FINAL REPORT

"LABORATORY STUDIES OF THE SENSITIVITY OF TROPOSPHERIC OZONE TO THE
CHEMISTRY OF SEA SALT AEROSOL"

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2. "Tropospheric HONO and Reactions of Oxides of Nitrogen with NaCl", R. Vogt and B. J. Finlayson-Pitts, Geophys. Res. Lett., 21, 2291 (1994).

I. OVERALL GOALS OF THIS PROJECT

Ozone plays a critical role in both the chemistry and radiation balance of the troposphere. Not only does ozone react directly with unsaturated organics, but it also photolyzes at wavelengths below 320 nm to form electronically excited $O(^1D)$ atoms; these react, in part, with water to generate hydroxyl radicals (OH), the "universal atmospheric oxidant" believed to drive the chemistry of both remote and polluted atmospheres (Finlayson-Pitts & Pitts, 1986). Since ozone is a greenhouse gas and absorbs in the 300 nm region, it also impacts tropospheric radiation both in the infrared and the UV (Demerjian et al, 1980; Ramanathan, 1988). As a result, understanding the factors controlling tropospheric ozone levels is critical to our understanding of a variety of issues in global chemistry and climate change.

Chlorine atoms have the potential to contribute significantly to the ozone balance in the free troposphere. They can react directly with ozone,

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (1)$$
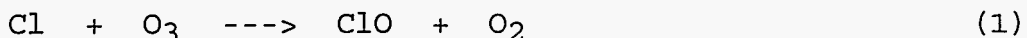
or alternatively, with organics:

$$Cl + RH \longrightarrow HCl + R \qquad (2)$$

The rate constant for reaction (2) is essentially diffusion-controlled, even for relatively small alkanes. The alkyl radical produced in (2) adds O_2 to form alkylperoxy radicals (RO_2) which, in the presence of sufficient NO, generate NO_2. Photolysis of NO_2 to produce ground state $O(^3P)$ atoms, which add to O_2, is the only known source of anthropogenic ozone. Hence chlorine atom-organic reactions may actually lead to the formation of ozone in the presence of sufficient NO.

Reactions of alkali halides in sea salt particles are a potential source of atomic chlorine, as well as to a lesser extent, bromine. In addition, salt particles have been generated in the troposphere in unusual situations such as the oil well burning in Kuwait (e.g. see Lowenthal et al, 1993), and in the stratosphere by the eruption of alkaline volcanoes such as El Chichon (Woods et al., 1985). Hence the reactions of these alkali halides, especially those producing precursors to atomic chlorine, are of great interest.

However, relatively little is known about the kinetics of these gas-solid "heterogeneous" reactions. In addition, the atmospheric fates of the gaseous halogen containing products of the salt reactions are not well known. Surprisingly, there is significant uncertainty in the absolute rate constants for the reactions of chlorine atoms even with the simple alkanes, and no data are

available for the reactions with biogenics. Finally, the mechanisms, intermediates and products of the Cl-biogenic reactions are unknown; these could serve as unique "markers" of chlorine atom chemistry in the troposphere, and hence are important to define.

II. SPECIFIC GOALS

The specific goals were as follows:

• To initiate studies of the reaction probabilities for the reactions of gaseous oxides of nitrogen with NaCl and NaBr;

• To initiate relative and absolute rate constant studies for the reactions of chlorine atoms with organics;

• To apply diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) to studying the reactions of N_2O_5 and HONO with NaCl;

• To extend our initial DRIFTS work on surface nitrate formed by NO_x reactions to studies of the effects of water and photochemistry on the surface species.

III. TECHNICAL REPORT

A. Reaction Probabilities for the "Heterogenous" Reactions of Oxides of Nitrogen with NaCl and NaBr.

1. Knudsen Cell Studies.

We have designed and constructed a Knudsen cell for measurement of gas-solid reaction probabilities. The design is somewhat different from that used in the classic work of Golden et. al. (1973), in that only one chamber, rather than two, is used. The salt is covered with a movable plate so that the gas concentration can be first monitored in the absence of the salt, and then by simply lifting the plate, in its presence. This design avoids the need to correct for different cell volumes and temperatures as is the case when two chambers are used.

