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

Progress Report
for the Period February 1994 to January 1995
and
Request for Continued Funding for the Period
August 1, 1995 - July 31, 1996

Prepared by

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February 1995

MASTER

Prepared for

THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-91-ER61208

DOE/ER/61208--4

D.O.E. Grant NO. DE-FGO2-91-ER61208

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ABSTRACT

Biogenically produced reduced sulfur compounds from the marine envirnoment, deliver a sulfur burden to the atmosphere which is about half as large as that due to sulfur oxides produced by fossil fuel combustion. The multiphase chemical processes for these species must be understood in order to evaluate the relative roles of biogenic and combustion produced sulfur oxides over the oceans. The aim of the studies funded by the subject DOE grant is to measure parameters governing the heterogeneous chemistry of the species occuring in the marine environment. During the past year, uptake studies for the sulfur species MSA, DMSO, $DMSO_2$, DMS, OCS, CS_2, H_2S, and CH_3SH have been finalized. Studies of the reactive uptake of Cl_2 and Br_2 by Br^- and I^- solutions as a function of temperature have been completed. The uptake of O_3 by aqueous NaI solutions has also been studied for the purpose of comparison. We have begun co-deposition studies and have obtained some preliminary results for the codeposition with ozone of DMS, DMSO, $DMSO_2$ and MSA. For the next phase of the work, a new horizontal bubbler apparatus was designed and built and construction to improve the detection sensitivity of the apparatuses was begun. Altogether during 1994, 8 articles have been accepted for publication and 2 Ph.D. dissertations have been submitted and approved.

MEASUREMENTS FOR TRACE GASES ACTIVE IN THE MARINE ENVIRONMENT

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Biogenically produced reduced sulfur compounds from the marine envirnoment, including dimethylsufide (DMS), hydrogen sulfide (H_2S), carbon disulfide (CS_2), methyl mercaptan (CH_3CH) and carbonyl sulfide (OCS), deliver a sulfur burden to the atmosphere which is about half as large as that due to sulfur oxides produced by fossil fuel combustion. These species and their partial oxidation products dimethyl sulfoxide (DMSO), dimethyl sulfone ($DMSO_2$) and methane sulfonic acid (MSA) contribute to aerosol and CCN production in clean marine air. Furthermore, oxidation of reduced sulfur species will be strongly influenced by NO_x/O_3 chemistry in marine atmospheres. The multiphase chemical processes for these species must be understood in order to understand the relative roles of biogenic and combustion produced sulfur oxides over the oceans. The aim of the studies funded by the subject DOE grant is to measure parameters governing the heterogeneous chemistry of the species occuring in the marine environment.

We have developed two experimental techniques which make it possible to study various aspects of heterogeneous gas-liquid interactions. The basic approach in all our studies is to bring gas molecules in contact with a liquid surface and then examine how the gas enters the liquid, how it leaves it and what chemical reactions occur at the gas-liquid interface. Experiments are performed as a function of gas-liquid contact time, temperature and appropriate additives. In the first method, suitable for measuring relatively large gas uptakes ($\gamma_{meas} > 5x10^{-4}$), the gas phase species interacts with a controllable stream of monodispersed droplets of known size, temperature and chemical composition. In the second method, used to measure the uptake of gases with relatively smaller uptakes (γ_{meas} in the range 10^{-4} to 10^{-7}), the trace gas to be studied is contained in controlled bubbles rising through the liquid of interest.

Following is the Work Statement in our proposal of January 1994; D.O.E. Grant NO. DE-FGO2-91-ER61208

Work Statement

(i) Co-Deposition of Gases; The Study of Chemistry at the Interface. Studies will be performed with the reduced sulfur compounds DMS, OCS, CS_2, H_2S, CH_3SH co-deposited with H_2O_2, O_3, NO_2 and NO_3. The NO_3 experiments will be performed by co-depositing the sulfur species with O_3 and NO_2 . ion of F with HNO_3. These studies will be completed during the first year of the new funding period.

(ii) Photochemistry. The effect of visible and near UV light on the production of liquid phase free radicals will be examined. Test solutions containing controlled and variable amounts of dissolved oxidants (H_2O_2, NO_2^-, NO_3^- and O_3) or cationic additives (Ca^{++}, Mg^{++}, Fe^{++}, Fe^{+++}, Cu^{++} and Mn^{++}) and carboxylic or sulfite anionic additives will be used in bubble column experiments illuminated with varied and controlled (photon flux/wavelength) light. This work will be performed during the first and second years of the new funding period.

(iii) Exploratory Development of Droplet Ablation/Vaporization Techniques to Improve the Sensitivity of Droplet Train Experiments. Pulsed excimer laser and/or charged droplet ablation/evaporation techniques for the isolated droplet train after its interaction with the trace gas flow will be tested and evaluated to determine if they can be utilized in conjunction with mass spectrometric detection to significantly extend the sensitivity range of the droplet train technique to smaller uptake coefficient species and/or reduced trace gas partial pressure conditions. This work will be completed during the second year of the new funding period.

