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Smog Chamber Experiments of SOA Formation from Gasoline Exhaust and Light Aromatics

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Experiments where gasoline exhaust was exposed to UV-radiation to examine Secondary Organic Aerosol (SOA) formation were performed in a smog chamber. The Aerosol Mass Yield (formed SOA/reacted precursor mass) was determined and compared with the yield from a pure precursor experiment in the chamber and from results reported in literature. Preliminary results show that the majority of the organic aerosol mass emitted from idling gasoline cars is secondary. Further, the SOA yields when taking only C6-C10 light aromatics into account are within a similar range to pure precursor experiments, suggesting that light aromatics are dominating precursors in gasoline exhaust SOA.

Introduction

Aerosol particle mass formed by oxidation of volatile organic compounds (VOCs) in the atmosphere is generally denoted as secondary organic aerosol (SOA). SOA formation from combustion processes is a subject that is not well understood, because it involves a large number of complex physical and chemical processes such as the oxidation and gas to particle transformation of VOCs (Hallquist *et al.*, 2009). A key concept is the Aerosol Mass Yield; it is the ratio between the formed SOA and reacted precursor mass. Previous studies (Ng *et al.*, 2007), (Hildebrandt *et al.*, 2009) have determined the yield for photo oxidation in experiments with single light aromatics such as toluene and xylene. The results indicate that the yield is higher for experiments in low-NO_x conditions than under high NO_x-conditions. The mass concentration of organic aerosol particles may also influence the yield

In this paper we report some preliminary results from photo-oxidation experiments in a smog chamber for exhaust from idling gasoline cars. The aim was to examine the SOA formation from gasoline exhaust and compare the results with model experiments using a mixture of toluene and xylene (TX).

Methods

The experiments were performed in a 6 m³ Teflon (FEP) chamber, housed inside a larger 22 m³ thermally insulated stainless steel enclosure. Important characteristics of the chamber and the experimental conditions are listed in table 1 (Nordin *et al.*, 2009). The chamber background was estimated by irradiating pure air containing ammonium sulphate seeds. The OA concentration was < 0.5 µg/m³ after 5 h irradiation. Gasoline

exhaust or a mixture of toluene and m-xylene (TX), were exposed to UV-radiation (black lights, peak intensity at 350 nm) in the chamber. The vehicle exhaust was diluted using an ejector diluter (1:10) and injected to the chamber at a flow rate of 0.00083 m³/s (50 lpm) via a heated stainless steel inlet (140 °C). An idling gasoline car (Volvo V40, 1998) was used. Toluene and m-xylene were injected to a glass bulb and added to the chamber through evaporation in the pure precursor experiments. A summary of results from the three experiments is given in table 3. Nebulized ammonium sulfate (20-50 µg/m³) was utilized as condensation seeds in all experiments. Additional NO was added in the Gasoline 1 and TX experiments. The experiments were monitored by several particle characterization instruments and gas analyzers as shown figure 1 and table 2, including a High Resolution Time of Flight Aerosol Mass Spectrometer (HR-TOF-AMS) and a Proton Transfer Reaction Mass Spectrometer (PTR-MS).

To estimate the Aerosol Mass Yield:

$$(Y = \frac{C_{SOA}}{C_{VOC}})$$

the concentration of formed SOA and reacted light aromatics was determined. In order to get an accurate measure of the total formed SOA, particle losses to the walls in the Teflon chamber were accounted for. This was done by determining the ratio between sulphate and organics in the particle phase (AMS) in every data point and assuming that the wall loss corrected sulphate concentration was constant. The AMS data were then scaled to the initial volume concentration from the SMPS. The wall loss correction method is described by Hildebrandt *et al.* (2009). To convert the volume concentration to mass concentration, an OA effective density of 0.00130 kg/m³ and 0.00177 kg/m³ for the ammonium sulphate was used. The SOA density was independently determined using the Differential mobility analyzer – aerosol particle mass analyzer method.

