine if they can undergo further oxidation with OH radicals and O_3. Both gas and particle phase products were analyzed to distinguish between the aging effects in the two phases.

Experimental

York University Smog Chamber
(8 m^3 Teflon bag surrounded by 24 UV lights)

Aging Experiments

- Introduce $(NH_4)_2SO_4$ seed particles
- Inject β-pinene, isopropyl nitrite (OH source) and NO
- Mixing time: 1 hour
- Lights are turned on initiating reaction

Performed 2 times:
- Lights are turned off after complete depletion of β-pinene
- Inject isopropyl nitrite (5 times higher) or O_3
- Mixing time: 1 hour
- Lights are turned on initiating aging (For OH Aging)
- Reaction times range : 6 hours

Measurements

- *Tandem DMA-CNC* : determine particle size distribution and organic particulate mass concentration
- *Chemiluminescence NO_x analyzer* : measures NO and NO_x concentrations
- *GC-FID* : monitors β-pinene concentration
- *API 365-APCI MS/MS* :
  - Atmospheric pressure chemical ionization source
  - Triple quadrupole mass analyzer
  - Analyze chemical composition of oxidation products and monitors reaction profiles

*Counter flow membrane denuder (CFMD): Separates gases from particles to investigate particle phase products

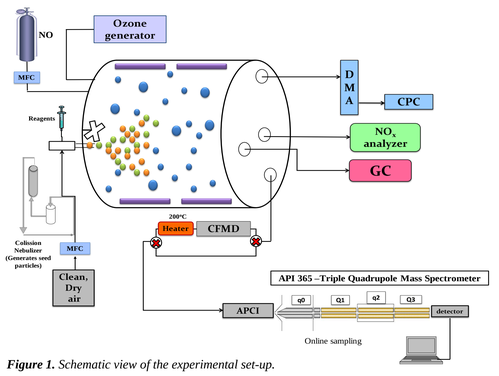

Figure 1. *Schematic view of the experimental set-up.*

Results

1. OH Induced Aging

Previously in our study, the chemical composition of gas and particle phase products generated from β-pinene photo-oxidation were studied and a number of products were identified. During aging experiments, the products times profiles were acquired by monitoring selected precursor to product ion pairs signal over the course of the reaction (SRM time profiles) to examine their formation during the β-pinene photo-oxidation and also their fate under aging condition.

Nopinone which is the major primary product of β-pinene photo-oxidation shows a sharp decay upon OH exposure which indicates its further oxidation during aging (Figure 2). By initiating β-pinene oxidation, organic particles were formed resulting in an increase in the organic particulate mass concentration. Over the lights off period, the particulate mass remained pretty constant and after lights being turned on (more OH production) for aging, a rise in the particulate mass was observed which indicates further formation of SOA mass (Figure 3).

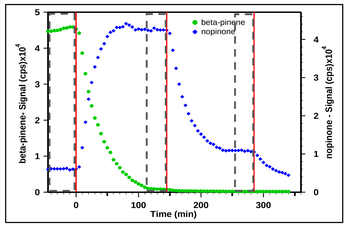

Figure 2. *Tme profiles for the ion pairs 137→81 (green marker) and 139→121 (blue marker) representing particle phase β-pinene and nopinone respectively. The grey boxes show the mixing time when the lights were off and the vertical red lines indicate the time at which the lights were turned on .*

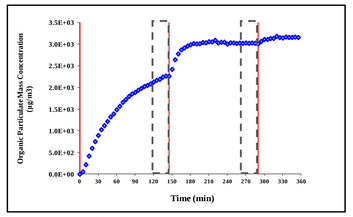

Figure 3. *Time profile of organic particulate mass concentration during β-pinene OH induced aging experiment.*

❖ Carboxylic acid products

A number of carboxylic acid products have been previously identified including pinalic 3-acid, norpinic aicd and pinic acid. In the acquired time profiles of these acids, a rise in signal was observed after they were exposed to OH radicals (after 2nd lights on) which indicates additional formation of these carboxylic acids products during aging (Figure 4). During the same time period, the nopinone profile showed a rapid decay in signal suggesting that it was a source of further carboxylic acid products formation.

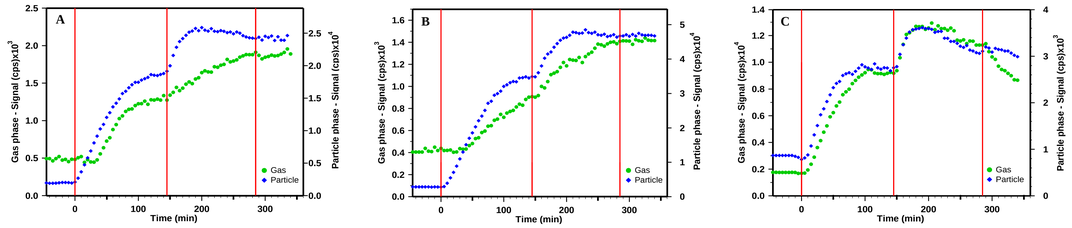

Figure 4*. SRM time profiles for (A) pinalic 3-acid (171→125), (B) norpinic aicd (173→127) and (C) pinic acid (187→141). The gas and particle phase are distinguished using green and blue symbols respectively.*

❖ Nitrate products

The main observation from the nitrate products profiles (C10 aldehyde nitrate, C10 hydroxy nitrate and C10 dihydroxy nitrate) was that after they were exposed to OH radicals, their signal started to decrease (Figure 5). This indicated that nitrate products, in contrast with the carboxylic acid products, were not formed from nopinone oxidation. Mechanisms of their formation indicates they were formed via β-pinene oxidation[1].