In initial studies, the sensitivity of the mass spectrometer for the gases was not as great as desired. This was due to the use of a skimmer at the interface between the first vacuum chamber, to which the Knudsen cell is connected, and the second which housed the quadrupole. This skimmer was part of the mass spectrometer design when it was originally interfaced to a fast flow discharge system. We have replaced the skimmer with a larger orifice into the

quadrupole chamber, which has increased our sensitivity by approximately an order of magnitude, sufficient for these studies.

The first set of experiments planned is to determine the reaction probability for the reaction of N_2O_5 with H_2SO_4/H_2O mixtures. A variety of studies have measured this reaction probability to be 0.06-0.1 over a range of temperatures and acid-water compositions (Fried et al, 1994 and references therein), so that it can be reliably used as a test of our Knudsen cell. One problem is that low temperatures are required to maintain a sufficiently low water pressure to carry out these studies; a -95° C temperature bath is being purchased through other sources of support and will be used to carry out this testing of our cell. In the meantime, preliminary studies of the HNO_3-NaCl reaction are being carried out for comparison to the XPS studies below.

A postdoctoral fellow, Dr. Ruaidhri Neavyn, is working on this system.

2. X-Ray Photoelectron Spectroscopy (XPS) Studies of the Reaction of NaCl with HNO₃.

In collaborative work with Professor John Hemminger and Mickey Laux (a Ph.D. student) at the University of California, Irvine, we have measured the reaction probability for the reaction of HNO_3 with NaCl:

$$HNO_3{}_{(g)} + NaCl{}_{(s)} \longrightarrow NaNO_3{}_{(s)} + HCl{}_{(g)} \qquad (3)$$
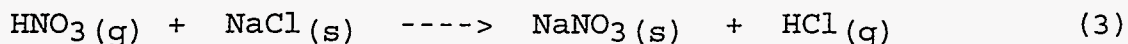
This measurement is important because the gaseous halogen-containing product, HCl, is not as readily converted to atomic chlorine in the troposphere as are the photochemically active products of other NO_x reactions. Thus HCl does not absorb light in the actinic region, and is only slowly converted by reaction with OH into Cl; competing with this is the efficient scavenging of HCl, removing it via both wet and dry deposition.

X-ray photoelectron spectroscopy (XPS) was used to measure the reaction probability for reaction (3). A single crystal of NaCl was exposed to measured amounts of gaseous HNO_3 through a doser whose conductance could be used to calculate the total number of molecules incident on the face of the crystal. The surface nitrate formed was measured as a function of the total dose of HNO_3 using XPS, from which a reaction probability of $(4\pm2)\times10^{-4}$ was obtained.

. This reaction probability is sufficiently small that the reaction of N_2O_5 with NaCl is likely to be competitive with HNO_3 at night when significant concentrations of N_2O_5 can build up. This is

important, since unlike reaction (3), the N_2O_5 reaction produces $ClNO_2$ which photolyzes readily to chlorine atoms.

This has been published in Geophys. Res. Lett.; a reprint is found in the Appendix.

B. Reaction Kinetics for Chlorine Atom Reactions with Organics

1. *Relative Rate Studies*.

We have carried out relative rate measurements for the reactions of atomic chlorine with the simple alkanes ethane, propane, *i*-butane and *n*-butane. These studies were carried out using a small quartz cell in which mixtures of Cl_2 with two organics were photolyzed. The loss of the organics was followed with time using GC. From the relative rate equation,

$$\ln [X]_o/[X] = \{k_X/k_Y\} \ln [Y]_o/[Y] \tag{I}$$

the ratio of the rate constants k_X/k_Y can be obtained from the rates of loss of the individual organics.

Table 1 shows our measured values of three pairs of relative rate constants, determined both in air and in He and over a wide range of reactant concentrations. Those for ethane/propane and isobutane/*n*-butane differ by less than 10% from the measurements of Atkinson and Aschmann (1985) and Wallington et al. (1988). That for ethane/*n*-butane differs from the other two relative rate measurements by ~18%, significantly greater than is the case for the first two pairs of organics and greater than expected for relative rate methods. In addition, the relative rate results differ from the ratios of the absolute rate constants by ~15-20% for the ethane-propane-*n*-butane pairs. It is not clear why this is the case, making the absolute rate constant measurements (see below) even more important.

