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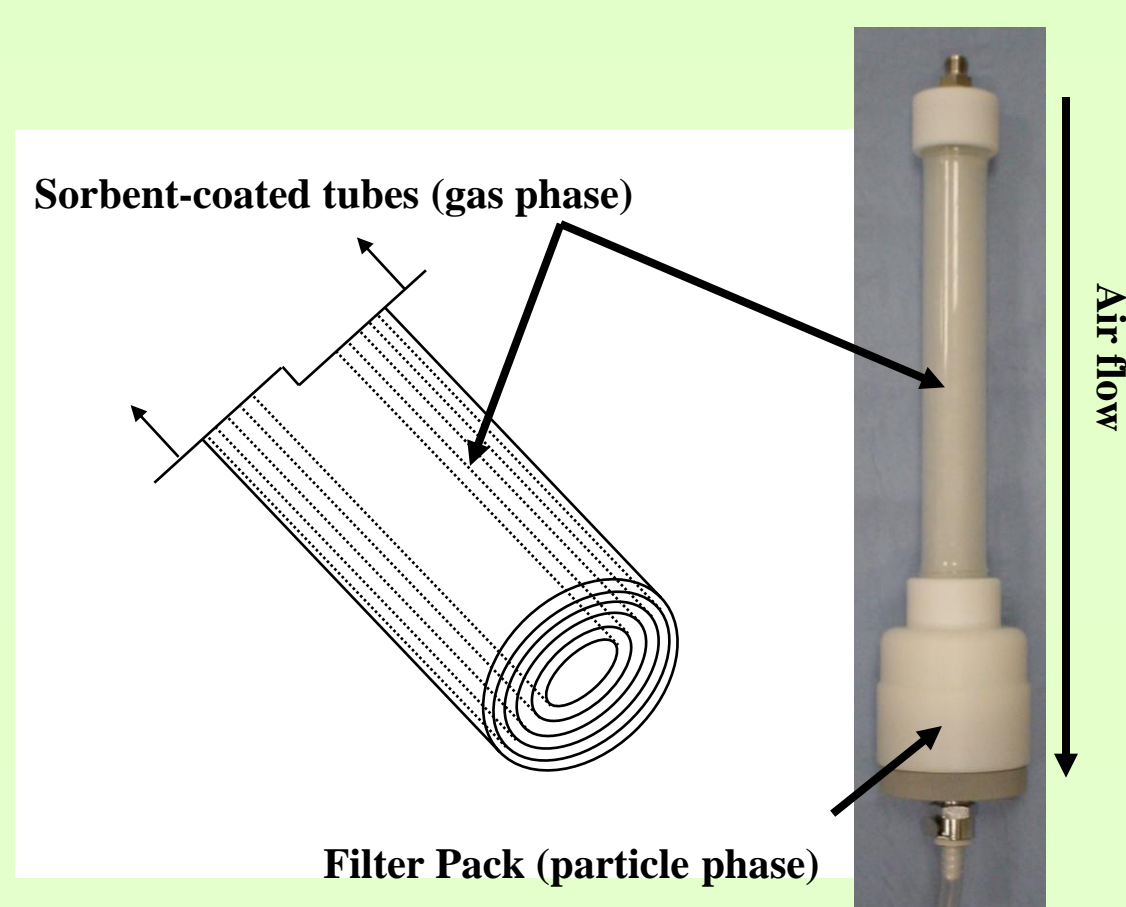
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Introduction

