Title

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Journal

Geophysical Research Letters, 21(15)

ISSN

00948276

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Publication Date

1994-07-15

DOI

10.1029/94GL01196

Peer reviewed

GEOPHYSICAL RESEARCH LETTERS, VOL. 21, NO. 15, PAGES 1623-1626, JULY 15, 1994

X-ray photoelectron spectroscopic studies of the heterogenous reaction of gaseous nitric acid with sodium chloride: Kinetics and contribution to the chemistry of the marine troposphere

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Abstract. We report here the first measurement of the reaction probability (ϕ) at 298 K for the reaction (1) $HNO_{3(g)}$ + $NaCl_{(s)}$ ---> $HCl_{(g)}$ + $NaNO_{3(s)}$, ϕ = (4 ± 2) x 10^{-4}, which was determined using X-ray photoelectron spectroscopy to follow the formation of nitrate on the surface of single crystals of NaCl. Along with recent kinetic data for the reaction $N_2O_{5(g)}$ + $NaCl_{(s)}$ ---> $ClNO_{2(g)}$ + $NaNO_{3(s)}$, we show that in the dark with typical relative concentrations of N_2O_5 and HNO_3, the N_2O_5 reaction should be competitive with, and may exceed, that of HNO_3. The reactions of NO_2 and $ClONO_2$ with NaCl are expected to be much less important. Thus, the tropospheric production of chlorine atoms via photolysis of $ClNO_2$ from the N_2O_5 reaction is anticipated, which has the potential to impact the ozone balance in the troposphere.

Introduction

Sea salt particles generated by wave action in the marine troposphere [Woodcock, 1953; Blanchard, 1985] should have a chemical composition reflecting the solids in sea water, primarily NaCl with smaller amounts of other species such as bromide [Kester et al., 1967]. However, the ratio of chlorine to sodium is often less than that in sea water [Junge, 1956; Martens et al., 1973; Cicerone, 1981; Prospero et al., 1983; Keene et al., 1990] and appears in some cases to be related to the presence of oxides of nitrogen [Martens et al., 1973], which is consistent with finding excess nitrate in the particles. While nitrate may not account for all of the "missing chlorine" [Keene et al., 1990, 1993a; Chameides and Stelson, 1992, 1993], it represents a significant fraction.

Based on the work of Cadle and coworkers [Robbins et al., 1959; Cadle & Robbins, 1960], it has often been assumed that the reaction responsible for the chloride deficit and excess nitrate is that of gaseous nitric acid with sodium chloride:

$$HNO_{3(g)} + NaCl_{(s)} \text{--->} HCl_{(g)} + NaNO_{3(s)} \qquad (1)$$

Subsequently, it was shown that other nitrogen oxides such as NO_2, N_2O_5 and $ClONO_2$ also react with NaCl [Schroeder and Urone, 1974; Chung et al., 1978; Finlayson-Pitts, 1983; Finlayson-Pitts et al., 1989; Behnke et al., 1991; Zetzsch and Behnke, 1992; Finlayson-Pitts, 1993]:

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

$$N_2O_{5(g)} + NaCl_{(s)} \text{--->} ClNO_{2(g)} + NaNO_{3(s)} \qquad (3)$$

$$ClONO_{2(g)} + NaCl_{(s)} \text{--->} Cl_{2(g)} + NaNO_{3(s)} \qquad (4)$$

In contrast to reaction (1), reactions (2)-(4) produce photochemically reactive products, which photolyze in the troposphere to atomic chlorine. While ClNO and $ClNO_2$ have not been detected in the troposphere, there is some evidence for Cl_2 [Keene et al., 1993b; Pszenny et al., 1993; Spicer, 1992].

Chlorine atoms may play a role in the formation and fate of tropospheric ozone, since they react directly with O_3. Alternatively, atomic chlorine can abstract hydrogen from alkanes even faster than OH, leading to the formation of O_3 in the presence of NO_x [Finlayson-Pitts and Pitts, 1986].

