Determination of Nitric Acid Uptake Onto Sodium Chloride Particles

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Purpose

- Determine the uptake coefficient of the reaction

$NaCl_{(s)} + HNO_{3(g)} \rightarrow NaNO_{3(s)} + HCl_{(g)}$

by single particle mass spectrometry.

- Elucidate the mechanism by which nitric acid is
  - transformed on deliquescent NaCl particles.

Methods

- Single particle laser desorption ionization mass spectrometry was used to obtain mass spectra.
- Mono-disperse NaCl droplets (d_p~100 nm, RH 90%)
  - were mixed with several known nitric acid vapor concentrations under laminar flow conditions.
- The measured compositions of the particles as a function of contact time were used to determine kinetic parameters.

Results

- The magnitude of gaseous nitric acid uptake is greater for NaCl droplets than for NaCl dry particles.
- The reaction rate increases with increasing nitric acid concentration.
- Reactive uptake coefficients decrease with increasing nitric acid concentration.
- A Langmuir dissociative mechanism can be invoked to explain the uptake phenomenon.

Background

The reactions of sea salt particles with gas-phase species has garnered interest because of its importance in the cycling of halogens in the atmosphere.[1] Depending on the concentrations of the other reactants in the environment, the reaction of nitric acid with sea salt particles can increase or deplete ozone concentrations. In order to assess the significance of this reaction in the polluted coastal troposphere, the kinetics and mechanism warrant further study.

Single Particle Aerosol Mass Spectrometry

- Single particle mass spectrometry has proved to be a powerful tool for the investigation of the physicochemical characteristics of particulate matter.[2]
- Particle phase reactions have been observed in both laboratory and field settings using this technique.
- Relative response factors for internally-mixed binary aerosols have been developed to relate the ion signal intensity to the chemical composition of the particle.
- In this work, we use quantitative concentration measurements to determine the reactive uptake coefficient for this important heterogeneous reaction.

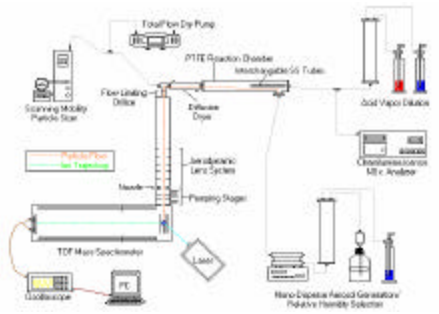

Figure 1 is an illustration of the experimental apparatus. The change in particle composition is monitored with a single particle TOF mass spectrometer. Nitric acid vapor reacts with sodium chloride droplets in the flow tube reaction chamber. Kinetic runs are performed as a function of nitric acid concentration and contact time.

Standard Response

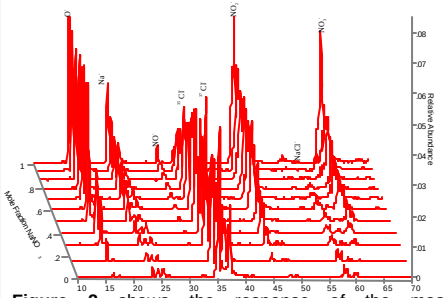

Figure 2 shows the response of the mass spectrometer to particles that were prepared with different known chemical compositions. It should be noted that for the analysis, ion intensities from individual spectra are measured and then averaged to calculate their response, shown below.

Relative Ion Response vs. Composition

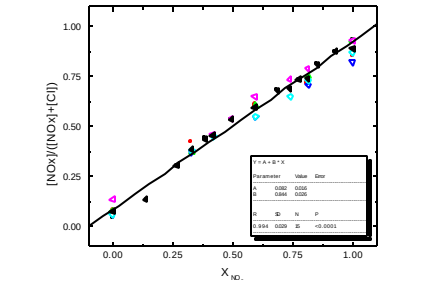

Figure 3 demonstrates the linearity of response for internally mixed binary NaCl/$NaNO_3$ aerosols.

Kinetics Calculations

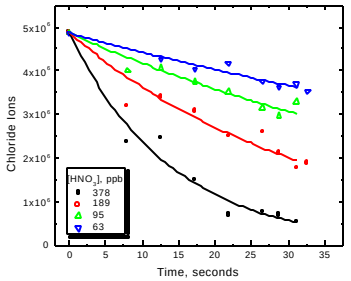

Figure 4 displays the change in chemical composition of the aerosol as a function of contact time and nitric acid concentration in the reactor. The measured loss rate of NaCl (molecules/cm^3/sec) is:

$$\frac{\partial[NaCl]}{\partial t} = \frac{\pi d_p^3 \rho_p W_{NaCl} N_A}{6 V_r}\left(\frac{\partial X_{NaCl}}{\partial t}\right)$$

where d_p is the dried particle diameter, ρ_p is the density of sodium chloride, W_{NaCl} is the formula weight, X_{NaCl} is the mole fraction of NaCl in the detected particle, N_A is Avogadro's Number, and V_r is the volume of the reactor. The reactive uptake coefficient is be given by:

$$\gamma = \frac{\frac{\partial[NaCl]}{\partial t}}{\frac{\pi c d_d^2}{4 V_r}[HNO_3]}$$

where the numerator, given as the number of collisions that lead to reaction, is normalized by the total number of collisions of the nitric acid gas molecules and a single particle. In this equation d_d is the droplet diameter; c is the average molecular speed of nitric acid. This equation assumes first order kinetic gain to the particle, that is the observation of nitrate in the particle is coincident with loss of HCl.

Diffuso-Reactive Length

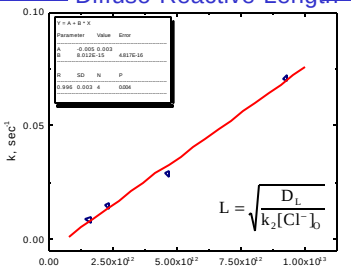

Figure 5 shows the dependence of the rate coefficient on nitric acid concentration. The diffuso-reactive length is a parameter used to describe where the reaction takes place in the droplet. By calculating the $[Cl^-]_0$ in the droplet, it can be computed.[4] In this case L = 4 nm for d_d = 100 nm.

Langmuir Dissociative Mechanism

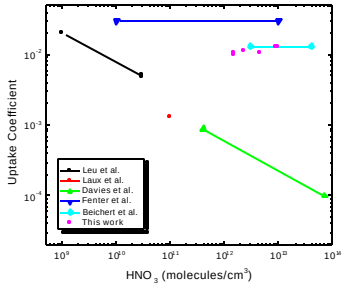

Figure 6 shows the reactive uptake coefficient for HNO_3 on NaCl from different laboratories as a function of $[HNO_3]$.[4]

A one-site Langmuir dissociative mechanism predicts that γ is independent of $[HNO_3]$ at high relative humidity.

Conclusions

- With proper experimental conditions, laser desorption ionization mass spectra can be used to quantitatively determine the chemical composition of a particle in real time.
- This information can be exploited to perform kinetic experiments of reactions that are important in the atmosphere.
- A one-site Langmuir dissociative mechanism can describe the uptake kinetics.
- The results are in good agreement with previous studies.[1]
- Future experiments will elucidate the effects of relative humidity and particle size on the kinetic parameters.

References

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Acknowledgements

- NSF Grant CHE – 0098831
- Dr. Burnaby Munson, University of Delaware
- Dr. David Kane, Philip Morris Incorporated
- Derek Lake, University of Delaware
- Berk Oktem, University of Delaware
- Frederick Cox, University of Delaware