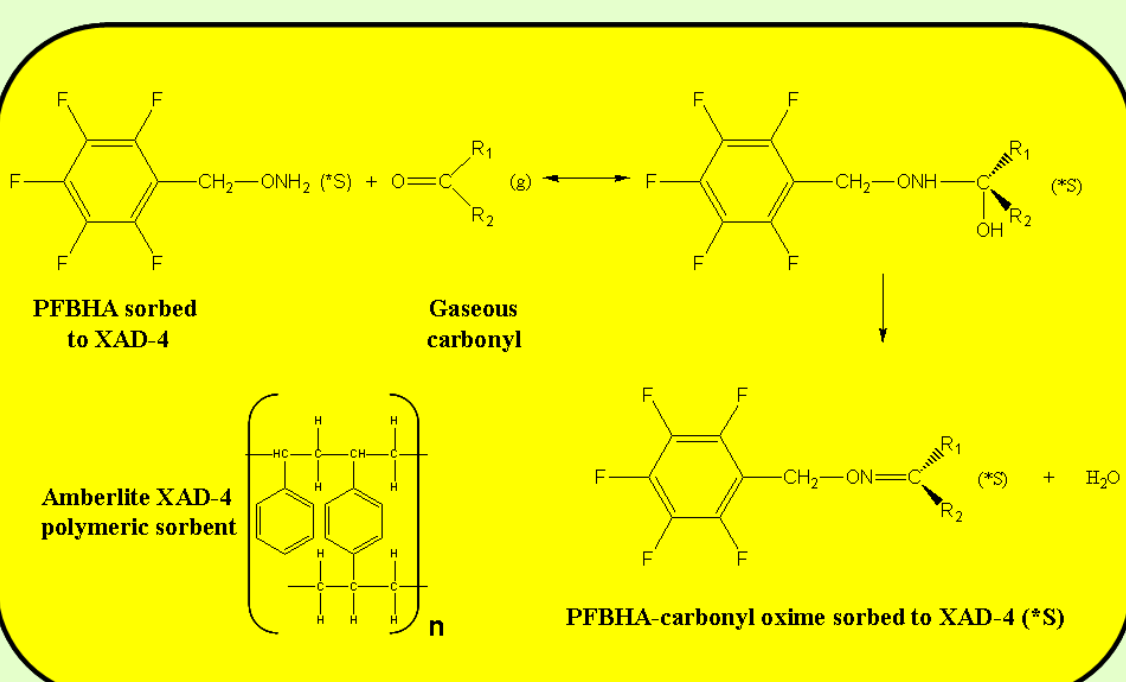
A new denuder-filter sampling system has been developed to collect gas and particle-phase products arising from the atmospheric oxidation of VOCs. The denuder is coated with a mixture of XAD-4 resin and the derivatizing agent *O*-pentafluorobenzyl hydroxyl amine (PFBHA) which reacts specifically with compounds containing aldehyde and ketone functional groups. The filter is also coated with PFBHA to derivatize the particle-phase products. The derivatized compounds are detected by GC-MS. The performance of the denuder was tested on a wide range of polar organic compounds including aromatic aldehydes, phenols, benzoquinones, furans and smaller carbonyls such as glyoxal and methylglyoxal. Once tested the method was successfully applied to simulation chamber studies of isoprene and 1,3,5-trimethylbenzene (1,3,5-TMB) photo-oxidation in order to investigate the gas/particle partitioning behaviour of the products formed. Experiments were carried out in atmospheric simulation chambers both at University College Cork and the Paul Scherrer Institut, Switzerland. GC-MS was employed for the identification and quantification of derivatized species. Partitioning (K_p) values for products are then calculated from their concentrations in the particle (C_p) and gas (C_g) phase and the aerosol mass concentration (TSP), $K_p = \frac{C_p}{C_g \text{ TSP}}$

Denuder-filter

The efficiency of the denuder-filter system has been previously tested in a series of experiments at UCC. The PFBHA coated denuder was observed to efficiently collect a range of carbonyl compounds over short sampling periods.