Key to the evaluation of the relative importance of reactions (1)-(4) and the potential production of chlorine atoms are their gas-solid reaction probabilities, (ϕ), defined as the fraction of gas-solid collisions leading to reaction. Reaction (2) has been shown to be second order in NO_2 for the reaction with dry NaCl, and assuming that N_2O_4 is the reactant, ϕ for the N_2O_4-NaCl reaction of (6 ± 2) x 10^{-5} was obtained [Vogt and Finlayson-Pitts, 1994]. For dry solid NaCl, a lower limit to ϕ for the reaction (3) of N_2O_5 was established to be >2.5x10^{-3} by directly measuring the $ClNO_2$ product [Livingston and Finlayson-Pitts, 1991]. Using a less direct approach, Zetzsch and coworkers reported that the sticking coefficient for N_2O_5 on particles of NaCl at relative humidities from 71-92% was ~0.03, with approximately 30% of the N_2O_5 uptake leading to $ClNO_2$ formation even at the highest relative humidities [Behnke et al., 1991; Zetzsch and Behnke, 1992]. For reaction (4) of $ClONO_2$, ϕ has been measured to be 5 x 10^{-3} at 298 K and 225 K (Timonen et al., 1994).

However, to date no kinetic data for reaction (1) have been reported. Knowledge of ϕ for this reaction is critical, since if this reaction is very fast, it may overwhelm the contributions of reactions (2)-(4) and lessen the likelihood of chlorine atom production, at least via these mechanisms.

We report here X-ray photoelectron spectroscopic studies of the kinetics of reaction of gaseous HNO_3 with solid NaCl at 298 K. We show that the nitric acid reaction is sufficiently slow that the generation of $ClNO_2$ via reaction (3) at night will be at least comparable to, and likely faster than, the production of HCl in reaction (1).

Paper number 94GL01196
0094-8534/94/94GL-01196$03.00

Experimental

Reaction (1) was followed by using X-ray photoelectron spectroscopy (XPS) to quantify the surface Cl^- and NO_3^- as a function of exposure of the NaCl to gaseous HNO_3. An ESCALAB MKII photoelectron spectrometer (VG Scientific) was used in these experiments. The ESCALAB MKII is a multi-technique surface analysis instrument based on an ultra-high vacuum (UHV) system which consists of three separately pumped interconnected chambers (spectroscopy , sample preparation , and fast sample entry chambers). The XPS experiments were carried out in the spectroscopy chamber, which is equipped with a standard Mg/Al twin anode X-ray source and a 150 mm radius hemispherical electron energy analyzer. Al K_α X-rays (1486.6 eV) and an analyzer pass energy of 20 eV were utilized for all experiments.

Freshly cleaved square NaCl single crystals [(100) orientation] of 5.0 mm edge length and approximately 1.0 mm thickness were clamped to a heatable copper sample holder. This holder was equipped with a thermocouple for monitoring the sample temperature. The samples were heated to 473 K to remove any physisorbed water and other impurities. XPS spectra of the samples treated in this manner showed no oxygen or other impurities.

Nitric acid exposures were carried out in the sample preparation chamber of the instrument to avoid contamination of the spectroscopy chamber with HNO_3. An all glass capillary doser mounted on the preparation chamber, as shown in Figure 1, allowed high doses of HNO_3 at the sample in a quantifiable manner without increasing the preparation chamber pressure substantially. The doser consists of a dry HNO_3 source (vapor above a HNO_3/H_2SO_4 50:50 v/v solution) attached via a capillary tube (conductance = 2 x 10^{-6} liter sec^{-1}) to the UHV system. Under our conditions of UHV, any small amounts of water possibly present in the HNO_3 do not adsorb to the salt surface. The glass doser system was passivated by exposure to HNO_3 prior to these experiments, and a capacitance manometer (Baratron) was used to measure the driving HNO_3 pressure. During dosing, the sample sat in the chamber ~1mm in front of the capillary exit. Knowledge of the capillary conductance and driving HNO_3 pressure allowed calculation of the number of nitric acid molecules incident on the sample each second. Complete sets of experiments were carried out at HNO_3 pressures of 7 and 10 Torr with identical results.

