MEASUREMENT OF HETEROGENEOUS CHEMICAL PROCESSES RELEVANT TO AEROSOL SURFACES AND TRACE GASES ACTIVE IN THE MARINE ENVIRONMENT

Final Report
Period August 1, 1991 to June 30, 1998

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Final Report

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Measurement of Heterogeneous Chemical Processes Relevant to Aerosol Surfaces and Trace Gases Active in the Marine Environment

Period Covered: August 1, 1991 to June 30, 1998

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1. Introduction

Ocean produced reduced sulfur compounds including dimethylsulfide (DMS), hydrogen sulfide (H₂S), carbon disulfide (CS₂), methyl mercaptan (CH₃CH) and carbonyl sulfide (OCS) deliver a sulfur burden to the atmosphere which is roughly equal to sulfur oxides produced by fossil fuel combustion. These species and their oxidation products dimethyl sulfoxide (DMSO), dimethyl sulfone (DMSO₂) and methane sulfonic acid (MSA) dominate aerosol and CCN production in clean marine air. Furthermore, oxidation of reduced sulfur species will be strongly influenced by NO₂/O₃ chemistry as well as halogen and ammonia chemistry in marine atmospheres. The multiphase chemical processes for these species must be understood in order to study the evolving role of combustion produced sulfur oxides over the oceans.

The work funded by the DOE/ACP has proceeded generally along the lines described in the original proposal. Using our droplet apparatus we measured the uptake of MSA, DMSO, DMSO₂, SO₂ and, NH₃. The uptake of gas phase Cl₂ and Br₂ as a function of aqueous Br⁻ and I⁻ concentration and O₃ and Br₂ as a function of I⁻ concentration was also studied in detail. Studies were performed as a function of temperature and yielded mass accommodation coefficients and where applicable reaction rates for the species.

In order to study the uptake of less soluble gas phase species we developed two new apparatuses using controlled bubbles within the liquid of interest. The devices were carefully characterized. Using the new techniques, detailed uptake studies have been completed for DMS, H₂S, CS₂, CH₃SH, OCS, O₃, NO₂, CO₂, N₂O and formaldehyde. Experiments were performed as a function of pH, ionic strength (i.e. NaCl and (NH₄)₂SO₄ concentrations and H₂O₂ concentration. To simulate the interaction of SO₂ with sulfuric acid aerosols, a detailed uptake studies were initiated for gas phase SO₂ by aqueous sulfuric acid in the presence of oxidants H₂O₂, O₃ and HONO. The results of these experiments were used to obtain Henry's law coefficients, "salting out" Setchenow coefficients and where applicable, reaction rates for the species.

Important features of chemical interactions at the gas-liquid interface were noted. For several species such as SO₂, NH₃, CH₂O, Cl₂ and Br₂ the results are not explainable by bulk phase chemistry. Instead, the uptake measurements for these species indicate that reactions at the gas-liquid interface dominate the gas uptake and that chemistry at the interface is very different from that occurring either in the gas or the liquid phase. Reactions may be orders of magnitude faster at the interface than either in the gas or in the liquid phases. It was also observed, that in the process of uptake, some species form a chemisorbed complex at the gas-liquid interface which is likely to participate in the heterogeneous chemistry of the species. The results of our studies have led to the development of models that are shedding light on the mechanisms of uptake for both reactive and non-reactive gas phase species.

Fourteen manuscripts describing the work sponsored in part by our DOE grant have been published in refereed journals and five additional manuscripts are in preparation. Four graduate students completed their Ph.D. research during the grant period. More than 60 invited talks describing the funded research were presented by the members of the research group.
2. Results.

- The following tasks have been accomplished during the period of the grant:

a). Detailed uptake studies have been completed for MSA, DMSO and DMSO₂ using the droplet apparatus. Uptake was studied as a function of temperature, droplet pH and NaCl concentration. Published in *J. Geophys. Res.* Publication 2, listed in section 3.

b). A vertical bubble column apparatus was constructed to study gas-liquid interactions of molecules with smaller uptake coefficients, in the range 10⁻⁴ to 10⁻⁷. The apparatus was tested and carefully calibrated. This involved extensive gas liquid chemistry studies of species with known thermodynamic and kinetic properties. Published in *Environ Sc. Technol.* Publication 3, listed in section 3.

