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FINAL REPORT

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

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APPENDIX. Reprints/ preprints of the publications listed in Section V from this research are attached.

I. BACKGROUND

Both the chemistry and radiation balance of the troposphere are largely determined by ozone. 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,

or alternatively, with organics, and in the presence of NO_x , generate O_3 :

Reactions of alkali halides in sea salt particles are a potential source of atomic chlorine, as well as to a lesser extent, bromine (Finlayson-Pitts, 1993). Salt particles have been observed many hundreds of kilometers inland (Shaw, 1991). They have also 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). There are clear indications that chlorine chemistry, and to a greater (and somewhat surprising) extent bromine chemistry, goes on at high latitudes at polar sunrise (Jobson et al., 1994). 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 was significant uncertainty in the absolute rate constants for the reactions of chlorine atoms even with the simple alkanes and alkenes, and

no data were available for the reactions with biogenics, even though there is evidence that they are produced by processes in the oceans (e.g. Bonsang et al., 1992; Moore et al., 1994). 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.

In addition, measurements of CH_3Cl in the marine boundary layer and in seawater over the Labrador Sea by Professor Robert Moore of Dalhousie University in Halifax, Canada, suggested that there must be some reaction actually producing this compound in air. One possibility is the Cl-DMS reaction, where the fate of the adduct, which accounts for ~50% of the reaction at one atm. in air, is unknown. However, no measurements of CH_3Cl in this reaction have been reported.

II. OVERALL GOALS

The overall goals of this research were as follows:

- To identify "heterogeneous" reactions of sea salt particles which produce photochemically active halogen compounds, and to measure the kinetics of these reactions, including the effects of water vapor;
- To elucidate the kinetics and mechanisms of the gas phase reactions of the atomic halogens produced on photolysis of the photochemically active products of the sea salt reactions.
- To collaborate with scientists from Battelle, Columbus and PNNL in Richland, Washington (who are also in the DOE Atmospheric Chemistry Program) in exploring the atmospheric implications of our studies through field and modeling work.

III. RESULTS

Results in each area are highlighted in the following section and described in detail in the papers listed in Section V below and included in the Appendix. The number of the paper (see Section V) is used as the reference in the following summary.

A. HETEROGENEOUS REACTIONS OF SEA SALT AND ITS COMPONENTS

The results of our studies of heterogeneous reactions of sea salt and its components with oxides of nitrogen and ozone can be summarized as follows:

- The reactions of NO_2 and N_2O_5 with NaCl and NaBr were shown to give nitrate, not nitrite as proposed by other research groups (Junkermann et al., 1994). Hence these reactions will not serve as a source of gas phase HONO as proposed (paper #1).

