

Deployment of a Chemical Ionization Mass Spectrometer during the NOPP Calspan Chamber Experiments

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LONG-TERM GOALS

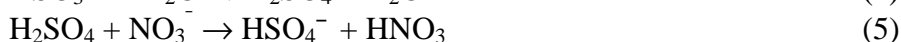
The long-term goal of this research is to develop a detailed understanding of the photochemical processes leading to formation and destruction of tropospheric free radicals, and their interaction with sulfur and other cycles to lead to products such as aerosols and acids.

OBJECTIVES

This research will focus on development of modern instrumentation to make free radical measurements aboard aircraft platforms, at ground-level sites and in laboratory situations. These instruments will then be deployed to collect free radical concentrations at a variety of atmospheric environments including both polluted and background regimes. This includes planning and development of new measurement programs as well as participation in programs initiated by other researchers and institutions. The important part of the research, though, is the analysis and interpretation of the measured quantities that leads to new understanding and impetus for further study.

APPROACH

A single-channel chemical ionization (CIMS) mass spectrometer was deployed during the NOPP chamber experiments at the Calspan Environmental Chamber in western New York in October and November 1999. This program was organized by Dr. William Hoppel of Naval Research Laboratories and Dean Hegg of Washington State University. The experiments were designed to understand nucleation phenomena, cloud processing and other aspects of aerosol formation, growth and oxidation chemistry. The CIMS instrument was designed to measure peroxy radicals through chemical conversion to sulfuric acid (H_2SO_4) in the inlet by the addition of NO and SO_2 . Measurements of OH (by addition of SO_2 only) and H_2SO_4 (addition of no reagents) are also possible, but the inlet design was not optimized for these molecules. The chemical reactions exploited in this measurement are as follows.



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The instrument consists of a vacuum system, inlet, flow control, electronics and data acquisition and is shown schematically in Figure 1.

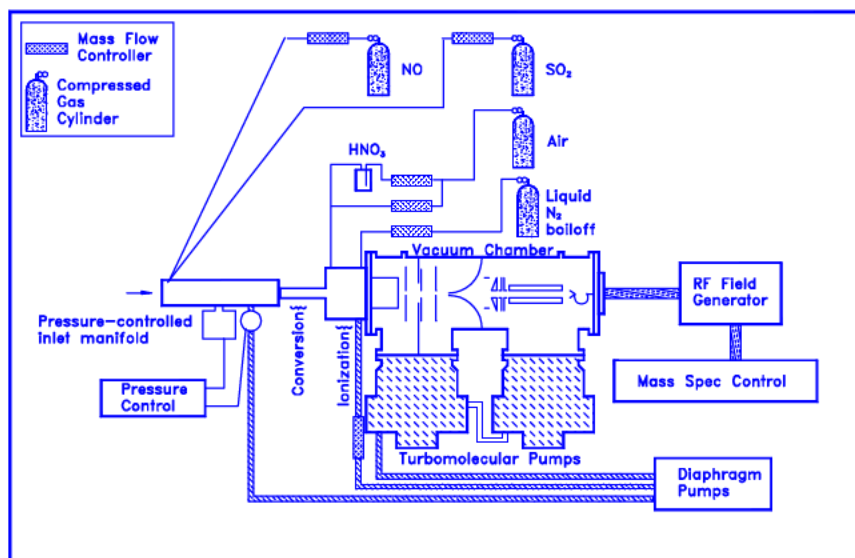


Figure 1. Schematic diagram of CIMS instrument.

Calibration of the response of the instrument to radicals is accomplished through the 184.9 nm photolysis of a known mixture of water vapor in air. The photolysis intensity is measured by the NO yield in the photolysis of a known mixture nitrous oxide (N_2O) in air. Detection limits are typically 10^7 radicals cm^{-3} in 30 seconds or less.

The successful completion of several of the chamber experiments required a controlled source of OH radicals. The original plan was to use the photolysis of ozone (O_3) in the presence of water vapor, but the chamber lamps were found to emit insufficient light in the O_3 absorption region for significant photolysis to occur. Instead, an alternative method involving the photolysis of formaldehyde (CH_2O) in the presence of NO was devised. CH_2O photolysis produces HO_2 radicals, in part, and these are converted to OH by reaction with NO. This source produced enough OH to produce significant sulfuric acid aerosols by way of the oxidation of sulfur dioxide (SO_2).

The application of a photochemical box model to the interpretation of the preliminary results proved useful in the design of the following experiments. It was used as a tool in the sensitivity of various species concentration to input parameters, so that a range of conditions of, for example, sulfuric acid production rates, could be examined.

WORK COMPLETED

Radical (OH and HO_2+RO_2) concentration data were collected for a number of experiments in the Calspan chamber. These data have been reduced from their raw form to concentration – time series in a format agreed by the science team at a workshop at NRL in February 1999. Various team members have collected the data they need for analysis of particular experiments.