For the gasoline exhaust experiments the yield was calculated for 5 types of light aromatic compounds, Benzene, Toluene, Xylenes, C9 and C10-Aromatics. Complementary tube sampling for GC-MS analysis was also performed to get specific species based concentrations at the beginning and end of the experiment.

Gasoline 2 and TX have similar initial light aromatics to NO ratio, about 20 times higher than that in the Gasoline 1 experiments (where NO was added).

Table 1: Characteristics of the Lund University Smog Chamber and the experimental conditions in this study.

Dimensions	Relative Humidity	Temperature	Photolysis rate
1. 52 * 1. 83 *2. 13 m (6m ³)	5 – 10 %	23 ±2 °C	0.16 min ⁻¹

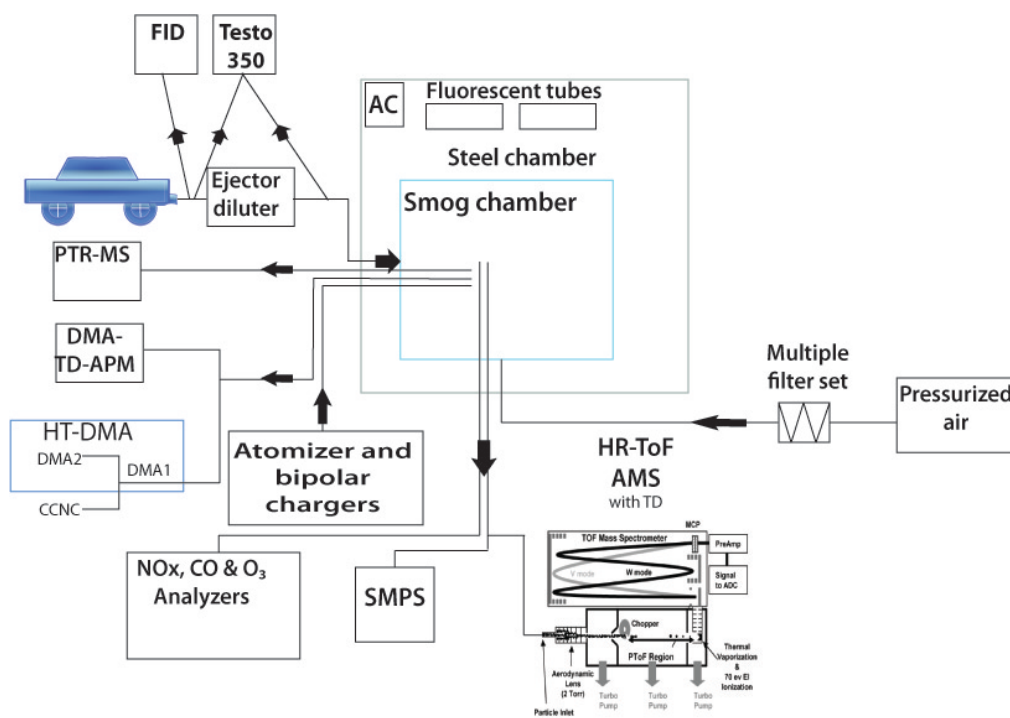


Figure 1: The measurement setup, cf. table 2 for additional information.

Table 2: Explanations of the abbreviations in figure 1 together with references to literature that further describes the measurement technique.

Abbreviation	Long form	Measuring quantity	Reference
SMPS	Scanning Mobility Particle Sizer	Size distribution	
HR-TOF-AMS + TD	High Resolution- Time of Flight- Aerosol Mass Spectrometer + Thermo denuder	Chemical composition of particles/Volatility	(DeCarlo <i>et al.</i> , 2006) (Eriksson <i>et al.</i> , 2010)
DMA-TD-APM	Differential Mobility Analyzer-Thermo Denuder-Aerosol Particle Mass Analyzer	Effective density	(Park <i>et al.</i> , 2003) (Rissler <i>et al.</i> , 2010)
HT-DMA	Hygroscopic Tandem-Differential Mobility Analyzer	Cloud activation properties	(Wittbom <i>et al.</i> , 2010)
PTR-MS	Proton Transfer Reaction-Mass Spectrometer	Concentration of VOCs	