After each HNO_3 dose, XPS peak areas for N, Cl, O and Na were measured after standard Shirley-type background substraction. Standard XPS sensitivity factors for N, O and Cl (0.489, 0.721, 0.925 respectively, relative to the F sensitivity factor of 1.00) were used to quantify the surface concentrations of these elements [Wagner, et. al., 1981]. The XPS sensitivity factor for Na is not well established in the literature [Wagner, et.al., 1981; Castle and West, 1980], so we used a relative sensitivity factor of 3.8, developed for our instrument, which gives a Na:Cl ratio of 1:1 for freshly cleaved, clean NaCl.

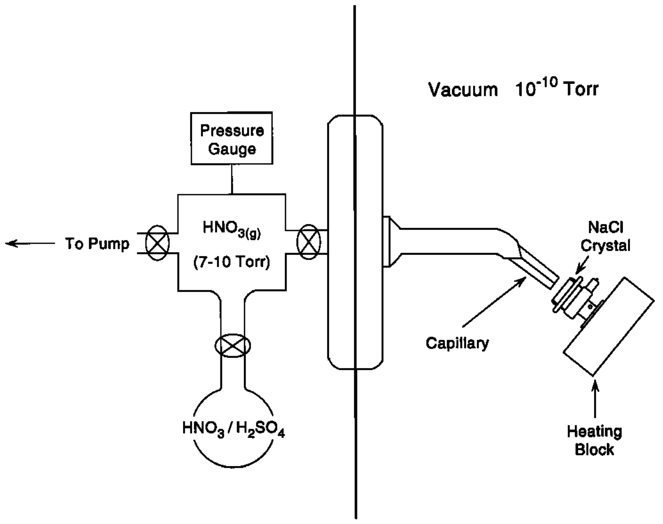

Figure 1. Schematic of glass capillary doser apparatus.

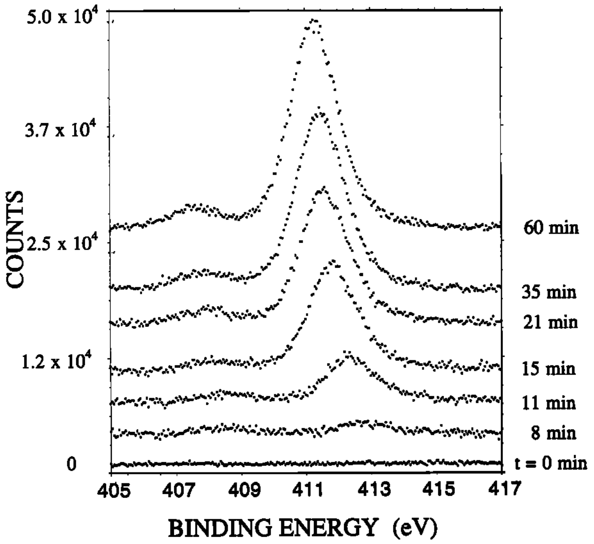

Figure 2. X-ray photoelectron spectra of the nitrogen region (N 1S) following various exposures of a single crystal of NaCl (100) to HNO_3. The binding energy scale has not been corrected for charging effects as described in the text.

Results

The XPS spectra in Figure 2 show the increase in the N 1S photoelectron peak following cumulative exposure times to HNO_3. The binding energy scale has not been corrected for the small amount of sample charging which occurs as a result of exposure of the insulating NaCl sample to X-rays. The amount of sample charging can be quantified by comparison to the Na 1S binding energy. The charging-corrected binding energy of the N 1S peak is 407.2 eV, indicative of a nitrate species on the surface [Moulder, et. al., 1992]. The small feature seen at lower binding energy at longer exposure times is due to NO_2^-, which we have shown in separate experiments is due to X-ray photolysis of NO_3^- as observed in other studies (Johnson, 1970). Our experiments were carried out with minimal X-ray exposure to avoid significant conversion of NO_3^- to NO_2^-.