Table 1: Relative Rate Constants for Chlorine Atom Reactions with Simple Alkanes[a]

Pair of Compounds	This Study	Atkinson & Aschmann (1985)	Wallington et. al. (1988)	Lewis et. al.[b] (1980)
Ethane/Propane	0.441±0.036	0.476±0.022	0.484±0.039	0.363±0.049
Ethane/n-Butane	0.283±0.047	0.324±0.009	0.344±0.026	0.244±0.034
i-butane/ n-butane	0.655±0.049	0.695±0.009	0.671±0.042	0.649±0.078

[a]Errors shown are two standard deviations.
[b]Relative rate values shown are the ratios of the absolute measurements.

Since the rate constants for the chlorine atom reactions with the unsaturated biogenics will be pressure dependent, we also tried some runs using these cells and repressurizing to one atmosphere total pressure after each sample was removed for GC analysis. The rate constants obtained had much poorer precision and exhibited some systematic errors.

As a result, we have set up a relative rate system employing a collapsible Teflon reaction chamber which allows a constant pressure to be maintained while sampling over the course of an experiment. We have constructed a bank of fluorescent lights for photolysis of the Cl_2-organic mixtures in the 50 L Teflon chambers, and are using larger loops on the gas sampling valve to increase the sensitivity by a factor of ~40. This will allow us to work in the low ppm-high ppb range more closely approximating concentrations found in the troposphere.

Currently working on this project are Ms. Lisa Abato and Mr. Mark Ragains, with the assistance of Dr. Ruaidhri Neavyn who used a similar system for his Ph.D. work in Ireland. Lisa worked on this as part of her senior research project required of all of our undergraduates for their B.S. degree; she graduated in December and worked full time on the project until she entered the Ph.D. program at the University of California, Irvine, this fall. Mark is a high school teacher who is working on this as part of his Master's degree. He is supported by a Research Corporation "Partners in Science" grant which covers his summer stipend for 1994 and 1995.

2. *Absolute Rate Constant Measurements.*

Our fast flow discharge system which has been used for OH kinetics measurements in the past has been converted for application to Cl atom kinetics. We are using resonance fluorescence of Cl at 139 nm, excited by a microwave discharge in a dilute (0.1%)Cl_2/He mixture.

Initial studies were carried out using a discharge of a 1% Cl_2/He mixture as the source of chlorine atoms. Problems with irreproducibility were encountered, even after treatment of the discharge region with phosphoric acid and "preconditioning" by discharging O_2 as suggested by Lewis et. al. (1980). It appears that unlike H_2 and F_2, Cl_2 does not efficiently nor reproducibly discharge. As a result, varying amounts of atomic chlorine were produced, along with significant concentrations of the undissociated Cl_2. The latter reacted with the alkyl radicals produced in the initial reaction (2), to regenerate Cl:

$$Cl_2 + R \longrightarrow RCl + Cl \qquad (3)$$
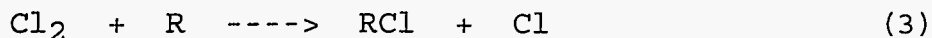
In addition, the undissociated Cl_2 was photolyzed by the resonance lamp to generate atomic chlorine.

To resolve these problems, we are now using the reaction of fluorine atoms with HCl as a source of Cl:

$$F + HCl \longrightarrow HF + Cl \qquad (4)$$

Atomic fluorine can be generated by discharge of a dilute F_2/He mixture. We have studied the discharge of F_2/He in the past in a fast flow discharge system interfaced to a mass spectrometer and have shown that F_2 can be discharged with essentially 100% efficiency.

In these initial studies, the signal to scattered light was also not sufficient for our purposes. With rate constants of $\sim 10^{-10}$ cm^3 molecule^{-1} s^{-1}, it is necessary to start with initial organic concentrations of the order of 10^{11} molecules cm^{-3} in order for the reaction to occur with measurable decays of Cl over the time scale of about 50 ms. This necessitates having initial chlorine atom concentrations $<10^{10}$ atoms cm^{-3}, and hence a sensitivity of $\sim 10^8$ atoms cm^{-3}.