PROGRESS REPORT

During the past year, uptake studies for the sulfur species MSA, DMSO, $DMSO_2$, DMS, OCS, CS_2, H_2S, and CH_3SH have been finalized. This work has been described in three manuscripts which have been accepted for publication.

The studies of the reactive uptake of Cl_2 and Br_2 by Br^- and I^- solutions as a function of temperature have been completed. The uptake of O_3 by aqueous NaI solutions has also been studied for the purpose of comparison. The magnitude of the measured halogen uptake and its functional dependence on ion concentration are not in accord with a simple bulk phase reaction mechanism. The data indicate that reactions at the gas-liquid interface have a significant role in the gas uptake process. The atmospheric implications of the halogen uptake results have been examined. This work has been submitted and accepted for publication.

We have begun co-deposition studies and have obtained some preliminary results for the codeposition with ozone of DMS, DMSO, $DMSO_2$ and MSA. The uptake of DMS alone and the DMS codeposited with O_3 are shown in Figure 1. An enhanced uptake due to the presence of ozone is clearly evident but the results are not yet adequately defined for a quantitative determination.

Altogether during 1994, 8 articles have been accepted for publication and 2 Ph.D. dissertations have been submitted and approved. Abstracts for the articles and the dissertations are enclosed.

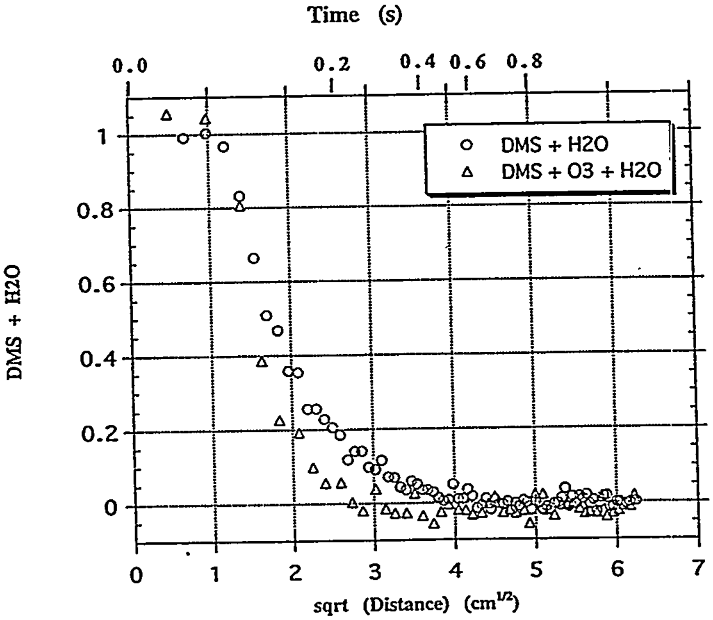

Figure 1. The effect of ozone on the uptake of DMS.

For the next phase of the work, we had to make two significant modifications of the apparatus. Detection sensitivity had to be improved both for the droplet and the bubble column apparatuses. In addition, the bubbler apparatus had to be redesigned.

Detection sensitivity. The new experiments in progress require improved detection sensitivity and mass discrimination. Greater sensitivity is especially important in co-deposition studies where the two species are in contact with each other in their gas phase and may in some cases react. Experiments have to be performed at gas densities as low as possible to minimize this effect. In the case of NO_2, which is a key atmospheric trace gas, the species in the aqueous phase reacts with itself. Therefore, in order to study the heterogeneous reactions of NO_2 with aqueous additives, here again we must work with densities as low as possible in order to minimize NO_2 - NO_2 reactions.

Up till now mass detection in the apparatus was done with a UTI model 100C quadrupole system which was originally designed for use as a residual gas analyzer. The systems are being re-designed to use a model EXM300 quadruple mass spectrometer. This spectrometer is a precision built instrument designed specifically for research applications. The following features make the Extrell system superior: An efficient electron impact axial ionization source for molecular beam sampling, an electrostatic lens assembly which allows control of ion focusing (particularly useful when sampling ions made outside of the mass spectrometer vacuum chamber), greater mass resolution resulting from lager diameter quadrupole rods and the capability for positive and negative ion detection with signal processing in both analog and pulse counting modes. These features give improved ion transmission and detection sensitivity.

In our apparatus, the trace gas is always in the presence of water vapor which is in equilibrium with the liquid. Therefore, with electron-bombardment ionization, detection of species with masses close to that of water has been impossible so far. This includes the detection of NO, OH, and ammonia. We have modified our detection system so that the ionization of the species can be achieved both by electron bombardment and also by photon ionization. Using the hydrogen Lyman alpha line produced by a microwave discharge lamp we are now able to selectively ionize some species while leaving the water in its neutral state. We have been able to detect ammonia and NO in the presence of water vapor using our UTI mass spectrometer.