Figure 3 shows the time dependence of the N, O and Cl peaks obtained from spectra similar to those in Figure 2. The nitrate concentration (N and O) increases steadily with exposure to saturation values, while the Cl concentration at the surface of the sample decreases. Note that the O:N ratio is 3:1 as expected for a surface nitrate species (the decrease in Cl cannot be easily correlated to the increase in N and O since the beam interrogates more than the surface layer and probes at different depths for each element). Since the exposure time is proportional to the total number of gas-solid collisions, the instantaneous reaction probability (reactive sticking coefficient) is directly related to the slope of the uptake curve.

An average sticking coefficient, ϕ, can be obtained by

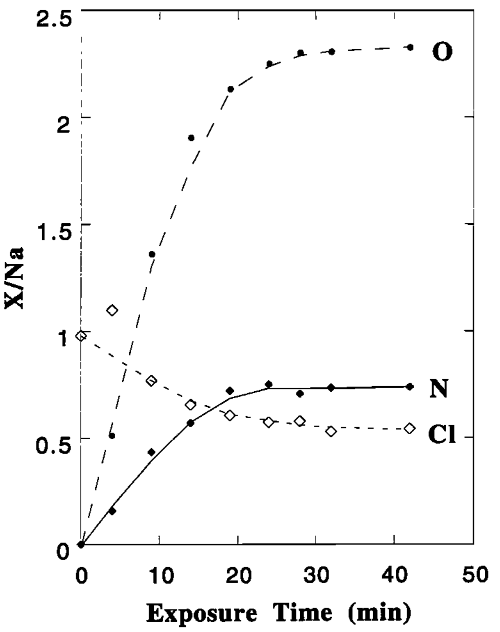

Figure 3. Uptake curves for O(1S), N(1S), and Cl(2P) as a function of time of exposure of HNO_3 to NaCl(100). The data are plotted as ratios of element peak area to the Na (1S) peak area corrected using sensitivity factors as described in the text (The sensitivity factors used were: O, 0.721; N, 0.489; Cl, 0.925).

dividing the number of nitrate species on the surface at saturation by the number of HNO_3 molecules incident on the sample required to reach saturation. We estimate the number of nitrate species on the surface at saturation by assuming that each nitrate replaces one chloride ion. The (100) face of NaCl has 6.4×10^{14} Cl atoms per cm^2 of surface area [Kittel, 1986]. The number of molecules incident on the sample surface, ΔN, can be calculated from the conductance of the doser capillary using Equation (I) [Chambers et al., 1989]:

$$\Delta N = (3.48x10^{13})[1+(3750)(L)/R]^{-1}\,(1/TM)^{1/2}\,PR^2\Delta t\, f \qquad (I)$$

R and L are the capillary radius and length in µm and cm respectively, P is the dosing pressure in Torr, T is the temperature in K, M is the dosing gas molecular weight in kg/mol, Δt is the dosing time for saturation in seconds, and f is the fraction of molecules from the doser that strike the sample surface, approximately 0.5 based upon the geometrical arrangement of the dosing system. In the calculation of ϕ, we assume that the saturation point for nitric acid exposure corresponds to replacement of one monolayer of Cl atoms with nitrate. This assumption is certainly good to 50%, and is reasonable based on the drop in the Cl signal. The resulting ϕ of reaction 1 is then calculated to be $(4 \pm 2) \times 10^{-4}$, where the uncertainty is dominated by our estimate of the possible systematic errors due to the assumptions inherent in this calculation.

Discussion

This is the first report of the reaction probability for the HNO_3-NaCl reaction at 298 K, which is found to be one to two orders of magnitude slower than the corresponding reaction of N_2O_5. This may be due to steric factors involved in the gas-solid interaction, and/or to the strength of the initial interaction between the gas and the NaCl. Solid N_2O_5 is believed to exist as $NO_3^-NO_2^+$ [Cotton and Wilkinson, 1972], which may also be the case for N_2O_5 as it initially adsorbs on the salt surface. The ionized structure may interact more strongly with the ionic NaCl, increasing the rate of the reaction.