- The photochemistry of nitrate formed on the surface of NaCl by reaction with NO_2 or HNO_3 was shown to be different from bulk crystalline NaNO_3 . Thus, the nitrate disappears upon photolysis but nitrite is not formed, as happens in the NaNO_3 photolysis. It appears that the surface nitrate may photolyze to $\text{NO}_2 + \text{O}^\cdot$, rather than $\text{NO}_2^\cdot + \text{O}$. This may help to regenerate active forms of NO_x from HNO_3 in the atmosphere (paper #2).
- The kinetics of reaction of NO_2 with NaBr were studied using diffuse reflectance infrared spectroscopy (DRIFTS), and shown to be similar to the NaCl reaction (paper #3). In addition, transmission electron microscopy studies carried out in a collaborative effort by Professor Hemmingers group confirmed earlier indications from DRIFTS studies that the surface nitrate could be crystallized into NaNO_3 by exposure to water vapor (paper #3). This explains why small sea salt particles are sometimes observed to be almost devoid of chlorine; these are likely NaNO_3 crystallites formed by this recrystallization of surface nitrate, followed by shattering off to form a small separate crystal.
- A new free radical intermediate, $\text{ClNO}_2^\cdot$, was identified in the NO_2 -NaCl reaction using EPR. This may be the central intermediate in the NO_2 reactions and is an interesting example of a particle-bound free radical particle, an area of great current interest in terms of the new particle standards (see paper #4).
- The reaction of HNO_3 with NaCl was shown in Knudsen cell studies to be controlled by small amounts of water bound to the salt surface (paper #7).
- Studies of synthetic sea salt showed that there was much more water on this surface, which also controlled the reactivity (paper # 15). This suggests that at least in terms of HNO_3 uptake and reaction, the behaviour of sea salt particles above and below the deliquescence point may be much more similar than anticipated. This may also prove to be the case for other reactive gases such as ClONO_2 , which are currently being studied.
- DRIFTS studies showed that the small amounts of crystalline hydrates in the mixture of salts in sea salt control the reactivity (paper #8). This suggests that while NaCl is the major component, using it as a model compound should be done with caution.
- Studies using our new aerosol chamber show that Cl_2 is generated from the reaction of O_3 with wet sea salt particles in the presence of UV light (paper # 16). This could provide a continuous, daytime source of chlorine atoms in the marine boundary layer (paper # 16).
- Other reactions and sources of atmospheric oxides of nitrogen were studied. These included the possible formation of N_2O from the $\text{O}(^1\text{D})$ reaction with CO_2 in the presence of NO. This was shown not to occur at a significant rate (paper #14).
- A review of tropospheric chemistry, including halogen chemistry, was carried out for an invited article in *Science* (paper #11).

B. KINETICS AND MECHANISMS OF REACTION OF ATOMIC CHLORINE

- It had been suggested that the reaction of atomic chlorine with dimethyl sulfide in the marine boundary layer could be a source of CH_3Cl . We measured the yields of methyl chloride from this reaction and find they are too small to be significant (paper # 5).
- The kinetics and mechanism of reaction of chlorine atoms with isoprene have been studied. The reaction is very fast (paper #9) and in the absence of NO_x , generates unique chlorine-containing products which may prove useful as "markers" of chlorine atom chemistry in the marine boundary layer (paper # 12). In conjunction with these studies, data analysis techniques were examined and Monte Carlo studies carried out to assess the best methodologies to use (paper # 10).
- The kinetics of reaction of chlorine atoms with simple alkenes were studied using both relative rate and fast flow discharge techniques. The results, where comparable, were in excellent agreement and studies of the reactions of the deuterated compounds elucidated the reaction mechanisms, particularly the fraction of these reactions proceeding by abstraction rather than addition (papers #13 and 18).
- The kinetics of reaction of chlorine atoms with a series of biogenics were studied. A paper is under preparation and will be submitted within a few months.

D. COLLABORATION WITH BATTELLE COLUMBUS AND PNNL SCIENTISTS

A very beneficial part of this grant was the opportunity to interact and collaborate with other scientists in the DOE Atmospheric Chemistry Program, as well as from other institutions. These interactions with other scientists in ACP included studying the reaction products from the isoprene-chlorine atom reaction using atmospheric pressure ionization mass spectrometry (API-MS) (paper # 12) and the first specific identification and measurement of tropospheric Cl_2 (paper # 17). In the latter case, the PI worked with the PNNL scientists on the chemical aspects of the model and with the Battelle Columbus scientists to see which of the expected chlorine-containing gaseous products of the sea salt reaction could be detected by API-MS. We synthesized a variety of chlorine-containing products such as ClNO , ClNO_2 and ClONO_2 and provided them to Dr. Chet Spicer to test. Unfortunately, none of these particular compounds had a parent peak using API-MS, so the field studies focussed only on Cl_2 .

IV. STUDENTS, POSTDOCTORAL FELLOWS AND COLLABORATORS

A number of undergraduate and graduate students, and postdoctoral fellows participated in this research. In addition, there were a number of collaborative efforts involving scientists both from UCI and from other institutions. A summary follows:

A. STUDENTS

Undergraduates: Lisa Wingen, Jason Lee, Christopher Elliott, Christy Keoshian, Brandon Buehler and Alisa Ezell

Graduate Students: Mark Ragains, Lisa Wingen, Brian McGovney, Weihong Wang, Matthew Lakin, Michael Gebel, Dinh Quach

B. POSTDOCTORAL FELLOWS

Rainer Vogt, Peter Beichert, Ruaidhri Neavyn, Sarka Langer, Sean Pemberton, Trent Nordmeyer, Jochen Stutz, Kawon Oum, David DeHaan, Bill Barney, Tracy Caldwell

C. COLLABORATORS

From UCI: John C. Hemminger and James N. Pitts, Jr.