Above: The denuder-filter apparatus

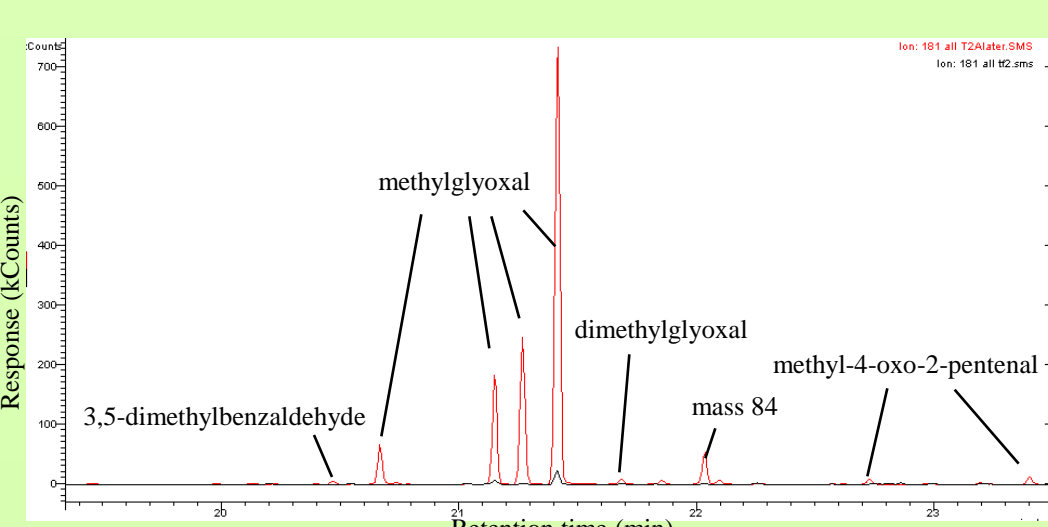
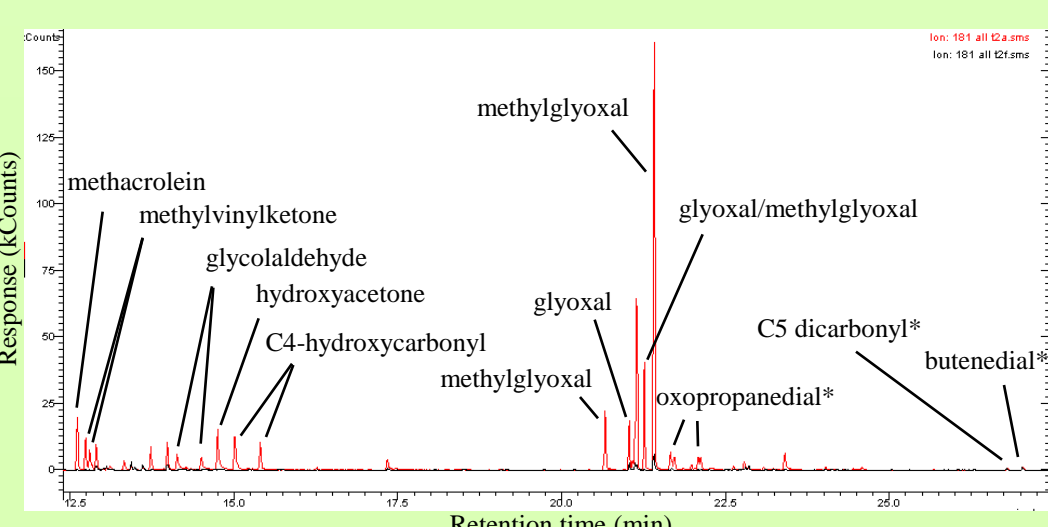


Above: The on-tube derivatization process

Gas phase carbonyls react with PFBHA at the denuder walls and are subsequently bound. Particles are efficiently transmitted through the denuder to a PFBHA coated filter.