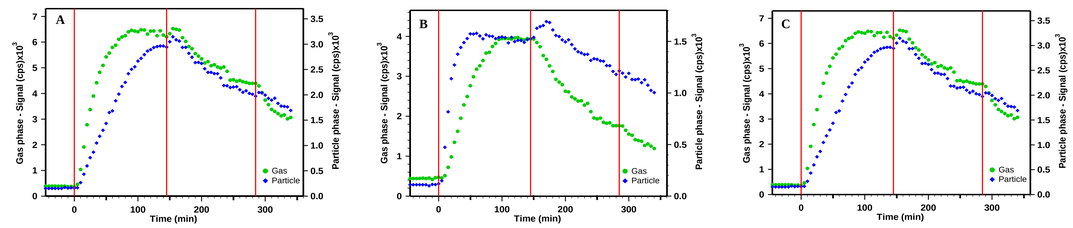

Figure 5. *SRM time profiles for (A) C10 aldehyde nitrate (214→168), (B) C10 hydroxy nitrate (216→152) and (C) C10 dihydrocy nitrate (232→151).*

❑ Additional SOA formation source

Observations from SRM profiles suggested that nopinone plays an important role in the additional formation of several oxidation products such as carboxylic acids during aging. In order to investigate how much nopinone contributes to additional SOA formation during aging, a number of nopinone experiments were carried out in the smog chamber under the same condition as in the β-pinene aging experiments (The nopinone yield after completion of β-pinene oxidation in the chamber was found to be 25% [2]). These results indicate that the organic mass concentration formed during the β-pinene aging experiments was higher in comparison to the nopinone experiments (Figure 6). This indicates that some other products also contributing to the additional organic mass formation during aging (e.g., hydroxy nopinone).

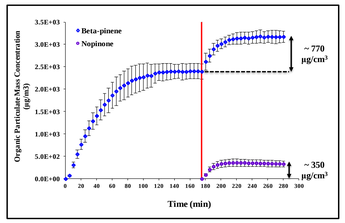

Figure 6. *Comparison of organic particulate mass concentration evolution from β-pinene OH induced aging (blue) and nopinone photo-oxidation experiments (purple).*

2. O_3 Induced Aging

For O_3 aging experiment, (to avoid NO_3 radical formation) dark ozonolysis experiments were performed in order to generate oxidation products which then were exposed to enhanced level of O_3. The results indicate that O_3 did not seem to have any significant impact on the nopinone pattern (Figure 7). It should be note that the observed slight decrease in nopinone profile is due to OH radicals formation in the system (since no OH scavenger was used). The particulate mass concentration profile before and after the O_3 exposure period demonstrated no change after 4 ppm O_3 and only a very slight increase after the 8 ppm O_3 level was reached (Figure 8). This indicated that aging with O_3 does not cause additional SOA mass formation except under very high O_3 level.

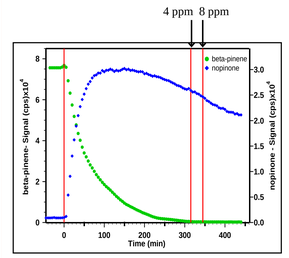

Figure 7. *Time profiles of β-pinene and nopinone. The addition time of O_3 is shown by red vertical lines and overall O_3 levels are marked by arrows for each addition.*

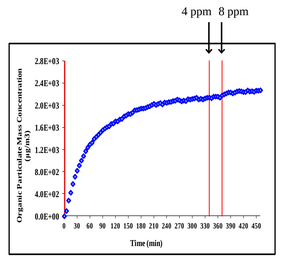

Figure 8. *Time profile of organic particulate mass concentration during β-pinene O_3 induced aging experiment. The addition time of O_3 is shown by red vertical lines and overall O_3 levels are marked by arrows for each addition.*

Conclusions

In this study the oxidative aging process of oxidation products derived from β-pinene precursor within the chamber has been investigated. The aging was much stronger for β-pinene OH induced aging compared with the very stable β-pinene dark ozonolysis system. The observed changes in chemical composition of products and additional production of SOA mass during OH induced aging can be explained by further oxidation of gas phase products, mainly nopinone, which produce compounds partitioning to the particle phase (i.e., carboxylic acids). No evidence was found for formation of high-molecular-weight species or any new oxidation products. These observations are consistent with those of other studies [3,4] .

References

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