c). Uptake studies were completed for the species of interest DMS, H₂S, CS₂, CH₃SH, OCS, O₃, NO₂ and N₂O using the vertical bubble column apparatus. Studies were performed as a function of temperature, pH, ionic strength (i.e. NaCl and (NH₄)₂SO₄ concentration) and H₂O₂ concentration. The results yielded Henry's law coefficients and the "salting out" Setchenow coefficients for the species. Published in *J. Geophys. Res.* Publication 4.

d). The uptake of gas phase Cl₂ and Br₂ by aqueous NaBr and NaI solutions has been studied as a function of concentration, temperature (263-293K) and gas-liquid interaction time (2-15 ms). The uptake of O₃ by aqueous NaI solutions has also been studied for the purpose of comparison. The data indicate that reactions of Y⁻ (Y = Br or I) via X₂ at the gas-liquid interface have a significant role in the gas uptake process. Published in *J. Phys. Chem.* Publication 6 listed in section 3.

e). A more versatile and accurate horizontal bubble train apparatus was constructed to study gas-liquid interactions of molecules with smaller uptake coefficients, in the range 10⁻³ to 10⁻⁸. The apparatus was tested and carefully calibrated. This involved extensive gas liquid chemistry studies of species with known thermodynamic and kinetic properties. Published in *Env. Sc. And Technology*, Publication 13 listed in section 3.

f). The uptake of gas phase ammonia by aqueous surfaces was measured as a function of pH, temperature, and gas liquid interaction time. The measured mass accommodation coefficient (~0.08 at 283K) exhibits a negative temperature dependence consistent with a cluster nucleation model. Time dependence of the uptake indicates that an ammonia surface complex is formed at the interface. Co-deposition NH₃:SO₂ studies were also performed. Manuscripts in preparation.

g). Studies were initiated using a droplet train apparatus, to measure the uptake of gas phase ammonia by sulfuric acid surfaces as a function of temperature (248-288 K), gas liquid interaction time (2-15 ms), and acid concentration (20-70 wt% sulfuric acid). Work in progress; manuscripts in preparation.

h). Uptake of SO₂ was measured as a function of acid concentration (pH 1.8 to 70 wt%) at 293 K and over the temperature range from 282 to 301 K at pH 1 using an horizontal bubble train apparatus. SO₂ uptake studies were also carried out in the presence of the oxidants, H₂O₂, O₃ and HONO in order to investigate oxidation pathways at high acid concentrations. Work in progress; manuscripts in preparation.

i). Using the droplet apparatus, previous SO₂(g) uptake studies were extended to higher pH up to pH = 14 at the temperatures of -10°C, 0°C, 10°C, 20°C. From the uptake data the rate constant $k_2$
for the reaction of SO$_2$(aq) with OH- was and the mass accommodation $\alpha$ was also measured as a function of temperature. Work in progress; manuscripts in preparation.

j). Studies were initiated using a droplet train apparatus of measuring isotope exchange for deuterated gas-phase acetic acid and ethanol in contact with water (H$_2$O) droplets. In these experiments, the gas phase species interacts with liquid droplets and the loss of the species is monitored. The loss of the species may be due to the entry of the molecules into the bulk or to a reaction of the species at the gas-liquid interface; in this case isotope exchange. These studies are yielding basic information about the nature of the gas-liquid interface. Work in progress; manuscripts in preparation.

Results and detailed discussion of this work are found in the published journal articles. Abstracts of the works in progress are found in Section 4 of this report.

3 Publications, Presentations and Educational Activities Resulting from Work Sponsored By DOE Grant DE- FG02-91ER61208

3. 1 Publications.


b) Articles in Preparation


3. 2 Invited Oral Presentations. During the period of the grant more than 60 invited talks were presented by our research group at various universities, scientific meetings and workshops. Following are the presentations of 1997 and 1998.

**LOCATION**

Air and Waste Management Meet, Toronto
ACS Atmosphere Symposium, Los Vegas, NV
ACS Atmosphere Symposium, Los Vegas, NV
N. Y. State, Dept. of Health, Albany, NY
Tufts University Medford, MA
Boston University
Research Institute for Innovative Technology, Tsukuba, Japan
Japan Atmospheric Environment Society Tokyo, Japan
NASA Atmospheric Effects of Aviation, Virginia Beach, VA
ACS Meeting, Dallas, TX

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**DATE**

June 11, 1997
Sept. 10, 1997
Sept. 10, 1997
Oct. 9, 1997
Oct. 7, 1997
Nov. 12, 1997
Feb. 9, 1998
Feb. 13, 1998
April 28, 1998
March 31, 1998
3.3 Education and Training.