GC-MS Analysis

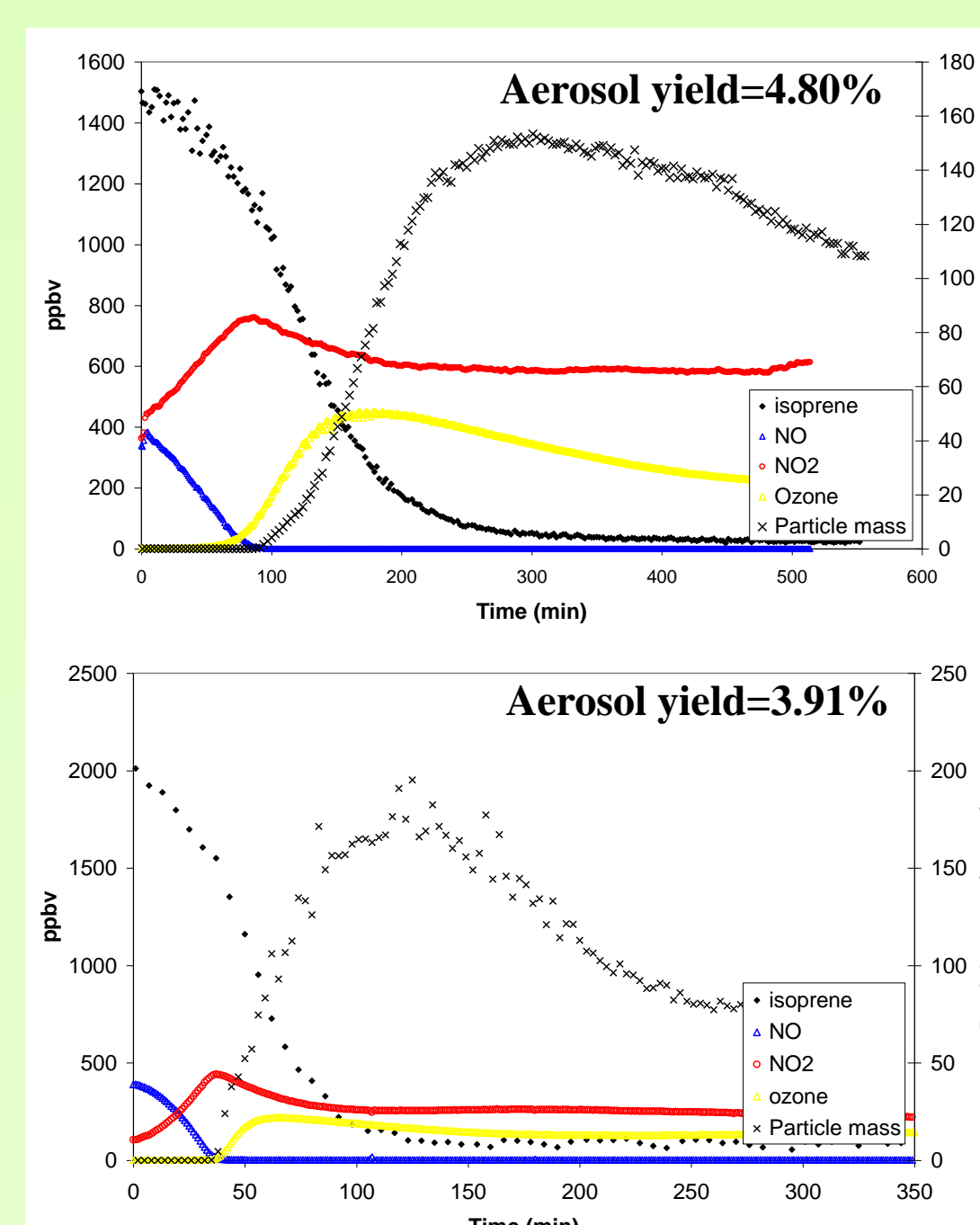
After sampling the denuder and filter are extracted and analyzed by GC-MS. At UCC a preconcentration step was introduced to increase the sensitivity of the method for particle phase carbonyls. Direct comparison of the responses in both phases is used to calculate partitioning values. Using appropriate standards gas and particle phase concentrations were then calculated.



Above: Reconstructed $m/z=181$ ion chromatograms of denuder (red) and filter (black) extracts in the isoprene (top) and 1,3,5-TMB (bottom) systems. (*tentatively identified)

Isoprene System

The photooxidation of isoprene was carried out at UCC and PSI under similar experimental conditions. Three denuder-filter samples were taken at regular intervals once the particle mass had reached a maximum in order to investigate the partitioning behaviour of the products formed. The reaction was faster at UCC due to the different lamps used for irradiation. Aerosol yields were calculated once particle mass had been corrected for wall loss. The yield observed at UCC was lower and may be due to the higher temperature at which the experiment was performed. Partitioning values were calculated for both experiments. For the experiments at UCC products in both phases were quantified by GC-MS using the appropriate standards or structurally similar substitutes.



Top: Concentration-time profile of isoprene photooxidation in the presence of NO_x at PSI

Bottom: Concentration-time profile of isoprene photooxidation in the presence of NO_x at UCC

