

EXECUTIVE SUMMARY

The goal of this Surface-induced Oxidation of Organics in the Troposphere (SOOT) HARC project (H101) was to investigate heterogeneous reactions relevant to formation of atmospheric trace gas species that are responsible for radical budget, oxidation of volatile organic compounds (VOC), and formation of ozone (O_3) in urban atmosphere. The ultimate objective of SOOT project was to elucidate missing sources of free radicals ($HO_x = OH + HO_2$) responsible for the rapid ozone production in the Houston airshed and the fundamental cause of the non-attainment status of the EPA 8-hour O_3 standard.

The project consisted of two phases, including laboratory experiments and field measurements. During Phase I, a laboratory study of the heterogeneous chemistry of nitrogen dioxide (NO_2) relevant to generation of nitrous acid (HONO) was performed using a flow reactor to measure the NO_2 uptake coefficients and HONO yields on different types of soot, including soot produced using different fuels and flame conditions and soot subjected to aging. During Phase II, simultaneous measurements of several key nitrogen compounds, including HONO, dinitrogen pentoxide (N_2O_5), and aerosols were conducted during a two-month period in 2009 at the University of Houston's Moody Towers. Also, a hybrid captured-air chamber was employed to examine the relevant heterogeneous reactions in a controlled ambient environment with known aerosol concentration and composition.

The results from our laboratory study indicate that conversion of NO_2 to HONO on soot is a fast process with HONO yields ranging between 6% to 100% and NO_2 uptake coefficients ranging between 4.0×10^{-4} and 6.4×10^{-3} . Based on our results for uncoated soot, we estimate that about 0.1 ppb of HONO can be ultimately produced in a polluted environment through heterogeneous reaction of NO_2 with freshly emitted soot aerosol. However, the capacity of soot to generate HONO in this reaction can be altered significantly when it becomes internally mixed with different coating materials. Coatings composed of organic acids enhance HONO production, increasing HONO concentration to about 1 ppb. Sulfate coatings under ambient relative humidity conditions reduce HONO production to zero. Pyrene coating has little effect on HONO generation.

Field measurements show that HONO levels often correlate with elevated ambient soot levels (as determined from low single scattering albedos (SSA) and the presence of low-density fraction in ambient aerosol), indicating that soot could play a role in HONO production. Mass-mobility measurements of particle effective densities indicate that aerosol in clean environment consisted mainly of ammonium sulfate internally mixed with organics. Under polluted conditions, aerosols were represented by external and internal mixtures of soot, ammonium sulfate, and a large fraction of organic components. Results of chamber studies show that within about 8 hours soot particles grow by about 30% and their effective density increases from 0.7 g/cm^3 to 1.4 g/cm^3 due to condensation of VOC oxidation products and soot core compaction. More than 10 ppb HONO could be formed inside the chamber with fresh soot whereas no detectable HONO production was observed in the presence of aged soot. Aging of soot particles significantly enhances their ability to absorb and scatter light, potentially reducing photolysis rates and retarding vertical transport in the atmosphere boundary layer.

From combination of laboratory and chamber studies, we conclude that fresh soot can contribute significantly to HONO production. Soot capacity to generate HONO is limited by the number of available reaction sites on the particle surface and has a strong dependence on the chemical composition of coating material.