From its inception about this project has included undergraduates, graduate students and postdoctoral researchers.

(a) Undergraduates. Three undergraduates have worked on this project. Two have gone on to pursue Ph. D. studies in chemistry and one has enrolled in medical school.

(b) Graduate Students. The following graduate students have been associated with this project:

Warren J. De Bruyn, graduated
Jianhong Hu, graduated
Erick Swartz, will graduate August 1998; has appointment as post doc at E.P.A.
Quan Shi will graduate August 1998; will have appointment as post doc at B.C.
Jayraj Boniface.
Yong Quan Li
Anatoli Chirokikh

Ph. D. Thesis

Warren J. De Bruyn, Theses Title: "The Heterogeneous Chemistry of Carbonyl Halides, Haloacetyl Halides and Biogenic Sulfur Species", December, 1994. Currently Research Associate at University of Miami.

Jianhong Hu, Theses Title: "Uptake of a Series of Gas-Phase Halogenated-Acetic Acids and Halogen Molecules by Aqueous Droplet Surfaces", December 1994, Currently Research Associate at University of Chicago.

(c) Postdoctoral Fellows. The following postdoctoral fellows have been associated with this project. Currently three of them have faculty positions, three work in research laboratories and one is currently working on the project.

Jane M. VanDoren Currently faculty member at Holy Cross
Jeffrey A. Shorter Currently working in a private corporation
Daniel Robinson Currently faculty member at Fitchburg State College
Oliver V. Rattigan Currently working at State University Albany, NY
Janice Cheung Currently working at Boston College

3.4 Collaborations. We have been in close contact with DOE scientists at Pacific North West Laboratory collaborating on heterogeneous chemistry issues of mutual interest.
4. Abstracts of Works in Progress

Uptake of Gas-Phase Ammonia 1:
Uptake by Aqueous Surfaces as a Function of pH

Abstract
The uptake of gas phase ammonia by aqueous surfaces was measured as a function of temperature, gas liquid interaction time and pH in the range 0 to 13. Uptake measurements at low pH yielded values of the mass accommodation coefficient (α) as a function of temperature. Time dependence of the uptake at high pH indicates that an ammonia surface complex is formed at the interface. A model using the concept of such a surface complex matches well the experimental results. The high pH data yielded values for the Henry’s law coefficient and the Gibbs energy for the surface complex. Co-deposition studies in which an aqueous surface, initially at pH = 4, was simultaneously exposed to both gas phase ammonia and SO2 were also performed. In such a co-deposition experiment, the species entering the liquid neutralize each other and as a result the uptake of each species is enhanced. Modeling calculations indicate that the uptake of each species is in accord with bulk phase kinetics.

Uptake of Gas-Phase Ammonia 2: Uptake by Sulfuric Acid Surfaces

Abstract
Using a droplet train apparatus, the uptake of gas phase ammonia by sulfuric acid surfaces was measured as a function of temperature (248-288 K), gas liquid interaction time (2-15 ms), and acid concentration (20-70 wt% sulfuric acid). The uptake coefficient increases as a function of acid concentration and reaches unity at about 50 wt% H2SO4. An analysis of the results indicates that this increased uptake is due to a reaction at the gas-liquid interface between NH3 and H+. These uptake experiments were also used to conduct a detailed study of gas transport to a moving train of droplets.