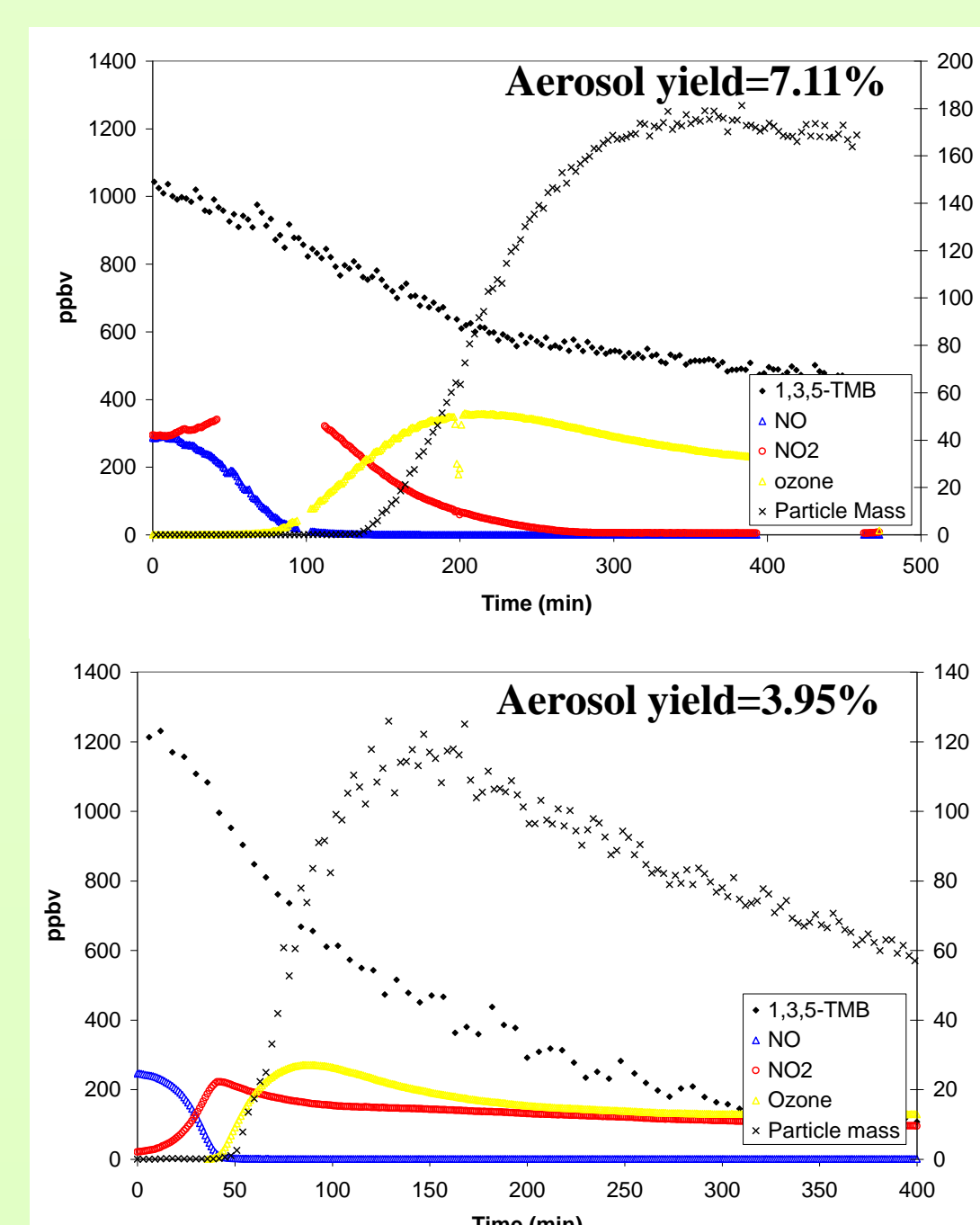
A range of carbonyl products were observed in the gas phase at PSI but only glyoxal and methylglyoxal were observed in the particle phase. However, a more efficient preconcentration step was employed at UCC enabling the quantification of a C5 unsaturated dicarbonyl* and butenedial* in the particle phase (*tentatively identified). These compounds represent a relatively small fraction of the SOA mass, but partition to a far greater extent than predicted by their vapour pressures.

| PARTITIONING VALUES | PSI sample1 | PSI sample2 | PSI sample3 | UCC sample1 | UCC sample2 | UCC sample3 |
|--|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| K_p glyoxal ($\text{m}^3\mu\text{g}^{-1}$) | 7.8×10^{-5} | 6.9×10^{-5} | 3.5×10^{-4} | 7.4×10^{-5} | 4.8×10^{-5} | 6.6×10^{-5} |
| K_p methylglyoxal ($\text{m}^3\mu\text{g}^{-1}$) | 7.4×10^{-5} | 8.6×10^{-6} | 4.0×10^{-5} | 4.0×10^{-5} | 1.1×10^{-5} | 1.1×10^{-5} |

| SOA COMPOSITION | UCC sample1 | UCC sample2 | UCC sample3 |
|------------------------------------|-------------|-------------|-------------|
| Glyoxal % of SOA | 1.13 | 0.68 | 0.78 |
| Methylglyoxal % of SOA | 1.32 | 1.09 | 1.17 |
| C5 unsaturated dicarbonyl % of SOA | 0.24 | 0.24 | 0.35 |
| Butenedial % of SOA | 0.42 | 0.35 | 0.38 |

