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Tropospheric HONO and Reactions of Oxides of Nitrogen with NaCl

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Abstract. Although nitrous acid is important in both the polluted and remote troposphere, as well as indoors, its mechanisms of production from oxides of nitrogen are not well known. The reactions of N_2O_5 with NaCl and NaBr in sea salt particles in the presence of water have been hypothesized recently to act as sources of particulate nitrite and which forms gaseous HONO. We report here the results of studies of the reactions of N_2O_5, HONO and NO_2 with NaCl using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to follow the formation of products on the salt surface. The infrared bands arising from species formed on the salt surface can be attributed to nitrate ions associated with water molecules; the presence of NO_3^- was confirmed by chemical analysis of the reacted salts. No nitrite was detected either by DRIFTS or by chemical analysis. Thus the reactions of sea salt particles with N_2O_5 in the troposphere are not expected to be significant sources of particle nitrite nor of gaseous HONO via conversion of the particle nitrite.

Introduction

Nitrous acid (HONO) is increasingly being recognized as a key species in both outdoor and indoor air environments [Perner and Platt, 1979; Platt et al., 1980; Pitts et al., 1985, 1989; Vecera and Dasgupta, 1991; Spicer et al., 1993]. In the troposphere, it photolyzes rapidly to produce OH [Finlayson-Pitts and Pitts, 1986], and in fact may be the major source of this highly reactive free radical at dawn in polluted urban atmospheres [Winer, 1985; Finlayson-Pitts and Pitts, 1986].

However, despite its potential importance in tropospheric chemistry, its mechanisms of formation are not well characterized, either qualitatively or quantitatively. A significant source [Finlayson-Pitts and Pitts, 1986; Akimoto et al, 1987; Svensson et al, 1987; Jenkins et al, 1988; Lammel and Perner, 1988] is believed to be the heterogeneous hydrolysis of NO_2:

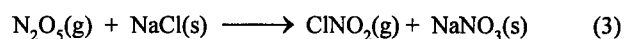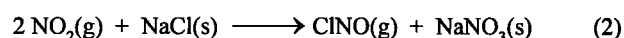$$2 NO_2 + H_2O \xrightarrow{\text{surface}} HONO + HNO_3 \qquad (1)$$
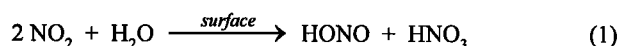
Based on the observed relationship between particle nitrite and sodium ions in the Arctic troposphere, Li [1993, 1994] suggested that sea salt might also be involved in the formation of nitrite. One possible mechanism proposed was the reaction of N_2O_5 with NaCl or NaBr, and subsequent hydrolysis of the nitryl halides.

Recently, Junkermann and Ibusuki [1992] used diffuse reflectance infrared Fourier transform spectroscopy to follow the infrared spectra of products formed on the surface of NaCl as it reacted with NO_2, N_2O_5 or HONO. They reported that, in the presence of water vapor, all three gave nitrite ions (NO_2^-) on the surface of the salt. They further suggested that gaseous HONO

could be ultimately formed from the particulate nitrite produced in the N_2O_5-NaCl reaction. The gas phase reaction products of a mixture of N_2O_5, O_3 and water vapor in air with NaCl were collected in a water-filled impinger for subsequent ion chromatographic analysis. In the absence of NaCl only 1% of the initial nitrogen could be recovered, most likely due to the loss of N_2O_5 to the 'wet' walls in the reaction chamber [Finlayson-Pitts and Pitts, 1986]. When NaCl was present, nitrite as well as chloride ions were observed in the impinger solution, corresponding to recovery of 2% to 3% of the total nitrogen.