Table 3: List of experiments, the initial concentrations are defined as when the UV-radiation starts

Experiment	NO (initial)/ NO ₂ (initial)/ O ₃ (final) concentration (ppb)	Initial C6-C10 concentration (ppb)	Initial light aromatics/ NO-ratio	Reacted light aromatics, C6-C10 ($\mu\text{g}/\text{m}^3$)	Wall corrected organic mass concentration ($\mu\text{g}/\text{m}^3$)	Aerosol Mass Yield
Gasoline 1	55/4/64	44	0.8	55.4	4.6	0.08
Gasoline 2	12/5/58	260	21.7	114	18.9	0.16
TX	63/7/88	1055	16.7	782	206	0.26

Results & discussion

The concentrations of sulphate, ammonium, organics and nitrates in the experiment ‘Gasoline 2’ is given in figure 2. The corresponding wall loss corrected concentration of salt seed, primary organic aerosol (POA) and SOA is given in figure 3. Note that SOA clearly dominates over POA after 5 h photo-oxidation.

The SOA formation starts after about 20 minutes, which corresponds to the time when the NO has reacted. In figure 3, the SOA formation has a steeper slope during the first hour of formation ($t= 20\text{-}80$ min), than the remainder of the experiment. The AMS mass spectra and the volatility of the SOA is described by Eriksson et al. (2010).

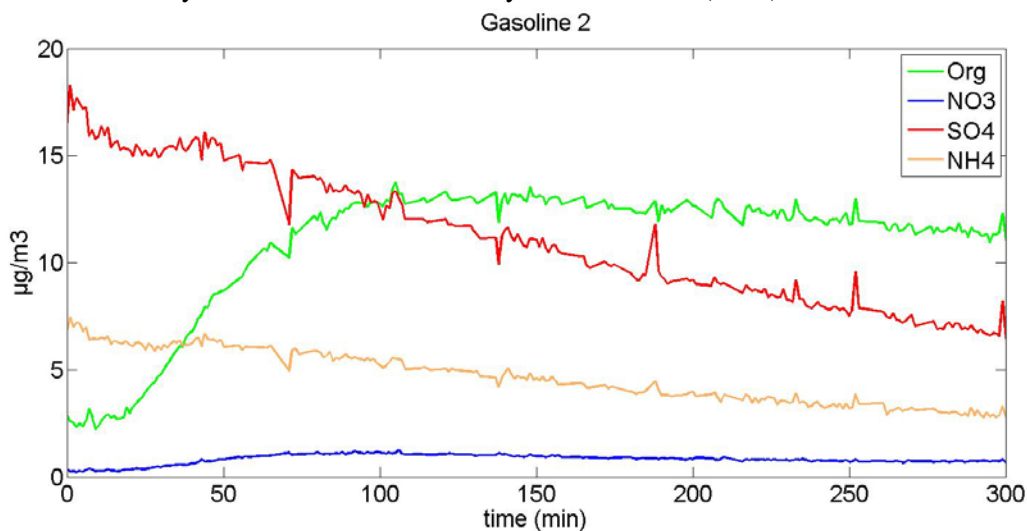


Figure 2: The chemical composition (AMS) from the gasoline 2 experiment. The UV-radiation starts at time=0.