As a result, we redesigned the detection port, fabricating it out of metal to ensure that the exciting light and detection system are held in a rigid, perpendicular alignment. We have also included in the design the capability of incorporating MgF_2 lenses to minimize the scattered light and maximize the signal. Studies are currently underway to test and optimize this new system.
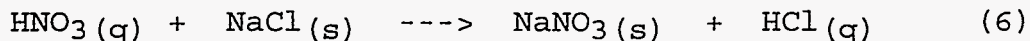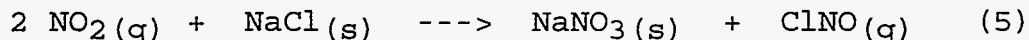
The first set of studies involves measuring the rate constants and temperature dependence of the Cl atom reactions with simple alkanes. As seen in Table 1 above, the rate constants measured using relative rate techniques for the ethane/propane and ethane/n-butane pairs differ somewhat from the corresponding ratios of rate constants determined using absolute rate methods. Accurate determination of the absolute rate constants for these simple alkanes will allow relative rate values from this and other laboratories to be converted to absolute values with considerably more confidence than is possible at the present time.

Initial studies give room temperature rate constants for the reactions of ethane, propane and n-butane of 4.78, 9.26 and 17.4 x 10^{-10} cm^3 molecule^{-1} s^{-1} respectively. From these data, the ratio of ethane/propane is 0.516 and ethane/n-butane is 0.275. Within the approximately 20% uncertainty associated with the ratio of the absolute rate constants, the agreement with our relative rate studies is excellent.

Dr. Peter Beichert, a postdoctoral fellow, is currently working on this system, with the advice and assistance of Dr. Rainer Vogt, a a postdoctoral fellow who has been working with me for over a year and who carried out similar studies for his Ph.D. work in Germany.

C. DRIFTS Studies of the Reactions of N_2O_5 and HONO with NaCl in the Presence and Absence of Water

Under NSF support, we have shown that diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) is a very effective technique for studying the kinetics and mechanisms of the reactions of gases with the alkali halides. In earlier work, (Vogt and Finlayson-Pitts, 1994a), the reactions of NO_2 and HNO_3 with NaCl were studied, and the kinetics of the NO_2 reaction measured. These reactions were shown to give NO_3^- on the NaCl surface as expected:

$$2 \ NO_{2(g)} \ + \ NaCl_{(s)} \ ---> \ NaNO_{3(s)} \ + \ ClNO_{(g)} \qquad (5)$$

$$HNO_{3(g)} \ + \ NaCl_{(s)} \ ---> \ NaNO_{3(s)} \ + \ HCl_{(g)} \qquad (6)$$

However, more importantly, the infrared spectra showed that the nitrate ion was formed in different surface environments, characterized by different infrared absorption bands and different time dependencies of their formation during the reaction.

Recently, Junkermann and Ibusuki (1992) applied DRIFTS to the reactions of N_2O_5 and HONO with NaCl. They also observed infrared bands due to products accumulating on the NaCl, but attributed them to nitrite, NO_2^-, rather than nitrate. This is potentially

important, as the reacted salts could thus act as a source of gaseous nitrous acid. HONO absorbs light strongly in the actinic region, giving OH with unit quantum yield. Hence the formation of nitrite could significantly impact the chemistry of any regions in which salt is present.

We have extended our initial work to include the N_2O_5 and HONO reactions, and find that the product infrared bands are identical to those we observed in the NO_2 and HNO_3 reactions. Indeed, it appears unlikely that HONO itself reacts; it is likely to be the NO_2 in equilibrium with the HONO which generates the product nitrate in this case. While there is some shift in the band positions when water is added to the system, it is reversible, indicating that water reversibly complexes with the NO_3^-.

In short, there is no evidence for nitrite formation in these systems. This has just been published in Geophys. Res. Lett.; a reprint is found in the Appendix.

Dr. Vogt has carried out this work, as well as the DRIFTS studies described below.