Uptake of Gaseous SO2 by Aqueous Sulfuric Acid:
Oxidation by H2O2, O3 and HONO

Abstract
Uptake of SO2 was measured as a function of acid concentration (pH 1.8 to 70 wt%) at 293 K and over the temperature range from 282 to 301 K at pH 1 using an horizontal bubble train apparatus. SO2 uptake studies were also carried out in the presence of the oxidants, H2O2, O3 and HONO in order to investigate oxidation pathways at high acid concentrations. Modeling of the uptake yielded Henry’s law coefficients and aqueous phase oxidation rate coefficients. Measured Henry’s law solubility of SO2 in H2SO4 is in good agreement with the current recommendation. Reaction rates of SO2 with H2O2 from pH 1 to 70 wt% H2SO4 show an inverse dependence on hydrogen ion concentration with measured rate coefficients lying on average within a factor of 4 of the bulk phase recommended values. Reaction of SO2 with O3 was measured over the range pH 1 to 70 wt% H2SO4. Good agreement with previous rate measurements was observed at pH 1. Above 30 wt% H2SO4 the reaction rate is independent of acid concentration and approaches a limit determined by the reaction rate of SO2(aq) with O3 in agreement with the mechanism of Hoigne et al.. Our data indicate that this rate is 6.6 x 10^{-3} M^{-1} s^{-1}, about a factor of three lower than the present recommended value. Reaction of SO2 with HONO was investigated from 20-70 wt% H2SO4. The rate increases with hydrogen ion concentration with measured values lying within a factor of 4 of the predicted values. The implications of these results for aerosol formation in aircraft plumes are discussed.
Uptake of SO₂

Abstract

Using the droplet apparatus, previous SO₂(g) uptake studies were extended to higher pH up to pH = 14 at the temperatures of -10°C, 0°C, 10°C, 20°C. To confirm our treatment of gas phase diffusion and generally test consistency of data, the uptake was measured with two droplet-generating orifices of diameter of 64 μm and 28 μm. The two orifices produce droplets of diameters differing by a factor of about 2.3. After diffusion correction the data obtained with the two orifices are consistent with each other. As was found in the earlier work, the uptake of SO₂ increases with pH due to increasing effective solubility of SO₂. In the newly studied higher pH region further increase in uptake is observed due to reaction of SO₃(aq) with OH-. The uptake is consistent with bulk phase solubility and pseudo first order bulk phase reaction of SO₂ with OH-. From the uptake data the rate constant k₄ for the reaction of SO₃(aq) with OH- was determined to be k₄ = 3x10⁹/mol s. This is to be compared to the gas phase reaction rate for the two species which is 4.8x10¹¹/mol s. The SO₃(aq) / OH- reaction rate is essentially constant in the temperature range studied. The mass accommodation α was also measured as a function of temperature can be expressed as α/1−α = exp (-ΔG/RT). Where ΔH = -7.78 kcal/mol and ΔS = -29.9 cal/(mol K). At -10°C α = 0.44.

Isotope Exchange for Gas-phase Acetic Acid and Ethanol at Aqueous Interfaces

Abstract

Isotope exchange for deuterated gas-phase acetic acid and ethanol in contact with water (H₂O) droplets was studied using a droplet train apparatus. In these experiments, the gas phase species interacts with liquid droplets and the loss of the species is monitored. The loss of the species may be due to the entry of the molecules into the bulk or to a reaction of the species at the gas-liquid interface; in this case isotope exchange. Studies were conducted as a function of pH in the range 0 to 14, droplet temperature in the range 291K to 263K and gas-liquid interaction time in the range 2 to 15 ms. In another set of studies, the uptake of normal gas-phase ethanol in contact with deuterated water (D₂O) droplets was measured. For deuterated acetic acid the isotope exchange probability with water molecules at the interface is near unity. On the other hand, isotope exchange probability for ethanol with surface water molecules at pH 7 is much smaller ranging from 0.033 at 263K to 0.051 at 291K. Ethanol isotope exchange is both acid and base catalyzed. The exchange probability therefore increases both toward low and high pH and levels off to a plateau at pH 2 and 12 respectively. The maximum value of the isotope exchange probability at the plateau is significantly less than one. For deuterated ethanol with water molecules (H₂O) at the interface it ranges between 0.14 and 0.18 with no clear trend in temperature. The maximum value of the isotope exchange probability for normal ethanol with deuterated water is about twice as large. Results are explained in terms of a kinetic model in which it is assumed that the surface adsorbed ethanol molecules are distributed between two distinct forms; a weakly adsorbed state, and a partially solvated state. Only the partially solvated molecules can interact with the near-surface ions in the interior of the liquid. A finite rate of entering the partially solvated state is responsible for the observed plateaus in isotope exchange at high and low pH. Parameters describing the gas uptake and isotope exchange processes are examined using two models to describe the surface species; surface nucleation and Gibbs surface excess.