The uptake of peroxy radicals by aerosols and cloud droplets (a side issue to the NOPP experimental goals) has been investigated. A method for bringing the radical concentrations and the particle surface area densities together to yield an estimate of the heterogeneous reaction probability of HO₂ and RO₂ onto these various surfaces has been performed. Examination of other chamber studies including the oxidation of dimethyl sulfide (DMS) by NO₃ radicals leading to aerosols has also begun.

RESULTS

Calculations for a number of conditions of aerosol size and number concentration of the uptake of peroxy radicals have been performed and indicate (in agreement with the literature) that it is indeed a very efficient process, with reaction probabilities approaching unity for all conditions. This is likely because there is efficient reaction of peroxy radicals within the aerosol since the solubility of HO₂ and RO₂ radicals is somewhat low. Results are similar for uptake onto cloud droplets. An example of the relative radical levels (typically around 100 pptv) before, during and after production of a cloud in the chamber is shown in Figure 2.

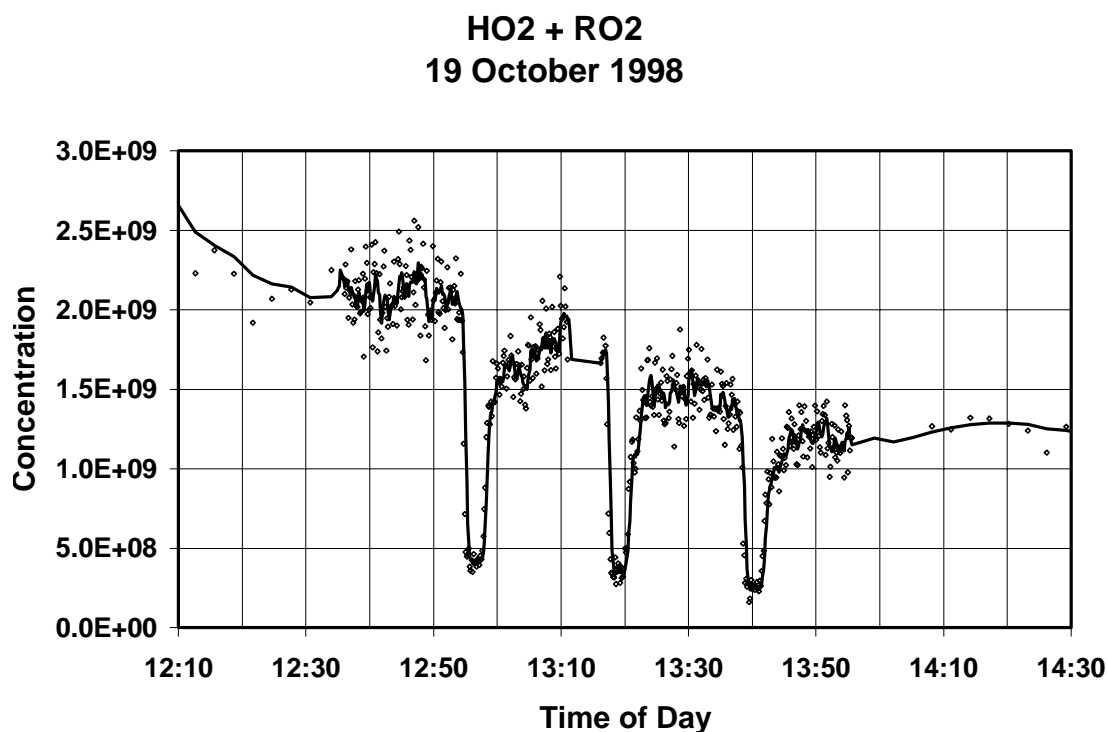


Figure 2. Peroxy radical levels measured during three cloud encounters.

Oxidation of DMS by NO₃ radicals leads to condensable products that ultimately form aerosols. Detailed evaluation of the data will lead to recommendations for further laboratory studies of DMS oxidation chemistry and parameters of use in chemical transport models.

IMPACT/APPLICATIONS

The direct measurement of radicals and sulfuric acid in these experiments will allow useful parameters to be extracted for use in understanding tropospheric aerosol and free radical chemistry.

These may lead to new understanding of the importance of these processes, to new laboratory and field experiments, and ultimately to an ability to predict the behavior and amounts of these species in the troposphere, particular the marine boundary layer.

TRANSITIONS

The CIMS method has been expanded to measurement of other molecules and this will lead to further enhancements in our understanding of tropospheric chemistry through future scientific studies.

RELATED PROJECTS

David Hansen and Fred Eisele of NCAR are examining the nucleation of sulfuric acid by measuring the amounts of small clusters using CIMS.

The peroxy radical CIMS is being deployed in several field measurement campaigns sponsored by NCAR/NSF and NASA.

REFERENCES

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