From Other Institutions: Jeffrey Wan (Queen's University, Canada), Robert Moore (Dalhousie University, Canada), Theo Brauers (KFA Juelich), Jand Ganske (Pepperdine University), Chet Spicer and Robert Plastridge (Battelle Columbus), Carl Berkowitz, Elaine Chapman, Jerome Fast and John Hubbe (PNNL).

V. PUBLICATIONS FROM THIS RESEARCH

1. "Tropospheric HONO and Reactions of Oxides of Nitrogen with NaCl", R. Vogt and B. J. Finlayson-Pitts, Geophys. Res. Lett. **21** 2291 (1994).
2. "Rate Constants for the Reactions of Chlorine Atoms with Some Simple Alkanes at 298 K: Measurement of a Self-Consistent Set Using Both Absolute and Relative Rate Methods", P. Beichert, L. Wingen, J. Lee, R. Vogt, M. J. Ezell, M. Ragains, R. Neavyn and B. J. Finlayson-Pitts, J. Phys. Chem., **99**, 13156 (1995).
3. "Unique Photochemistry of Surface Nitrate", R. Vogt and B. J. Finlayson-Pitts, J. Phys. Chem. **99**, 17269 (1995).
4. "Some New Laboratory Approaches to Studying Tropospheric Heterogeneous Reactions", R. Vogt, C. Elliott, H. C. Allen, J. M. Laux, J. C. Hemminger and B. J. Finlayson-Pitts, Atmos. Environ., **30** 1729 (1996).
5. "The Formation of Free Radical Intermediates in the Reactions of Gaseous NO₂ with Solid NaCl and NaBr -Atmospheric and Toxicological Implications", J. K. S. Wan, J. N. Pitts Jr., P. Beichert and B. J. Finlayson-Pitts, Atmos. Environ., **30** 3109 (1996).

6. "The Dimethyl Sulfide Reaction with Atomic Chlorine and Its Implications for the Budget of Methyl Chloride", S. Langer, B. T. McGovney, B. J. Finlayson-Pitts and R. E. Moore, Geophys. Res. Lett., **23**, 1661 (1996).
7. "Knudsen Cell Studies of the Uptake of Gaseous HNO_3 and Other Oxides of Nitrogen on Solid NaCl: The Role of Surface-Adsorbed Water", P. Beichert and B. J. Finlayson-Pitts, J. Phys. Chem., **100**, 15218 (1996).
8. "Diffuse Reflectance Infrared (DRIFTS) Studies of the Reaction of Synthetic Sea Salt Mixtures with NO_2 : A Key Role for Hydrates in the Kinetics and Mechanism", S. Langer, R.S. Pemberton, and B.J. Finlayson-Pitts, J. Phys. Chem. A, **101**, 1277 (1997).
9. "Kinetics and Mechanism of the Reaction of Cl Atoms with 2-Methyl-1,3-butadiene (Isoprene) at 298 K", M.L. Ragains and B.J. Finlayson-Pitts, J. Phys. Chem., **101**, 1509 (1997).
10. "Analysis of Relative Rate Measurements", T. Brauers and B.J. Finlayson-Pitts, Int. J. Chem. Kinetics, **29**, 665 (1997).
11. "Tropospheric Air Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons, and Particles", B. J. Finlayson-Pitts and J. N. Pitts, Jr., Science **276**, 1045 (1997).
12. "Unique Products of the Reaction of Isoprene with Atomic Chlorine: Potential Markers of Chlorine Atom Chemistry", T. Nordmeyer, W. Wang, M. L. Ragains, B. J. Finlayson-Pitts, C. W. Spicer and R. A. Plastringe, Geophys. Res. Lett. **24**, 1615 (1997).
13. "Inverse Kinetic Isotope Effect in the Reaction of Atomic Chlorine with C_2H_4 and C_2D_4 ", J. Stutz, M. J. Ezell and B. J. Finlayson-Pitts, J. Phys. Chem. A, **101**, 9187 (1997).
14. "An Upper Limit on the Production of N_2O from the Reaction of $\text{O}(^1\text{D})$ with CO_2 in the Presence of N_2 ", L. M. Wingen and B. J. Finlayson-Pitts, Geophys. Res. Lett. **25**, 517 (1998).
15. "Knudsen Cell Studies of the Reaction of Gaseous Nitric Acid with Synthetic Sea Salt at 298 K", D. O. De Haan and B. J. Finlayson-Pitts, J. Phys. Chem. A, **101**, 9993 (1997).
16. "Formation of Molecular Chlorine from the Photolysis of Ozone and Aqueous Sea-Salt Particles", K. W. Oum, M. J. Lakin, D. O. De Haan, T. Brauers and B. J. Finlayson-Pitts, Science **279**, 74 (1998).
17. "Observations of Molecular Chlorine in Coastal Air", C. W. Spicer, E. G. Chapman, B. J. Finlayson-Pitts, R. A. Plastringe, J. M. Hubbe, J. M. Fast and C. M. Berkowitz, Nature in press (1998).