D. DRIFTS and XPS Studies of the Effects of Water on Surface Nitrate

In our initial DRIFTS studies (Vogt and Finlayson-Pitts, 1994), we showed that nitrate in at least two different surface environments was formed at <5% reaction of the surface chloride. Figure 1 shows the spectrum after a small extent of reaction of NaCl with NO_2 (solid line), after exposure to water vapor below the deliquescence point (dashed line) and then after drying the salt by heating (dotted line). It is seen that exposure to water causes the peaks at 1333 and 1460 cm^{-1} due to the isolated nitrate ions to decrease, while broader peaks in the center similar to mixtures of bulk $NaNO_3$ mixed with NaCl grow in. Upon drying, this conversion of the isolated features to those typical of $NaNO_3$ is completed. This suggests that water on the surface even below the deliquescence point forms a quasi-liquid layer which mobilizes the surface ions. On drying, selective recrystallization into separate regions of $NaNO_3$ and NaCl occurs.

Further support for this interpretation comes from experiments in which this surface is again exposed to NO_2 or HNO_3. Figure 2 shows the third spectrum from Figure 1 (after reaction, water treatment and drying), as well as that after a subsequent exposure to NO_2. The reactions lead to new bands at 1333 and 1460 cm^{-1}, just as for a fresh NaCl surface, rather than to an increase in the broad bands characteristic of $NaNO_3$.

Studies are underway joint with Professor Hemminger's group at UC Irvine to confirm that selective recrystallization does indeed

