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Smog Chamber Studies on SOA Formation from Gasoline Exhaust and Pure Precursors

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Formation of Secondary Organic Aerosol (SOA) in the atmosphere is of importance both from a climate and health point of view. Photo-oxidation of aromatic Volatile Organic Compounds (VOCs) such as Toluene and Xylene (TX) gives contribution to SOA formation in the atmosphere. Anthropogenic combustion sources such as light duty traffic contribute to emissions of light aromatics in the atmosphere. Vehicles operating on idling or cold starts have particularly high VOC emissions since the oxidation catalyst has yet to reach its operation temperature. The mass yield (the ratio between formed SOA and reacted light hydrocarbons) and the chemical composition of the formed aerosol are important parameters for understanding the mechanisms of SOA formation. The aim of this work is to improve the knowledge about light aromatics contribution to SOA formation, by examining and comparing the chemical composition and mass yields from idling gasoline exhaust and pure precursors.

The experiments were performed in a 6 m³ Teflon (FEP) smog chamber, housed in a temperature controlled (22±1°C) 22 m³ steel chamber. Black lights (intensity peak~350 nm) are used to initiate photochemistry; the NO₂-photolysis rate is 0.23 min⁻¹. Gasoline exhaust was injected via a heated ejector dilutor and heated inlet (120 °C). The vehicle used in the experiments was a Volvo V40 (118 kW) (1998). A relevant operating mode with sufficient emission reproducibility was identified and used. It involved a cold start and driving until engine cooler water temperature of 55°C was achieved. Emitted aerosol was then sampled to the smog chamber for 5-10 min. Nebulized ammonium sulfate was utilized as condensation seeds in all experiments. In the precursor experiment mixtures, three of the most abundant light aromatics in the exhaust (Toluene, m-Xylene and 1.2.4-Trimethylbenzene) were injected through evaporation to the smog chamber. The experiments were monitored by particle characterization instruments such as, High Resolution-Time of Flight Aerosol Mass Spectrometer (HR-ToF AMS) and Aerosol Particle Mass Analyzer (APM). Proton Transfer Reaction Mass Spectrometer (PTR-MS) and complementary GC-MS analysis was used for VOC-monitoring. The mass concentration of formed SOA was corrected for wall losses using the method by (Hildebrandt *et al.*, 2009).

Preliminary results from three gasoline and two pure precursor experiments are shown in Table 1. The reacted VOC concentration is calculated from the C₆-C₁₀ data from PTR-MS. This can be used for mass yield

calculations, given the assumption that C₆-C₁₀ are the only SOA forming precursors. The fraction of organic signal at (m/z) 43, 44 (f₄₃, f₄₄) is derived from unity mass resolved AMS-data.

Table 1. Preliminary results from the campaign.

Exhaust/ Precursor	Initial VOC to NO - ratio	Reacted VOCs (µg/m ³)	Wall loss corrected SOA (µg/m ³)	f(43) f(44)
Gasoline	8.8	148	26	0.105 0.115
Gasoline	6.4	246	66	0.084 0.123
Gasoline	21.7	114	29	0.073 0.136
T + m-X	16.7	782	412	0.138 0.121
T + m-X +1.2.4- TMB	5.8	473	64	0.178 0.092

As shown in Table 1 the ratio between formed SOA and reacted light hydrocarbons for gasoline exhaust is higher than the ratio for pure precursors (for similar mass loadings), which indicates that a major part of the SOA in the gasoline experiments is formed from light aromatic hydrocarbons. The SOA formed in the gasoline experiments contains more highly oxidized material than the SOA from pure precursors. The gasoline exhaust but not the pure precursor experiments fit well with a recent compilation of AMS spectral features from atmospheric oxygenated organic aerosol (OOA) observations (Ng *et al.*, 2010). This suggests that pure precursor experiments do not recapture all of the complexity in the detailed SOA composition from idling gasoline exhaust.

Hildebrandt, L., *et al.* (2009). *High formation of secondary organic aerosol from the photo-oxidation of toluene.* *Atmos. Chem. Phys.* **9**: 2973-2986.

Ng, N. L., *et al.* (2010). *Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry.* *Atmos. Chem. Phys.* **10**: 4625-4641.

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