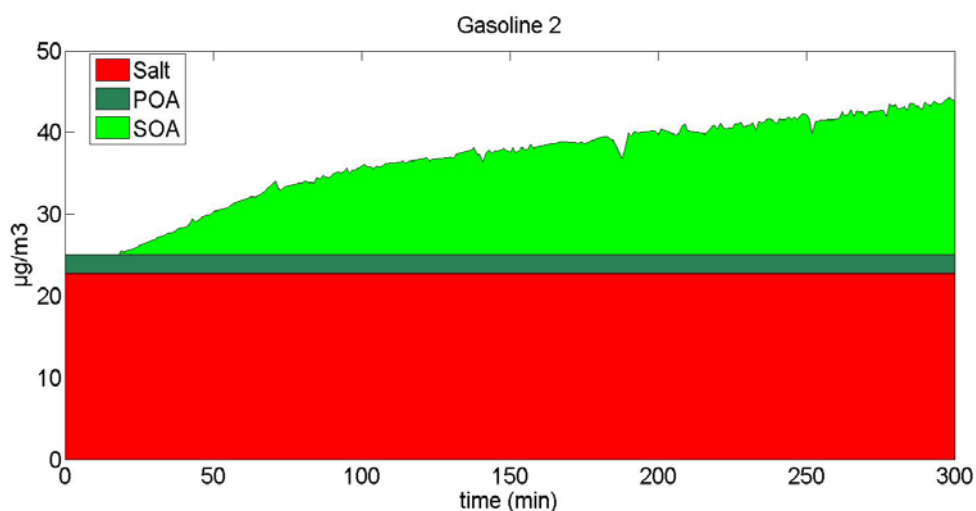


Figure 3: The estimated mass concentration from AMS-data, from the Gasoline 2 experiment. The UV-radiation starts at time=0.

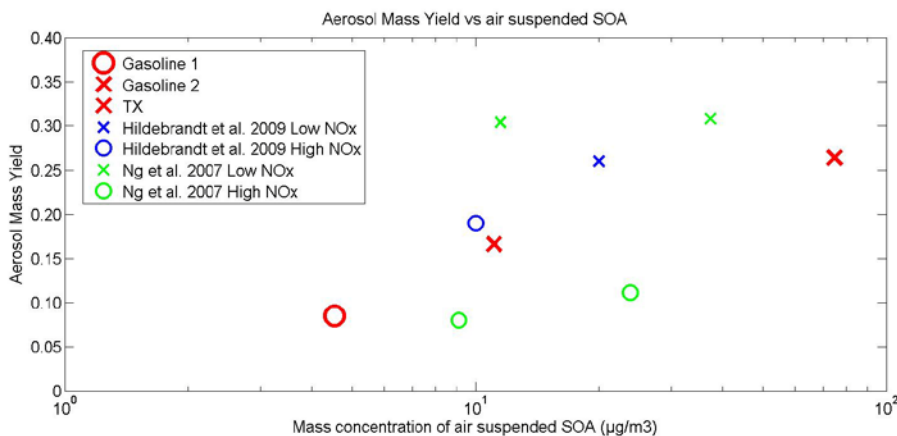


Figure 4: The Aerosol Mass Yield from our three experiments together with Toluene experiments from Ng *et al.*, 2007 and Hildebrandt *et al.*, 2009, vs. concentration of air suspended SOA for each experiment.

Yields from our experiments together with yields from pure precursor experiments are shown in figure 4. There is some distinction in terms of yield between the low and high NO_x experiments, the air suspended mass concentration seems to be of less importance.

Simulations using the AdChem model developed at Lund University suggest that the Gasoline 2 and TX experiments react under low NO_x conditions for the majority of the experiment. Typically the NO concentration approaches zero after about 30-60 min (Carlsson 2010). On the contrary, the Gasoline 1 experiment reacted under High NO_x conditions throughout the majority of the experiment.

In future campaigns more compounds such as C9 and C10 aromatics will be added to the pure mixture experiments in similar concentration as in gasoline exhaust. This will enable a more detailed comparison between the chemical characteristics and the yield of SOA from gasoline exhaust and pure precursor mixtures.

Conclusions

The Aerosol Mass Yield in the gasoline exhaust experiments is in the same range as yields for pure precursor experiments in the literature. Which indicates that the C6-C10 aromatics contribute to a majority of the SOA formation (Odum *et al.*, 1997).

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