The Extrell device is expected to be much more effective with the non-conventional ionization techniques. The ability of the device to easily switch between the negative and positive ion detection modes will greatly assist us in our effort to selectively detect the NOx, NOy and PAN species. For these experiments trace gas species will be "chemically" ionized via reaction with a suitable reagent ion, SF_6^- for example. Since the nitrogen oxides are strongly electronegative they form thermodynamically stable negative ions. Water vapor and helium, the major constituents of our flow gas, cannot react to form a stable negative ions and as a result the background mass spectrum will be very "clean". Chemical ionization also offers a very selective ionization scheme which will allow, for example, detection of NO_2 in the presence of HNO_3. In conventional electron impact ionization HNO_3 and NO_2 are indistinguishable since they are both detected as NO_2^+. Chemically ionizing HNO_3 in the presence of NO_2 with SF_6^- will result in two separate ions, $HNO_3{*}F^-$ and NO_2^-. Furthermore, H_2SO_4 vapor is easily detectable via H atom extraction and charge transfer to form HSO_4^-.

The design of the system has been largely demonstrated in other labs and is currently being adapted to the existing apparatus. The acquisition of the Extrell mass spectrometric system will greatly enhance the sensitivity and versatility of detection the range of chemical species of atmospheric interest.

A new horizontal bubble column apparatus. As mentioned in our proposal, one year ago, we constructed a bubble column apparatus to study the uptake of low solubility species such as ozone and the biogenic reduced sulfur species DMS, H_2S), CS_2), CH_3CH) and OCS. Using this apparatus we were able to conduct selected kinetics studies and we measured Henry's law and Setchenow coefficients for the species. Some disadvantages are inherent in that apparatus. Since the bubbles rise vertically through the liquid, driven by buoyancy, the trajectory of the bubbles from the injector to the surface is somewhat erratic. The depth from which the bubbles can be injected is limited and therefore the gas interaction time is also circumscribed to times less than about half a second. Most impairing however, is the limitation that the vertical bubbler presents to photo-chemical studies. Of necessity, there is always at least one centimeter of water between the UV light source and the gas in the bubble.

We have re-thought the bubbler apparatus and have designed and built an apparatus in which the bubbles move horizontal. The apparatus is shown in Figure 2. Water is pumped through the 0.40 cm i.d. qurtz tube at a speed of 20 to 50cm/sec. The trace gas of interest is injected into the liquid flow forming well defined bubbles that fill the tube and are carried by the flowing liquid. The length of the bubbles is between 0.4 and 1.2 cm depending on the gas and liquid flow conditions. In a controlled way 20 to 60 bubbles are formed per second in this way. A stroboscopically obtained photograph of the bubbles is shown in Figure 3.