However, in earlier studies [Finlayson-Pitts, 1983; Finlayson-Pitts et al., 1989; Vogt and Finlayson-Pitts, 1994], nitrate (NO_3^-) was observed using FTIR as a solid product of the reactions of dry NO_2 and N_2O_5 with NaCl, consistent with the identification of ClNO and $ClNO_2$ as the respective gas phase products:

$$2 NO_2(g) + NaCl(s) \longrightarrow ClNO(g) + NaNO_3(s) \qquad (2)$$

$$N_2O_5(g) + NaCl(s) \longrightarrow ClNO_2(g) + NaNO_3(s) \qquad (3)$$

This apparent conflict in the nature of the solid products formed in the reactions of NaCl with oxides of nitrogen could be resolved if the mechanism changed in the presence of water.

Because of the implications of such a change in mechanism on the tropospheric production of HONO, we have reexamined the solid products in reaction (3) using diffuse reflectance infrared spectroscopy combined with chemical analysis, and compare our observations to those from the HNO_3, NO_2 and HONO reactions. Nitrate is detected as the sole solid state product of all of these reactions, although its absorption bands are somewhat unusual compared to many literature spectra for NO_3^- due to the influence of the ion environment on the absorption spectra. There is no evidence for the formation of nitrite, ruling out the production and subsequent volatilization of particulate nitrite from the reaction of N_2O_5 and NaCl as a significant source of tropospheric HONO.

Experimental

The reactions of NaCl were studied in a diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) apparatus which has been described recently [Vogt and Finlayson-Pitts, 1994]. Briefly, the flow system consisted of a reaction chamber of ~20 cm^3 volume in which 250 mg of finely ground NaCl powder (Harshaw) was exposed to the nitrogen oxides and/or gaseous water. A slow flow of helium carrier gas (1.6-6.6 µmol s^{-1}) was pumped from the top of the salt surface through the pellet and out an opening at the bottom. The carrier gas pressure inside the chamber was typically 8 to 25 Torr. Reactive gases were added from bulbs of known volume to the carrier gas flow and gas concentrations were calculated from the measured pressure drop in the storage bulbs over time.

The reaction chamber was mounted in a Mattson RS Fourier Transform spectrometer equipped with a Harrick Scientific

diffuse reflectance attachment (Model DRA-2CS). Data from 64 scans (1 cm^{-1} resolution taken over 50 seconds) were averaged for each infrared spectrum.

Nitrogen dioxide was produced by the reaction of nitric oxide with excess oxygen and condensed at 195 K. Dinitrogen pentoxide was obtained by reaction of NO_2 with a twofold excess of 4% ozone in oxygen. It was trapped at 195 K, and the excess O_3/O_2 was pumped off. The bulbs and gas manifold used in these studies were conditioned by flushing several times with 10 Torr of N_2O_5. After this procedure, the IR spectra of the gaseous N_2O_5 measured in a 10 cm cell showed HNO_3 and NO_2 impurities which were estimated to be ≤20% and ≤10% of the N_2O_5 concentration, respectively. Nitrous acid was produced by slowly adding 10 ml 0.1 m $NaNO_2$ solution dropwise to 20 ml 0.5 m H_2SO_4 at 273 K [Sakamaki et al., 1983] and collecting the gases which evolved from this solution. The IR spectrum showed bands due to HONO, H_2O, NO_2 and NO, but not nitric acid.

Reacted pellets were analyzed chemically for nitrate and nitrite following the method of Greenberg et al. [1985]. The nitrate was reduced to nitrite on an activated Cd column and then converted to a highly colored azo dye by diazotization with sulfanilamide and coupling with N-(1-naphthyl)-ethylene-diamine. The absorbance of the dye was measured at 540 nm, giving a sensitivity of 2×10^{16} ions per 250 mg pellet. Nitrite was measured with the same sensitivity by omitting the reduction step.