DRIFTS Spectra after Reaction with NO_2, Exposure to H_2O and Heating

$[NO_2] = 4.5 \times 10^{14} \ cm^{-3}$ for 16 min

$P_{H_2O} = 17 \ m$ bar for 2 min

Heating: 413 K for 1.5 h
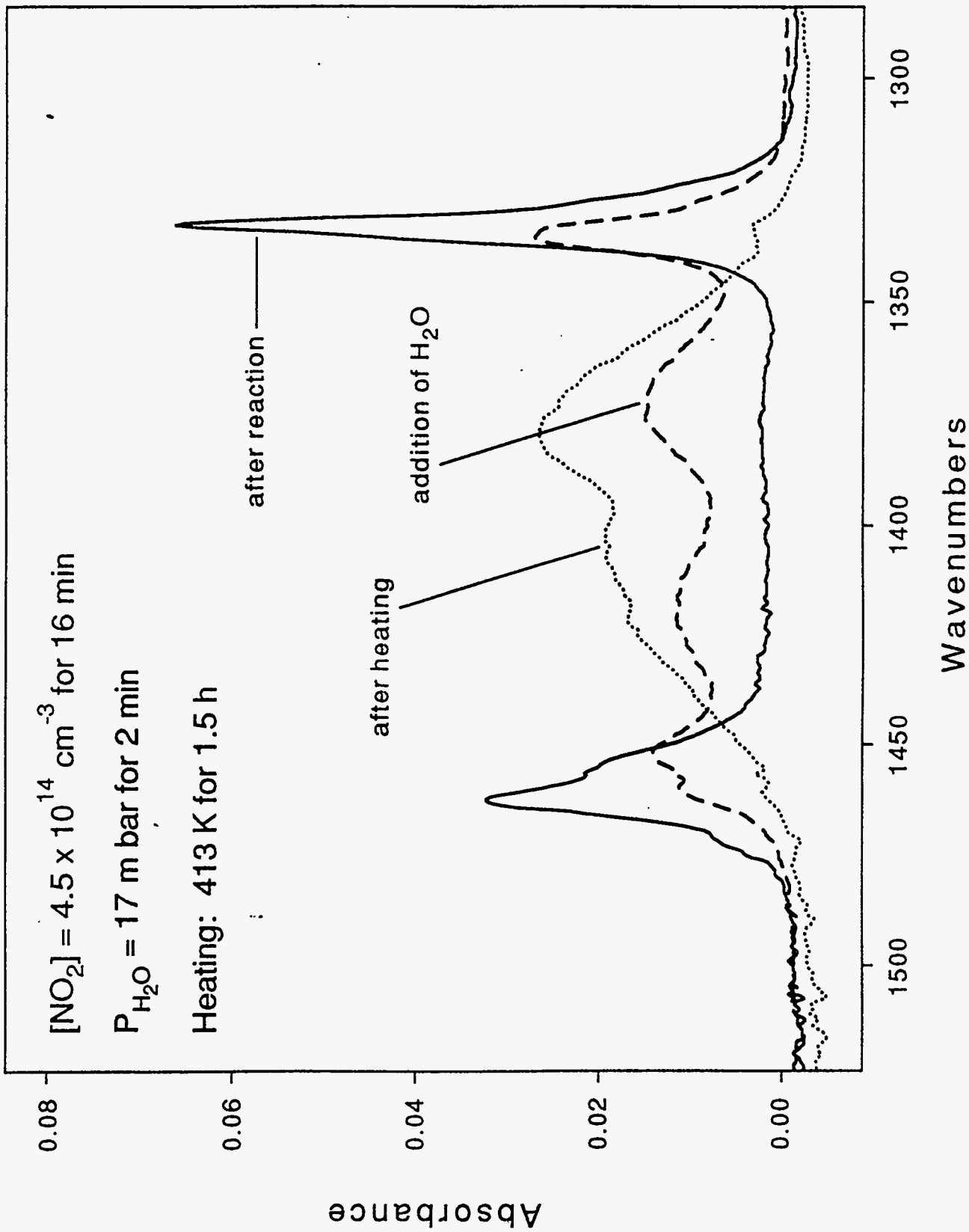
FIGURE 1

Effect of Reaction of NO₂ After NaCl Treatment with NO₂, H₂O and Heating

Initial Treatment:

$[NO_2] = 5 \times 10^{14}$ molecules cm^{-3}

$[H_2O] = 7$ mbar for 25 min

Heat at 413 K for 25 min

$+[NO_2] = 5 \times 10^{14}$ molecules cm^{-3} for 13 minutes

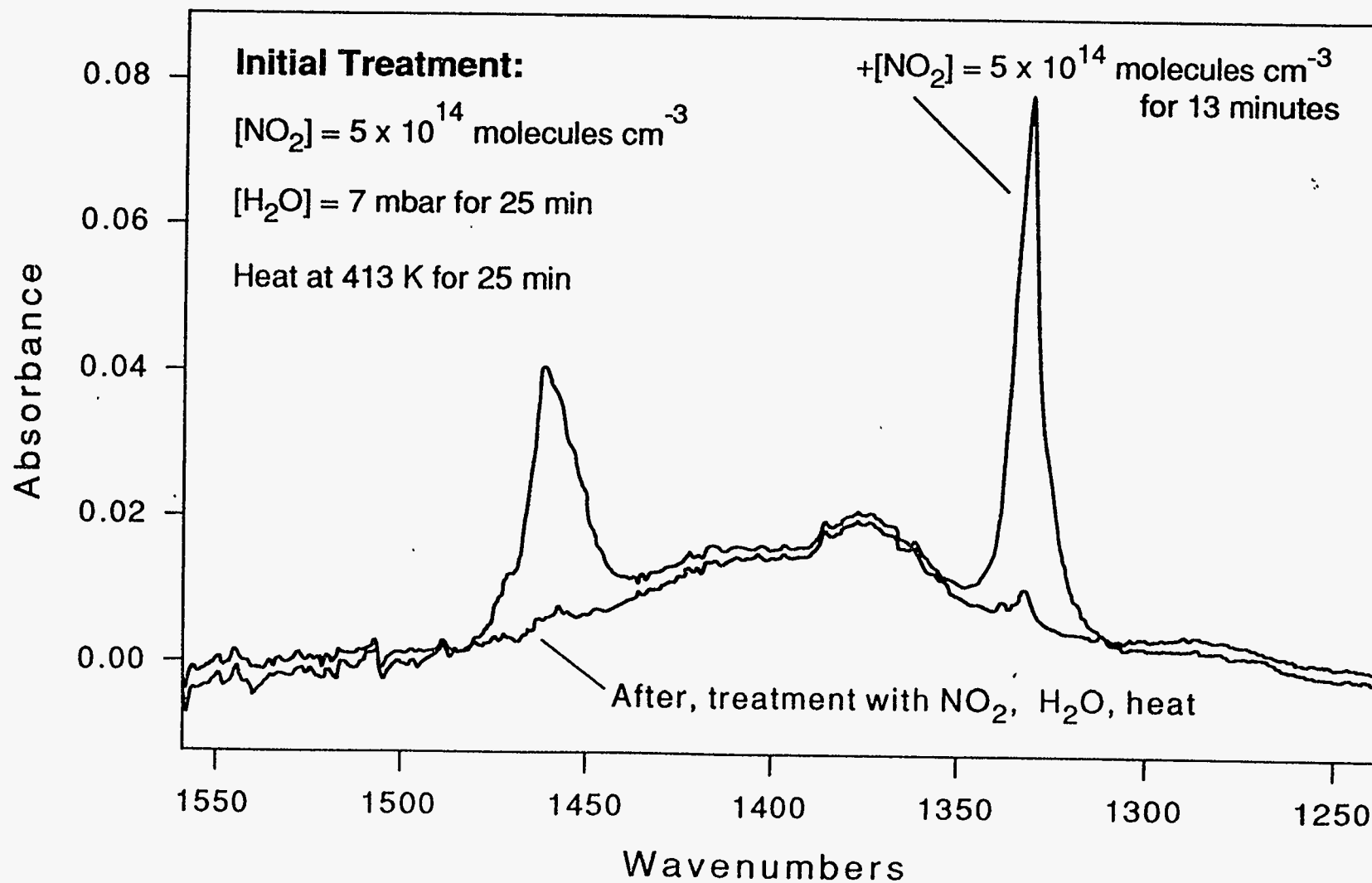After, treatment with NO₂, H₂O, heat

FIGURE 2

occur by applying transmission electron microscopy to these reactions. A graduate student, Ms. Heather Allen, is working on this project.

In addition, XPS studies are also being carried out by Mr. Mickey Laux, a graduate student, on single crystals of NaCl reacted with HNO_3 in which the regeneration of surface chloride after water treatment is being followed by XPS.

These results are quite exciting, in that this effect of water in mobilizing surface ions at water vapor pressures below the deliquescence point has not before been observed. It suggests that a quasi-liquid layer is formed, as has been hypothesized by Molina and coworkers is the case for polar stratospheric clouds (Molina, 1992; Abbatt et al, 1992). In this case, recycling of chloride to the surface will occur readily in the atmosphere, allowing essentially all of the particle chloride, not just that on the surface, to react. Indeed, this is consistent with the observation of particles collected in the same air mass having widely varying nitrate concentrations (Mouri & Okada, 1992); our results suggest this is not due to varying extents of reaction, but rather to selective recrystallization of particles containing nitrate.

E. Photochemistry of Surface Nitrate Species

An assumption which is usually made with respect to nitrate in sea salt particles is that it is conserved, i.e. that it does not react further. We have carried out initial studies using both XPS and DRIFTS which suggest that nitrate can be photolyzed to nitrite at wavelenghts below 290 nm. These species can be clearly distinguished using both methods.

More interesting is the effect of the substrate. If $NaNO_3$ crystals mixed with NaCl, or alternatively, what we interpret as our recrystallized $NaNO_3$ on the surface of NaCl, is photolyzed, NO_2^{2-} is formed. However, when our "isolated nitrate" ions are photolyzed, nitrate disappears, no nitrite is observed and a new peak due to an as yet unidentified species at approximately 2100 cm^{-1} is formed. Clearly the photochemistry depends critically on the environment surrounding the nitrate ion, the first time such an observation has been made in this system, to the best of our knowledge.

Dr. Vogt is carrying out the DRIFTS photochemistry studies.

IV. SUMMARY

In short, this project has been highly successful in initiating a variety of studies relevant to the issue of chlorine atom chemistry in the troposophere, and we anticipate that many of these approaches will be brought to fruition in the continuation of the grant. In addition, new portions of the project will be initiated, directed in particular to assisting in the design of field tests of this chemistry.

V. REFERENCES

Abbatt, J. P. D., Beyer, K. D., Fucaloro, A. F., McMahon, J. R., Wooldridge, P. J., Zhang, R. & Molina, M. J. (1992) "Interaction of HCl Vapor with Water-Ice: Implications for the Stratosphere", J. Geophys. Res., 97, 15,819-15,826.

Atkinson, R. & Aschmann, S. M. (1985) "Kinetics of the Gas Phase Reaction of Cl Atoms with a Series of Organics at 296±2K and Atmospheric Pressure", Int. J. Chem. Kinet., 17, 33-41.