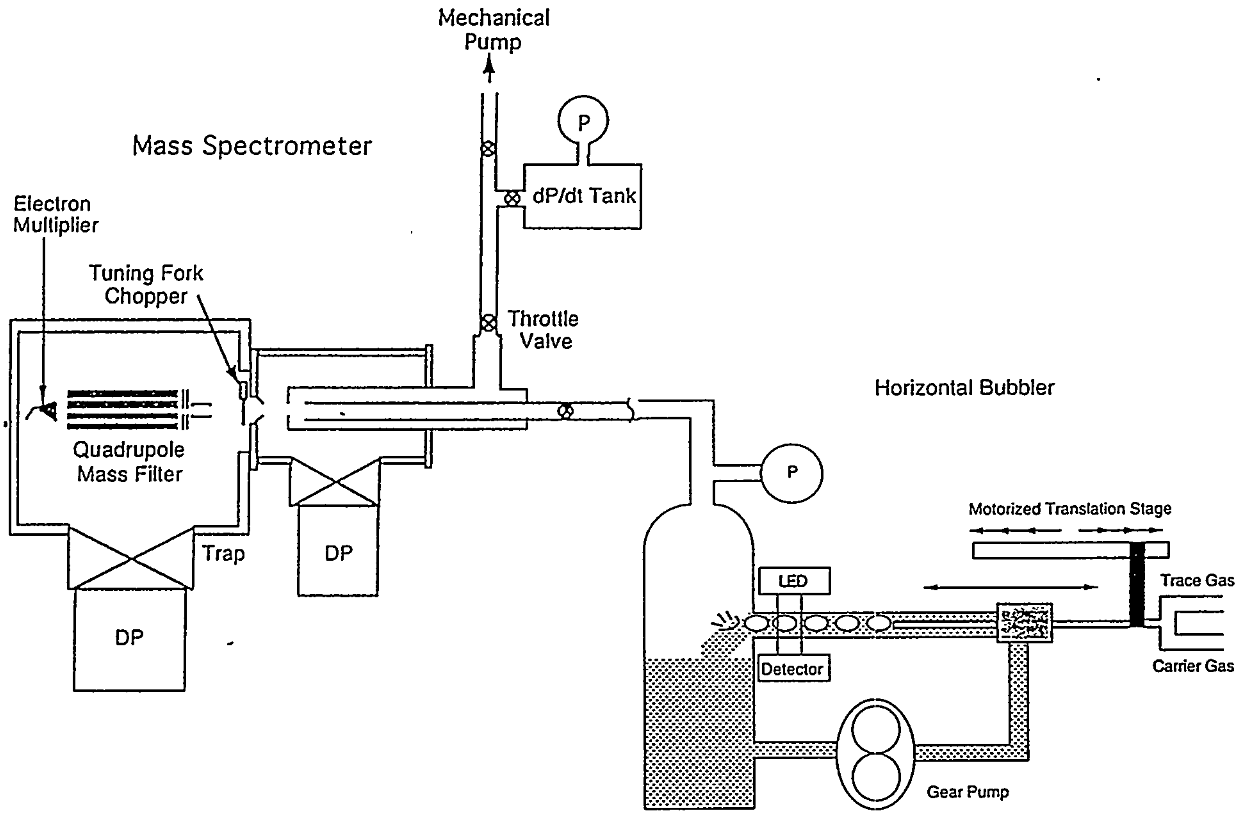

Figure 2. A new horizontal bubble column apparatus.

The construction of this apparatus was completed during the summer of 1994 and for the past five months we have been testing and parametrising the device. The formation of controlled bubbles under these conditions is unknown territory and we had to learn about the nature of the process. We have obtained our first quantitative results with this apparatus at the beginning of January. All the parameters in this device are now under control. We expect to obtain quantitative results by the middle of March.

We expect that this devise will become a highly useful apparatus for heterogeneous kinetic studies. Photo-chemical interaction studies will be possible since in this apparatus the bubbles and therefore the gas is in close contact with the glass tube and the water layer between the glass and the UV light source is estimated to be less than quarter of a millimeter. When the new apparatus and the modifications are completed we will proceed with the work as outlined in the original work statement.

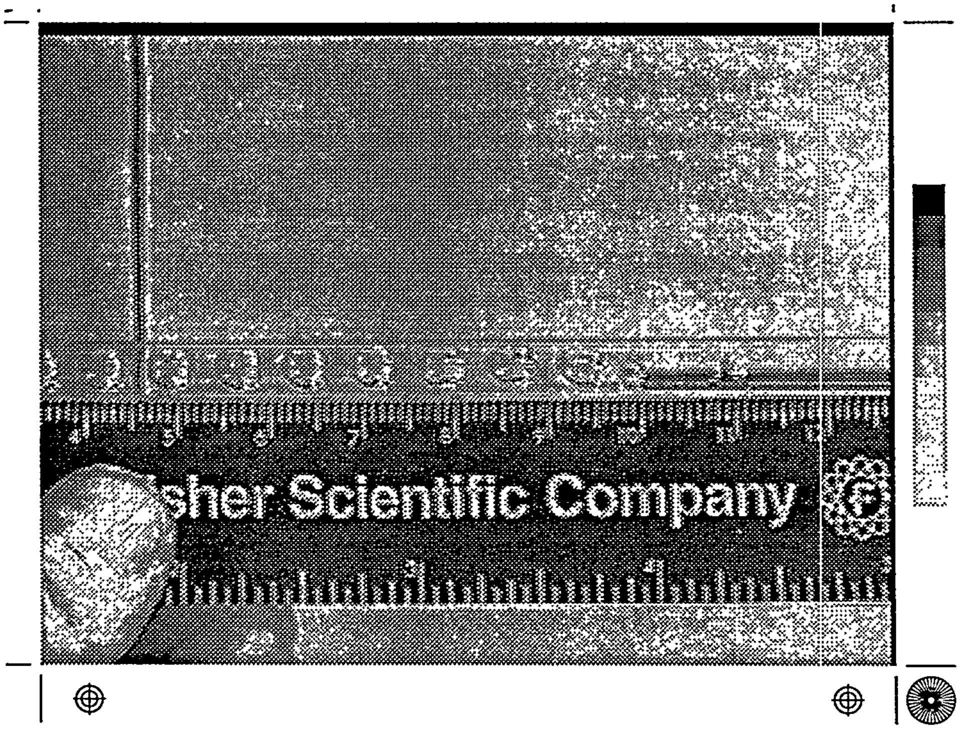

Figure 3 Stroboscopically obtained photograph of the bubbles

Publications and Presentations Resulting from Work Sponsored by DOE Grant DE-FGO2-91ER61208

Publications

1. "Laboratory Studies of Atmospheric Heterogeneous Chemistry" D.R. Worsnop, M.S. Zahniser, C.E. Kolb, Davidovits, P., Hanson, D.R., Ravishankara, A.R., Keyser, L.R., Leu, M.-T., Williams, L.R., Molina, M.J., and Tolbert, M.R. To be published in Current Problems in Atmospheric Chemistry J.R. Barker, ed. in the Advances in Physical Chemistry C.-Y. Ng, ed.