Results and Discussion

Reaction of N_2O_5 with NaCl

Figure 1 shows a time series of spectra recorded at 298 K as an N_2O_5/He mixture passed through the NaCl. The surface is relatively dry, since the salt had been heated for 2 hours to 420 K in a helium carrier gas stream prior to reaction to drive off adsorbed water. As seen by comparison to the dotted curve in Figure 1, the position and appearance of the bands are identical to those observed in experiments where NaCl was reacted with HNO_3, or as we have shown earlier, with NO_2 [Vogt and Finlayson-Pitts, 1994]. These bands at 1462, 1380, 1333 (v_3), as
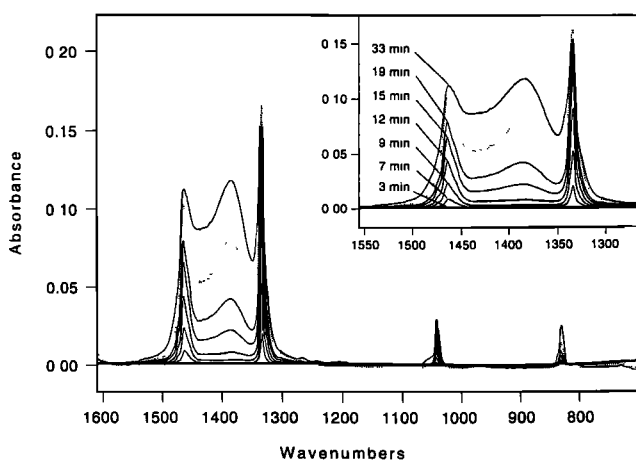
Figure 1. Diffuse reflectance infrared absorption spectra in the 1600-700 cm^{-1} region from the reaction of NaCl with N_2O_5 (5×10^{13} molecules cm^{-3}) over 33 min in the absence of water. For comparison, the dotted curve shows a spectrum recorded after 7 min from the reaction of HNO_3 (1.3×10^{14} molecules cm^{-3}) with NaCl.
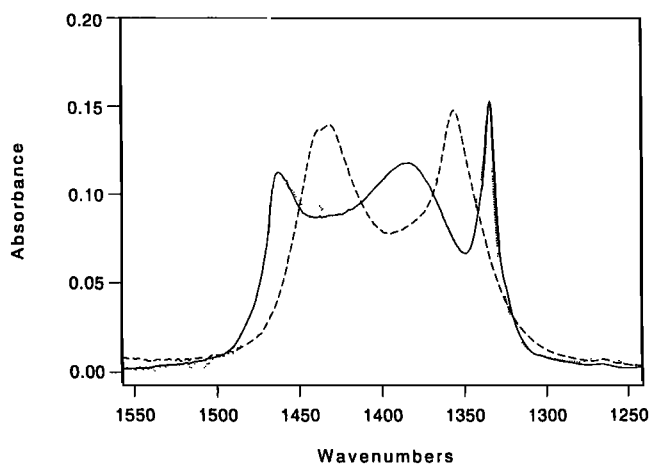
Figure 2. Absorption spectra from the reaction of NaCl with N_2O_5 (5×10^{13} molecules cm^{-3}, for 30 min) (solid curve), after subsequent addition of 5 Torr water vapor for 2 min (dashed curve), and after the gas phase and most of the adsorbed water had been pumped off for 60 min (dotted line). The weak band at 1265 cm^{-1} is attributed to an organic impurity commonly observed in this system [Vogt and Finlayson-Pitts, 1994].

well as 1042 (v_1) and 831 cm^{-1} (v_2) have been attributed to the fundamental vibrations of nitrate ions located in different surface environments of the sodium chloride lattice. No band attributable to NO_2^- at ~1270 cm^{-1} was detected.

Chemical analysis of the reacted pellets established that all of the N_2O_5 which had passed through the salt had been converted into NO_3^- ions. No NO_2^- was detected, from which an upper limit to its yield was estimated to be 5% of the nitrate formed in an experiment in which 40% of the surface chloride was reacted.

To study the influence of adsorbed water on the IR bands, an NaCl pellet which had been reacted with N_2O_5 was exposed to 5 Torr water vapor, equivalent to 21% relative humidity at 298 K. As seen in Figure 2, the DRIFTS spectrum in the v_3 region changed dramatically, with two strong absorption features at 1430 cm^{-1} and 1350 cm^{-1} (dashed curve) replacing the three bands at 1462, 1380 and 1333 cm^{-1} (solid curve). The exact position of the bands depended on the water vapor pressure. The bands at 1042 and 831 cm^{-1} became broader in the presence of water but did not shift in position.

