"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,

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]  
(1)

or alternatively, with organics, and in the presence of NO\textsubscript{x}, generate O\textsubscript{3}:

\[ \text{Cl} + \text{RH} \rightarrow \text{HCl} + \text{R} \]  
(2)

\[ \text{R} + \text{O}_2 \rightarrow \text{RO}_2 \]  
(3)

\[ \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \]  
(4)

\[ \text{NO}_2 + \text{h} \nu \rightarrow \text{NO} + \text{O}^3\text{P} \]  
(5)

\[ \text{O}^3\text{P} + \text{O}_2 \rightarrow \text{O}_3 \]  
(6)

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$_3$Cl 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$_3$Cl 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$_2$O$_5$ 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 NO₂ or HNO₃ was shown to be different from bulk crystalline NaN0₃. Thus, the nitrate disappears upon photolysis but nitrite is not formed, as happens in the NaN0₃ photolysis. It appears that the surface nitrate may photolyze to NO₂⁺ + O⁻, rather than NO₂⁻ + O. This may help to regenerate active forms of NOₓ from HNO₃ in the atmosphere (paper #2).

• The kinetics of reaction of NO₂ 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 NaN0₃ 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 NaN0₃ crystallites formed by this recrystallization of surface nitrate, followed by shattering off to form a small separate crystal.

• A new free radical intermediate, ClNO₂⁻, was identified in the NO₂-NaCl reaction using EPR. This may be the central intermediate in the NO₂ 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 HNO₃ 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 HNO₃ 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 ClONO₂, 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 Cl₂ is generated from the reaction of O₃ 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 N₂O from the O(¹D) reaction with CO₂ 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$_3$Cl. 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


VI. REFERENCES


Leu, M.-T., Timonen, R. S., & Keyser, L. F. (1995) "Heterogeneous Reactions of HNO_3(g) + NaCl(s) → HCl(g) + NaNO_3(s) and N_2C_5(g) + NaCl(s) → ClNO_2(g) + NaNO_3(s)", J. Phys. Chem., 99, 13203-13212.