As a first approximation, the rate of reaction (1) can be compared to those of reactions (2)-(4) via the rates of nitrate formation, given by equation (II):

$$d[NO_3^-] / dt = \phi C = \phi A[G](RT/2\pi M)^{0.5} \qquad (II)$$

A is the surface area of the solid and [G] the concentration of the gas with a molecular weight M. This approach assumes that diffusion of the gas to the surface is not rate-limiting, which may not be the case for very fast reactions. It also assumes that the reactivity of the single crystals of NaCl studied here is the same as that for small particles of NaCl in the troposphere. Given that sea salt particles collected in marine atmospheres are also highly crystalline upon drying and typically of the order of a few microns in diameter, the use of single crystals as a model should be appropriate for the reaction of dry sea salt particles, i.e.: at low relative humidity (RH). Further studies are needed to define ϕ for the concentrated solutions characteristic of high RH's.

In a moderately polluted urban atmosphere, typical peak concentrations of HNO_3 and NO_2 can be taken as 5 ppb and 100 ppb respectively [Finlayson-Pitts and Pitts, 1986]. The concentration of N_2O_4 in equilibrium with 100 ppb NO_2 at 298 K is calculated to be 0.069 ppt using the well known equilibrium constant for the NO_2/N_2O_4 equilibrium [Stull and Prophet, 1971]. While N_2O_5 has not been detected directly in the troposphere, those of the precursors NO_3 and NO_2 have been measured. From the equilibrium (5,-5)

$$NO_3 + NO_2 \text{<---->} N_2O_5 \qquad (5,-5)$$

and measured NO_3 and NO_2 concentrations, N_2O_5 has been calculated to be as high as 10-15 ppb [Atkinson et al., 1986], with 1 ppb being more typical. Under more remote conditions, the concentrations of the gaseous reactants will be much smaller, but the ratios of their concentrations may not be much different. Hence the same conclusions will apply.

At these concentrations of HNO_3 (5 ppb), N_2O_4 (0.069 ppt) and N_2O_5 (1 ppb), taking the rate of the HNO_3-NaCl reaction to be 1, the relative rates of nitrate formation were calculated from $\phi[G](M)^{-0.5}$ (eq. II) to be 2×10^{-6} for N_2O_4 and >1 for N_2O_5, taking the lower limit of 2.5×10^{-3} for the reaction probability for reaction (3). Based on the work of Zetzsch and coworkers [Behnke et al., 1991; Zetzsch & Behnke, 1992], the relative rate for the N_2O_5 reaction could be approximately an order of magnitude faster.

The concentration of $ClONO_2$ is not known; modeling studies suggest that global levels in marine atmospheres could be of the order of ~ 5 ppt (Singh and Kasting, 1988) which gives a relative rate of 1×10^{-2}, much smaller than the HNO_3 and N_2O_5 reactions.

Because NO_3 photolyzes rapidly at dawn [Finlayson-Pitts and Pitts, 1986], the equilibrium (5,-5) shifts, destroying N_2O_5. Thus the N_2O_5 reaction is a dark reaction, while HNO_3 can occur throughout the day. However, given the rapidity of the N_2O_5 nighttime reaction, it appears likely to be significant under many tropospheric conditions compared to the 24 hour HNO_3 reaction. While this conclusion applies to dry NaCl, the presence of significant amounts of water on the surface could alter the absolute and relative kinetics. Studies are planned to clarify this issue.

In short, while the NO_2/N_2O_4 and $ClONO_2$ reactions are unlikely to be important (unless enhanced by surface photochemistry and/or the presence of water), that of N_2O_5 is expected to at least be competitive with, and may exceed the HNO_3 reaction under moderately polluted conditions. The generation of $ClNO_2$ in the marine troposphere and its subsequent photolysis to produce atomic chlorine is thus potentially important in the oxidation of organics in these regions and in the formation and fate of tropospheric ozone.

Acknowledgments. We are grateful to the National Science Foundation (Grants No. ATM-9005321, ATM-9222769 and ATM-9302475) and the Department of Energy for support. We thank Dr J. N. Pitts Jr. for helpful discussions and comments on the manuscript, Dr. Jerry Tang for assistance with the XPS experiments, and Dr. Ming-Taun Leu for permission to cite unpublished work.

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(Received March 23, 1994; accepted May 6, 1994.)