

EPA Gas Phase Chemistry Chamber Studies

D.J. Luecken (1), and T.E. Kleindienst (2)

(1) National Exposure Research Laboratory, U.S. Environmental Protection Agency, MD-84, Research Triangle Park, NC, 27711, (2) ManTech Environmental Technology, Inc., Research Triangle Park, NC, 27709

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Extended Abstract

Gas-phase smog chamber experiments are being performed at EPA in order to develop databases that can be used to evaluate a number of current chemical mechanisms for inclusion in EPA's regulatory and research models. This work differs from that being performed in other institutions because the emphasis at EPA is on examining a variety of different mechanisms, rather than developing a single mechanism, and evaluating the appropriateness of each one for the various types of applications of air quality models at EPA. The mechanisms that we are currently studying include the Carbon Bond IV 99 (CB4-99) (Adelman, 1999), the SAPRC99 mechanism (Carter, W.P.L., 1999, private communication), and an updated version of the RACM mechanism (Stockwell, et. al., 1997). In addition, the database will provide information for studying a variety of mechanisms formulated using the newly-developed Morphecules method (Jeffries et al., 1999). In keeping with this objective, the experimental conditions in the chambers are chosen to stress the mechanisms and enhance the differences among mechanisms. By providing slightly different chamber conditions and experimental conditions than are found in other existing smog chambers, the EPA chamber data expands the database of experiments that are available for robust mechanism evaluation.

Two smog chambers are available, each consisting of 9000-L rectangular bags completely constructed of either 2- or 5-mil FEP Teflon film, and housed within two opposing high-reflectivity UV light banks mounted on an aluminum frame. The chamber has Teflon ports in a bottom panel and a fan is used to thoroughly mix the reactants in the chamber. Cooled air from an A/C unit is circulated in the ballast cavity and between the chamber walls and lights in order to maintain a near constant temperature of 26 °C during the simulation. One of the chamber frames is constructed to allow it to be rolled outside to conduct experiments in natural sunlight. When used indoors, the chambers are irradiated by a system of 122 cm fluorescent bulbs, with radiation in the wavelength range 300-350 nm generated with UV-340 black light bulbs, and radiation in the wavelengths 350-400 nm generated with standard F40-BL bulbs. This combination has been designed to match, to the extent possible, the distribution of solar radiation between 300 and 400 nm with a fluorescent bulb system.

Prior to an irradiation, the chamber is flushed for 24 to 48 hours with ultrazero air generated in-house with an Aadco pure air generator. Background samples are taken to verify that levels of hydrocarbon and carbonyl compounds are negligible (>50 ppbC) prior to the addition of reactant. Irradiations are typically performed until a peak is reached in the ozone concentration or for 12 hours. During the experiments, temperature, relative humidity, and light intensity are

continuously measured. NO and NO_x are continuously quantified using a chemiluminescent monitor with a converter that reduces NO_x to NO. Because the NO_x from this instrument is subject to interferences from PAN and other organic nitrates, it is a good measure of NO+NO₂ only during the early stages of photochemical conversion. Ozone is continuously monitored during the experiment with a chemiluminescent monitor. Measurements of organic precursors and reaction products were identified by using GC with detection by flame ionization (FID), electron capture (ECD), or mass spectrometry (MS), with samples taken at 1 to 2 hour intervals, depending on the experiment. Peroxyacetyl nitrate (PAN) and other peroxyacyl nitrates were measured by GC/ECD at 1-hour intervals. Measurements of carbonyl compounds were obtained by bubbling sample air through a solution of 2,4-dinitrophenylhydrazine (DNPH) in acidified acetonitrile, producing carbonyl hydrazones which were separated and quantified by high performance liquid chromatography (HPLC). Concentrations of nitric acid were obtained by sampling with nylon filters followed by extraction in 10⁻⁵ perchloric acid solution and analysis by ion chromatography. Other instrumentation is currently being evaluated, and alternative analytical techniques that are being developed, include the measurement of organic nitrates by GC/ECD, determination of multifunctional carbonyl compounds with derivatization by pentafluorobenzylhydroxyl amine (PFBHA) followed by GC/MS analysis, and determination of hydroxylated compounds, including organic acids, by derivatization with BSTFA followed by GC/MS analysis. Exploratory work is being undertaken to determine whether new pattern recognition techniques utilizing UV absorption spectrometry can be used to measure NO₂ and HNO₂ directly.

The chamber-dependant reactions are characterized through the use of a limited set of characterization experiments consisting of single component studies of clean air, clean air/NO_x, CO/NO_x, formaldehyde/NO_x, and ethylene/NO_x experiments. Experiments are performed under dry conditions and at relative humidities between 50-60%.

Earlier experiments have been performed to study ozone formation potential from a series of reformulated gasoline and alternative fuel exhaust from new technology vehicles. These experiments have used authentic exhaust generated from several different vehicles with a dynamometer and have focused on ozone formation potential as a function of fuel type (Kleindienst et al., 1994). A set of experimentally-based reactivity parameters were developed for each fuel. Vehicles run using reformulated gas (RFG) and ethanol (E85) were found to produce roughly equal amounts of peak ozone for similar reaction conditions, almost twice as much as methanol-fueled (M85) vehicles, and over 4 times as much as vehicles run using compressed natural gas (CNG). (Measurements were made for standard VOC/NO_x ratios of 5.5) Another result of this work has been the creation of auto exhaust surrogates that were prepared as tank mixtures using whole fuel with a dozen additional components representing the major combustion-derived components. These surrogates have been shown to reliably reproduce ozone formation and other photochemical constituents and reactivity parameters compared to direct automobile exhaust.

Studies of branched and straight chain C₅-C₈ alkane reactions have been performed in the chamber. Although these compounds are not extremely fast reacting, they are emitted into the atmosphere in large quantities from automobile exhaust. For these studies we have combined dynamic and static chamber simulations to better identify and quantify multifunctional

oxygenated compounds, organic nitrate, and secondary product formation. The static smog chamber was used to provide moderate conversion of reactants to products without major influences due to sampling and dilution, allowing quantitative determination of the reactive hydrocarbon loss and of the product formation rates. Simulations were also done using a dynamic reactor consisting of a 1-L Pyrex bulb reaction vessel, which had been deactivated with dichlorodimethylsilane, and irradiated by F40-BL fluorescent bulbs. The dynamic simulations allowed complex organic compounds to be more easily observed and quantified by varying the extent of the reaction.

This year's experiments focus on studying complex mixtures of hydrocarbons, including both branched and straight chain members of each class in combinations similar to those found in rural and urban atmospheres. These mixtures are designed to test the effect of the hydrocarbon lumping schemes used in current chemical mechanisms versus the more explicit Morphecule-type approaches. We are also coordinating gas-phase smog chamber experiments with studies of aromatic and biogenic hydrocarbons performed in the PM chemistry program, by performing gas-phase only experiments for compounds which are also studied in the particle chamber.

Future plans include using enhanced analysis techniques to more completely characterize NO_y and product formation. We are establishing a protocol for the types of comparisons that must be done to thoroughly compare chemical mechanisms, using a Process Analysis approach. In conjunction with our modeling of the smog chamber data and comparison of results using different mechanisms, we hope to provide support for the clarification of uncertain reaction parameters in atmospheric chemical mechanisms.

References:

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