2. "Uptake of Gas Phase Sulfur Species Mathanesulfonic Acid, Dimethylsulfoxide, and Dimethyl Sulfone by Aqueous Surfaces". W. J. De Bruyn, J.A. Shorter P. Davidovits D. R. Worsnop, M. S. Zahniser, and C. E. Kolb *J. Geophys. Res.*, 99, D8, 16,927-16,932, (1994).

3 "Henry's Law Solubilities and Setchenow Coefficients for Biogenic Reduced Sulfur Compounds Obtained from Gas-Liquid Uptake Measurements". W. J. De Bruyn, E. Swartz, J.A. Shorter, P. Davidovits D. R. Worsnop, M. S. Zahniser, and C. E. Kolb. To be published May 1995, J. Geophys Res.

4. "Bubble Column Apparatus for Heterogeneous Chemistry Studies", J.A. Shorter, W. J. De Bruyn, J. H. Hu, E. Swartz, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb. To be published May 1995, Env. Sc. and Tech.

5. "Uptake of Haloacetyl and Carbonyl Halides by Water Surfaces", W. J. De Bruyn, J.A. Shorter P. Davidovits D. R. Worsnop, M. S. Zahniser, and C. E. Kolb. To be published May 1995, Env. Sc. and Tech.

6. "Reactive Uptake of Cl2 and Br2 by Aqueous Surfaces as a Function of Br- and I- Ion Concentration: The effect of Chemical Reactions at the Interface" J. H. Hu, Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb Accepted for publication J. Phys. Chem.

7. "Heterogeneous Atmospheric Chemistry of Alternative Halocarbon Oxidation Intermediates" C. E. Kolb, D. R. Worsnop, M. S. Zahniser, W. J. De Bruyn, J.A. Shorter and P. Davidovits To be published in ACS Symposium Series.

8. "The Uptake of Gas Molecules by Liquid Surfaces" Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb In preparation for the Discussions of the Faraday Soc.

Abstracts where available are enclosed.
Preprints and reprints have been sent to Drs. M.R. Riches and J.M. Hales.

Invited Presentations.

Location			Presenter
D.O.E. Workshop, Nasheville TN	Invited	Jan 19, 1994	P. Davidovits
Worchester Polytechnic Inst., Worchester, MA	Invited	Jan. 31, 1994	M. S. Zahniser
ACS National Meeting, San Diego, CA	Invited	March 15, 1994	D.R. Worsnop
A.C.S.San Diego CA	Invited	March 16, 1994	P. Davidovits
Symposium on the Phys.Chem.of Global Change, ACS Meeting - Ann Arbor, MI	Invited	June 1, 1994	C.E. Kolb
Atmospheric Effects of Aviation, Annual Meeting (NASA), Virginia Beach, Virgina	Invited	June 28, 1994	D.R. Worsnop
Gordon Conference, Plymouth State College, New Hampshire	Invited	July 20, 1994.	D.R. Worsnop
Symposium on Advances in Replacements for Ozone Depleting Compoumds, ACS Meeting -	Invited	August 24, 1994	C.E. Kolb
International Aerosol Conf,Los Angeles CA	Invited	August 29, 1994	P. Davidovits
Holy Cross Worcester MA	Invited	Sept. 30, 1994	P. Davidovits
Batelle Pacific Northweest Laboratories, Richland, Washington	Invited	October 17, 1994	D.R. Worsnop
ACP Annual Science Meeting (DOE), Seattle, WA.	Invited	October 18, 1994	D.R. Worsnop
Workshop on Data Needs for Aqueous ChemicalKinetics, NIST, Gaithersburg, MD	Invited	November 1, 1994	D.R. Worsnop
Centre for Atmospheric Chemistry, York University, North York, Ont.	Invited	November 10, 1994	D.R. Worsnop
Department of Chemistry, University of Waterloo, Waterloo, Ont.	Invited	November 11, 1994	D.R. Worsnop
Fall Meeting of Am. Geophys Union - San Francisco, CA - December 5, 1994	Invited	December 5, 1994	J.T. Jayne

Except where stated, the subject of all these talks was the interaction of molecules with aqueous surfaces.

Graduate thesis resulting from work supported by our DOE Grant.

1.
Theses Title: The Heterogeneous Chemistry of Carbonyl Halides, Haloacetyl Halides and Biogenic Sulfur Species
Number of Pages: 175 pages.
Author: Warren J. De Bruyn,
Date of Degree: December 1994,
Degree: Doctor of Philosophy

2
Theses Title: Uptake of a Series of Gas-Phase Halogenated-Acetic Acids and Halogen Molecules by Aqueous Droplet Surfaces
Number of Pages: 180 pages.
Author: Jianhong Hu
Date of Degree: December 1994,
Degree: Doctor of Philosophy

Abstracts are enclosed.