18. "Rate Constants and Kinetic Isotope Effects in the Reactions of Atomic Chlorine with *n*-Butane and Simple Alkenes at Room Temperature", J. Stutz, M. J. Ezell, A. A. Ezell and B. J. Finlayson-Pitts, J. Phys. Chem. in press (1998).

VI. REFERENCES

- 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.
- Fenter, F. F., Caloz, F., & Rossi, M. J. (1994) "Kinetics of Nitric Acid Uptake by Salt", J. Phys. Chem. **98**, 9801-9810.
- Fenter, F. F., Calos, F., & Rossi, M. J. (1996) "Heterogeneous Kinetics of N_2O_5 Uptake on Salt, with a Systematic Study of the Role of Surface Presentation (for N_2O_5 and HNO_3)", J. Phys. Chem. **100**, 1008-1019.
- Finlayson-Pitts, B. J. & Pitts, J. N. Jr. (1986) Atmospheric Chemistry: Fundamentals and Experimental Techniques. New York: Wiley (and references therein).
- Jobson, B. T., Niki, H., Yokouchi, Y., Bottenheim, J., Hopper, F., Leaitch, R. (1994). "Measurements of C2-C6 Hydrocarbons During the Polar Sunrise 1992 Experiment: Evidence for Cl Atom and Br Atom Chemistry", J. Geophys. Res., **25**, 355-25,368.
- Leu, M.-T., Timonen, R. S., & Keyser, L. F. (1995) "Heterogeneous Reactions of $\text{HNO}_3(\text{g}) + \text{NaCl}(\text{s}) \rightarrow \text{HCl}(\text{g}) + \text{NaNO}_3(\text{s})$ and $\text{N}_2\text{C}_5(\text{g}) + \text{NaCl}(\text{s}) \rightarrow \text{ClNO}_2(\text{g}) + \text{NaNO}_3(\text{s})$ ", J. Phys. Chem. **99**, 13203-13212.
- 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.
- Moore, R. M., Oram, D.E. & Penkett, S. A. (1994) "Production of Isoprene by Marine Phytoplankton Cultures", Geophys. Res. Lett., **21**, 2507-2510.
- Ramanathan, V. (1988) "The Greenhouse Theory of Climate Change: A Test by an Inadvertent Global Experiment", Science **240**, 293-299.
- Shaw, G. (1991) "Aerosol Chemical Components in Alaska Air Masses. 2. Sea Salt and Marine Products", J. Geophys. Res. **96**, 22,369-22,372.
- 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.