Bonsang, B., Polle, C. & Lambert, G. (1992) "Evidence for Marine Production of Isoprene", Geophys. Res. Lett. 19 1129-1132.

Demerjian, K. L., Schere, K. L. & Peterson, J. T. (1980) "Theoretical Estimates of Actinic (Spherically Integrated) Flux and Photolytic Rate Constants of Atmospheric Species in the Lower Troposphere", Adv. Environ. Sci. Technol., 10, 369-459.

Finlayson-Pitts, B. J. & Pitts, J. N. Jr. (1986) Atmospheric Chemistry: Fundamentals and Experimental Techniques. New York: Wiley (and references therein).

Fried, A., Henry, B. E., Calvert, J. G. & Mozurkewich, M. (1994) "The Reaction Probability of N_2O_5 with Sulfuric Acid Aerosols at Stratospheric Temperatures and Compositions", J. Geophys. Res., 99, 3517-3532.

Golden, D. M., Spokes, G. N. & Benson, S. W. (1973) "Very Low-Pressure Pyrolysis (VLPP): A Versatile Kinetic Tool", Ang. Chemie 12 534-546.

Junkermann, W. & Ibusuki, T. (1992) "FTIR Spectroscopic Measurements of Surface Bond Products of Nitrogen oxides on Aerosol Surfaces-Implications for Heterogeneous HNO_2 Production", Atmos. Environ., 26A, 3099-3103.

Laux, J. M., Hemminger, J. C. & Finlayson-Pitts, B. J. (1994) Geophys. Res. Lett., 21, 1623-1626.

Lewis, R. S., Sander, S. P., Wagner, S. & Watson, R. T. (1980) "Temperature-Dependent Rate Constants for the Reaction of Ground State Chlorine with Simple Alkanes", J. Phys. Chem. 84, 2009-2015.

Lowenthal, D. H., Borys, R. D., Rogers, C. F., Chow, J. C., Stevens, R. K., Pinto, J. P. & Ondov, J. M. (1993) "A Fine Particle Sodium Tracer for Long-Range Transport of the Kuwaiti Oil-Fire Smoke", Geophys. Res. Lett., 20, 691-693.

Molina, M. J. (1992) "The Probable Role of Stratospheric 'Ice' Clouds: Heterogenous Chemistry of the 'Ozone Hole'", in CHEMRAWN VII:

Chemistry of the Atmosphere: The Impact of Global Change, J. G. Calvert, Ed., Blackwell Sci. Publ., Oxford, U. K., in press.

Mouri, H. & Okada, K. (1993) "Shattering and Modification of Sea-Salt Particles in the Marine Atmosphere", Geophys. Res. Lett., 20, 49-52.

Ramanathan, V. (1988) "The Greenhouse Theory of Climate Change: A Test by an Inadvertent Global Experiment", Science 240 293-299.

Riemer, D.D., Milne, P. J., Zika, R. G. & Brand, L. E. (1994) "Observations of Marine Isoprene Production", 207th National Meeting of the American Chemical Society, San Diego, CA, March 13-18 (1994), Division of Environmental Chemistry, 34, 715.

Vogt, R. & Finlayson-Pitts, B. J. (1994a) "A Diffuse Reflectance Infrared Fourier Transform Spectroscopic (DRIFTS) Study of the Surface Reaction of NaCl with Gaseous NO_2 and HNO_3", J. Phys. Chem., 98, 3747-3755.

Vogt, R. & Finlayson-Pitts, B. J. (1994b) "Tropospheric HONO and Reactions of Oxides of Nitrogen with NaCl", Geophys. Res. Lett., 21, 2291-2294.

Wallington. T. J., Skewes, L. M., Siegl, W. O., Wu, C.-H. & Japar, S. M. (1988) "Gas Phase Reaction of Cl Atoms with a Series of Oxygenated Organic Species at 295K", Int. J. Chem. Kinet., 20, 867-875.

Woods, D. C., Chuan, R. L. & Rose, W. I. (1985) "Halite Particles Injected into the Stratosphere by the 1982 El Chichon Eruption", Science 230, 170-172.

APPENDIX

Reprints of Papers Published in *Geophys. Res. Lett.*