Project Personnel

Boston College	
Paul Davidovits	Principal Investigator
Jianghong Hu	Received Ph. D. Dec. 1994 now a postdoctoral fellow at University of Chicago
Warren DeBruyn	Received Ph. D. Dec. 1994 now a postdoctoral fellow at University of Miami
Erick Swartz	Graduate Student
Quan Shi	Graduate Student
Igor Tchertkov	Graduate Student
Jeyaraj Boniface	Graduate Student
Daniel Robinson	Research Associate
Aerodyne Research Inc.	
Douglas R. Worsnop	Co-Principal Investigator
Mark S. Zahniser	Co-Principal Investigator
Charles E. Kolb	Co-Principal Investigator
John T. Jayne	Researcher

ABSTRACTS AND BUDGET FOLLOW

Puhl. 2

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 99, NO. D8, PAGES 16,927–16,932, AUGUST 20, 1994

Uptake of gas phase sulfur species methanesulfonic acid, dimethylsulfoxide, and dimethyl sulfone by aqueous surfaces

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Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts

D. R. Worsnop, M. S. Zahniser, and C. E. Kolb
Center for Chemical and Environmental Physics, Aerodyne Research, Incorporated, Billerica, Massachusetts

Abstract. Biogenic reduced sulfur species are emitted from the oceans and then oxidized in the marine boundary layer. The gas/liquid interactions of these oxidized species must be understood in order to evaluate the relative contributions to marine boundary layer aerosol levels from anthropogenic and biogenic sources and to assess the overall impact of these aerosols on global climate. A key parameter in understanding these interactions is the mass accommodation coefficient, which is simply the probability that a gas phase molecule enters into a liquid on striking the liquid surface. The mass accommodation coefficients for dimethylsulfoxide, dimethyl sulfone, and methanesulfonic acid into water have been measured as a function of temperature (260–280 K), pH (1–14), and NaCl concentration (0–3.5 *M*). The experimental method employs a monodispersed train of fast droplets in a low-pressure flow reactor. The mass accommodation coefficients show a negative temperature dependence varying from ~0.1 to ~0.2 over the range of temperatures studied. The measured uptake is independent of pH and NaCl concentration in the ranges studied. The mass accommodation coefficients are well expressed in terms of an observed Gibbs free energy $\Delta G^{\#}_{\mathrm{obs}} = \Delta H^{\#}_{\mathrm{obs}} - T\Delta S^{\#}_{\mathrm{obs}}$ as $\alpha/(1-\alpha) = \exp(-\Delta G^{\#}_{\mathrm{obs}}/RT)$. The results are discussed in terms of a previously described uptake model. In the marine boundary layer, mass transfer of these species into aerosols will be limited by mass accommodation for aerosols with diameters of less than 2 μm.

Publ. 3.

Henry's Law Solubilities and Setchenow Coefficients for Biogenic Reduced Sulfur Species Obtained from Gas-Liquid Uptake Measurements

W.J. De Bruyn, E. Swartz, J. H. Hu, Jeffrey A. Shorter * and P. Davidovits
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Chestnut Hill, MA 02167

D.R. Worsnop, M.S. Zahniser and C.E. Kolb, Center for Chemical and Environmental
Physics, Aerodyne Research Inc., Billerica, MA 01821

Abstract. Biogenically produced reduced sulfur compounds, including dimethylsulfide (DMS, CH_3SCH_3), hydrogen sulfide (H_2S), carbon disulfide (CS_2), methyl mercaptan (CH_3SH) and carbonyl sulfide (OCS), are a major source of sulfur in the marine atmosphere. This source is estimated to contribute 25% to 40% of global sulfur emissions. These species and their oxidation products, dimethyl sulfoxide (DMSO), dimethyl sulfone ($DMSO_2$) and methane sulfonic acid (MSA), dominate the production of aerosol and cloud condensation nuclei (CCN) in the clean marine atmosphere. 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. Using a newly developed bubble column apparatus, a series of aqueous phase uptake studies have been completed for the reduced sulfur species DMS, H_2S, CS_2, CH_3SH and OCS. Aqueous phase uptake has been studied as a function of temperature (278K - 298 K), pH (1-14), H_2O_2 concentration (0-1 M), NaCl concentration (0-5 M) and $(NH_4)_2SO_4$ concentration (0-4 M). The Henry's law coefficients for CH_3SH and CS_2 were determined for the first time as were the Setchenow coefficients for all the species studied.