1,3,5-TMB System

The photooxidation of 1,3,5-TMB was also performed at UCC and PSI under similar experimental conditions and denuder-filter samples were taken at regular intervals once the particle mass had peaked. Again, the reaction proceeded more quickly at UCC and the yield was lower than observed at PSI, probably for the same reasons as the isoprene system. Methylglyoxal was the major gas-phase carbonyl product for the 1,3,5-TMB system. Although methylglyoxal was the only particle phase carbonyl observed at PSI, several other carbonyls were observed in filter extracts at UCC. This can be attributed to the improved extraction and preconcentration steps employed.



Top: Concentration-time profile of 1,3,5-TMB photooxidation in the presence of NO_x at PSI

Bottom: Concentration-time profile of 1,3,5-TMB photooxidation in the presence of NO_x at UCC

Methylglyoxal, methyl-4-oxo-2-pentenal, butenedial* and methylbutenedial* were quantified in the particle phase (*tentatively identified).

| PARTITIONING VALUES | PSI sample1 | PSI sample2 | UCC sample1 | UCC sample2 | UCC sample3 |
|--|----------------------|----------------------|----------------------|----------------------|----------------------|
| K_p methylglyoxal ($\text{m}^3\mu\text{g}^{-1}$) | 1.9×10^{-5} | 2.0×10^{-5} | 2.7×10^{-5} | 9.1×10^{-6} | 1.5×10^{-5} |
| K_p methyl-4-oxo-2-pentenal ($\text{m}^3\mu\text{g}^{-1}$) | | | 1.4×10^{-4} | 7.6×10^{-5} | 8.5×10^{-5} |

| SOA COMPOSITION | UCC sample1 | UCC sample2 | UCC sample3 |
|----------------------------------|-------------|-------------|-------------|
| Methylglyoxal % of SOA | 3.85 | 2.04 | 2.93 |
| Methyl-4-oxo-2-pentenal % of SOA | 3.49 | 1.97 | 1.96 |
| Butenedial % of SOA | 1.42 | 1.10 | 1.05 |
| Methylbutenedial % of SOA | 0.05 | 0.46 | 0.59 |

At UCC experiments were also carried out on both the isoprene and 1,3,5-TMB systems at higher precursor concentrations in order to increase the SOA mass formed yielding similar results with increased reproducibility.

Conclusions, Future Work and Acknowledgements

For both systems, dicarbonyls are found in the particle phase, indicating that this functionality is important for gas-particle transfer. For example, methacrolein, methyl vinyl ketone, glycolaldehyde and hydroxyacetone were observed in the gas phase for the isoprene system but were not observed in the particle phase (or were below the limit of detection of the method). The results indicate that the partitioning behaviour of dicarbonyl oxidation products cannot be explained by standard partitioning theory alone, e.g. Pankow (1994) [1,2]. Recently, simulated aerosol mass concentrations from the master chemical mechanism for alkylbenzenes were only found to agree reasonably well with experimental data once absorptive partitioning coefficients were corrected by a factor of 5-30 [3]. Therefore dicarbonyls may be undergoing particle phase reactions to form low-volatility products that remain in SOA. This can be explained by oligomerization processes which have been observed at PSI both for the 1,3,5-TMB and isoprene systems [4,5]. The presence of the small dicarbonyls glyoxal and methylglyoxal in the filter extracts of this study may thus be explained by the breakdown of high molecular weight oligomers during extraction and storage to yield the monomeric form.

Future work will include a detailed study of the partitioning of the photooxidation products of *p*-xylene in a series of experiments under varying conditions, for example different humidities and VOC/NO_x ratios.

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[1] Pankow, J. F. *Atmospheric Environment* 1994, 28, 185-188. [2] Pankow, J. F. *Atmospheric Environment* 1994, 28, 189-193. [3] Johnson *et al. Environmental Chemistry* 2005, 2, 35-48 [4] Kalberer *et al. Science* 2004, 303, 1659-1662. [5] Dommen *et al. Geophysical Research Letters* 2006, 33, L13805.