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Publ. 4

Bubble Column Apparatus for Gas-Liquid Heterogeneous Chemistry Studies

Jeffrey A. Shorter*, Warren J. De Bruyn, Jainhong Hu, Erick Swartz and Paul Davidovits,
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Eugene F. Merkert Chemistry Center,
Boston College,
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Douglas R. Worsnop, Mark S. Zahniser, and Charles E. Kolb
Center for Chemical and Environmental Physics
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Billerica, MA 01821

Abstract

A bubble column apparatus has been designed to conduct time resolved gas-liquid interaction studies of interest in atmospheric chemistry. In the apparatus, a low pressure gas flow, carrying trace gas diluted in helium carrier gas, is 'bubbled' through a flask containing 3.5 liters of temperature controlled liquid. The outlet gas flow is then sampled by a differentially pumped mass spectrometer. The position of the bubble injector, which determines the gas/liquid contact time, is computer controlled by means of a stepping motor. Modeling of the gas uptake and the validation of the apparatus performance are described. The apparatus in the present configuration can measure Henry's law coefficients (H) for non-reactive species in the range 0.01 to 2.0 M/atm. For reactive species (reaction rate k) the apparatus measures $Hk^{1/2}$ values in the range 0.08 to 100 (M/atm)$s^{-1/2}$.

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Public. 5

Uptake of Haloacetyl and Carbonyl Halides by Water Surfaces

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D. R. Worsnop, M. S. Zahniser, and C. E. Kolb,
Center for Chemical and Environmental Physics,
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Billerica, MA 01821

Abstract

Gas-liquid uptake studies have been completed for the carbonyl halides CCl_2O, CF_2O and the haloacetyl halides CCl_3CClO, CF_3CFO and CF_3CClO which are intermediate products from gas phase oxidation of volatile halogen-containing species in the atmosphere. The fluorine-containing species result from degradation of hydrochlorofluorocarbons (HCFCs) (proposed substitutes for chlorofluorocarbons, CFCs). The tropospheric lifetime of the halides depends on their dissolution in the aqueous phase, determined by Henry's law solubility (H) and hydrolysis rate (k_{hyd}). Using a bubble column apparatus, time resolved gas-liquid interaction experiments measured the product $Hk_{hyd}^{1/2}$. Studies were performed at 278K and pH = 1 to 13; for CCl_3CClO and CCl_2O, temperature was varied from 278 to 298K. From this work and results from other laboratories, limits on values of the product Hk_{hyd} were established and used to estimate a 'global' cloud processing rates of these halides. An ~30 day upper limit to their tropospheric lifetime implies that tropospheric removal of the halide degradation products is fast enough not to contribute to the ozone depletion potential of the parent HCFCs.

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Publ. 6

Reactive Uptake of $Cl_2(g)$ and $Br_2(g)$ by Aqueous Surfaces as a Function of Br^- and I^- Ion Concentration: The Effect of Chemical Reaction at the Interface

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Department of Chemistry, Merkert Chemistry Center
Boston College, Chestnut Hill, MA 02167

D. R. Worsnop, M. S. Zahniser, and C. E. Kolb
Center for Chemical and Environmental Physics
Aerodyne Research, Inc., Billerica, MA 01821

Abstract: The uptake of gas phase Cl_2 and Br_2 by aqueous NaBr and NaI solutions has been studied as a function of concentration ($2.5\text{x}10^{-4}$ to 0.5M), temperature (263-293K) and gas-liquid interaction time (2-15 ms). The uptake of O_3 by aqueous NaI solutions has also been studied for the purpose of comparison. These measurements were conducted in a droplet apparatus in which a stream of well defined droplets (120-250 μm in diameter) is passed through a low pressure flow tube containing the halogen molecules. Since the solubility of the halogen molecules X_2 (X = Cl or Br) is low, the measured uptake is primarily due to the aqueous reaction of the species with the halide ion Y^- (Y = Br or I) via $X_2 + Y^- \text{--->} XY + Y^-$. The magnitude of the measured halogen uptake and its functional dependence on ion concentration are not in accord with a simple bulk phase reaction mechanism. The data indicate that reactions at the gas-liquid interface have a significant role in the gas uptake process. On the other hand, the O_3 uptake shows no evidence of interfacial reaction. The atmospheric implications of the halogen uptake results are discussed.

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Pub. 8

Faraday Discussion April 19 to 21 1995

Entry of Gas Molecules into Liquids

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Abstract

Heterogeneous gas-liquid interactions play a fundamental role in many atmospheric processes. Pivotal for the understanding of such processes is the rate of gas uptake by the relevant liquid. Accurate experimental techniques have been developed to study uptake of gases by liquids. Gas-liquid interactions have been investigated for more than thirty gas phase species encompassing two classes of molecules: 1) those that do not react in the liquid but are readily solvated by it, and 2) those that have low solubility in the liquid but react in the liquid rapidly to form highly soluble species. Uptake studies of non-reactive gas molecules in water have been explained by a model which treats the water surface as a narrow region of a dense gas-like state within which trace gas/solvent collisions occur. Gas accommodation occurs via nucleation of solvent molecules. Uptake studies for reactive gas molecules, indicate that for some species reaction rates are much more rapid at the liquid interface than in the bulk liquid. In this work the results of non-reactive and reactive uptake experiments are brought together. The uptake model is briefly described, and the implication of the model for the kinetic nature of liquid surfaces is examined. New reaction driven uptake studies which provide clear evidence for reactions at the gas/liquid interface are presented. The nature of interfacial reactions and their connection to the uptake model are examined.

* Present address Department of Geophysical Sciences, The University of Chicago, Chicago IL 60637.

Thesis)

THE HETEROGENEOUS CHEMISTRY OF CARBONYL HALIDES, HALOACETYL HALIDES AND BIOGENIC SULFUR SPECIES

Warren J. De Bruyn
December 1994

ABSTRACT

Heterogeneous reaction pathways involving aqueous droplets in clouds and fogs have been recognized as major mechanisms for the chemical transformation of atmospheric trace gases. Here we examine the heterogeneous chemistry of two atmospheric systems using a previously developed fast droplet experiment and a new bubble column apparatus.

Gas-liquid uptake studies have been completed for the following series of carbonyl and haloacetyl halides; CF_3CFO, CF_2O, CF_3CClO, CCl_2O and CCl_3CClO. Some of these species have been shown to be degradation products of hydrochlorofluorocarbons and hydrofluorocarbons which have been proposed as substitutes for ozone depleting chlorofluorocarbons. The experiments yielded values for the product of the Henry's law coefficient (H) and the liquid phase hydrolysis rate constant (k) in the form $Hk^{1/2}$. Results indicate that the tropospheric removal of the degradation products is fast enough not to contribute to the ozone depletion potential of their parent species.

A series of aqueous phase uptake studied have also been completed for key biogenic sulfur species in the marine boundary layer. Reduced sulfur species of biogenic origin CH_3SCH_3, H_2S, CS_2, CH_3SH and OCS are a major source of sulfur in the marine atmosphere. These species and their oxidation products CH_3SO_3H (MSA), $(CH_3)_2SO$, (DMSO) and $(CH_3)_2SO_2$ ($DMSO_2$) dominate the production of aerosol and cloud condensation nuclei in the clean marine atmosphere. Henry's law coefficients and Setchenow saltout coefficients have been obtained for the reduced sulfur species and mass accommodation coefficients have been obtained for the oxidized sulfur species. The atmospheric implications of the results have been examined.

The species DMSO, $DMSO_2$ and MSA which exhibit relatively large uptake were studied with the fast droplet apparatus previously described in detail. The other species studied in this work exhibited uptakes too small to be measured with the droplet apparatus. A new more sensitive bubble column apparatus was developed for the study of these molecules.

In the bubble column apparatus, a low pressure gas flow, carrying trace gas diluted in helium carrier gas, is bubbled through a liquid. The bubbles and their transit through the liquid are carefully characterized. Measurements of gas depletion yield the desired parameters.

Key words: atmospheric chemistry, heterogeneous chemistry, carbonyl halides, haloacetyl halides, biogenic sulfur species, Henry's law coefficient, hydrolysis rate constant.

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UPTAKE OF A SERIES OF GAS-PHASE HALOGENATED-ACETIC ACIDS AND HALOGEN MOLECULES BY AQUEOUS DROPLET SURFACES

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December 1994

ABSTRACT

The importance of gas-liquid heterogeneous chemistry in the atmosphere has been recognized. It has been found that heterogeneous reactions could dramatically alter the chemical composition of the atmosphere. Here we examine the heterogeneous chemistry of two atmospheric systems using a well developed droplet apparatus. This method combines a monodisperse droplet stream with a low pressure flow reactor. The uptake of gas by the droplets is determined by measuring changes in gas phase density using a mass spectrometer as the droplet area is changed.

Gas-liquid uptake studies have been performed for the following series of halo-acetic acids (as well as acetic acid itself): CF_3COOH, CCl_3COOH, $CClH_2COOH$, CCl_2HCOOH, $CF_2ClCOOH$, and CH_3COOH. These species (except CH_3COOH) are the final degradation products of alternative chlorofluorocarbons. The mass accommodation coefficients for these species have been determined. Results indicate that the mass transfer of these halo-acids to atmospheric cloud droplets are not limited by mass accommodation.

The studies of the uptake of gas phase Cl_2 and Br_2 by aqueous surfaces as a function of Br^- and I^- ion concentration have also been completed. Since the solubility of the halogen molecules X_2 ($X = Cl$ or Br) is low, the measured uptake is primarily due to the aqueous reaction of the species with the halide ion Y^- ($Y = Br$ or I) via $X_2 + Y^- \text{--->} XY + Y^-$. The magnitude of the measured uptake and its functional dependence on the ion concentration are not in accord with simple bulk phase reaction of the species. The data indicate that reactions at the gas-liquid interface play a significant role in the gas uptake process. The atmospheric implications of the results have been examined.

Key words: atmospheric chemistry, uptake studies, halogenated-acetic acids, halogen molecules.