The changes in the 1400 cm^{-1} region spectrum are reversible, as seen from the spectrum observed after pumping off the water (Figure 2, dotted curve). The bands at 1333 cm^{-1} and 1460 cm^{-1} are regenerated, although with slightly lower intensity while the broad band in the 1350-1450 cm^{-1} region increased slightly. This broad band is believed to be due to crystalline $NaNO_3$ which forms after mobilizing the isolated nitrate ions in a quasi-liquid layer on the NaCl surface, followed by recrystallization upon drying of the surface [Vogt and Finlayson-Pitts, 1994].

Clearly, the new bands at 1430 and 1350 cm^{-1} are due to nitrate ions reversibly associated with H_2O. At 21% relative humidity the salt surface has significant amounts of adsorbed water [Barraclough and Hall, 1974], so that strong hydrogen bonding between water molecules and the negatively charged nitrate is expected. This will split the degeneracy of the v_3 asymmetric stretch, leading to the two observed bands. It is noteworthy that these bands are similar to those from the reaction of N_2O_5 with ice, and also assigned to the two components of the v_3 mode [Horn et al., 1994].
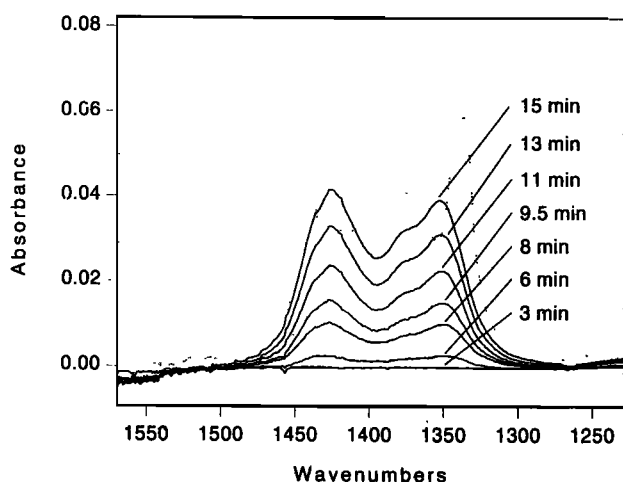
Figure 3. Absorption spectra measured over 15 min in the reaction of N$_2$O$_5$ ([N$_2$O$_5$]$_0$ $\cong$ 3.6x10^{13} molecules cm^{-3}) with NaCl having adsorbed water on the surface. (The actual N$_2$O$_5$ concentration was likely less than that cited because of the rapid surface hydrolysis of N$_2$O$_5$ [Finlayson-Pitts and Pitts, 1986]). Subsequent partial drying by purging with pure helium for 5 min led to the spectrum represented by the dotted curve.

The first DRIFTS studies of the reaction of N$_2$O$_5$ and NaCl [Junkermann and Ibusuki, 1992] were carried out in the presence of water, which could conceivably change the mechanism and products. This is important because under tropospheric conditions, significant concentrations of water will be present. To test this possibility, N$_2$O$_5$ was reacted with a salt pellet which had first been exposed to 2.5 Torr of water vapor in a helium carrier gas flow for 20 min. The absorbances of the bands due to adsorbed water centered at 3460 cm^{-1} and 1630 cm^{-1} were used to estimate the water partial pressure in the reaction chamber during the experiments.

Figure 3 shows the spectra obtained when salt with adsorbed water reacted with N$_2$O$_5$. The infrared bands at 1430 and 1350 (as well as 1050 and 832 cm^{-1} which are not shown here) are the same as those formed upon reaction in the absence of water, followed by exposure to water (see Figure 2). Subsequent partial drying using a flow of pure helium leads to a spectrum (dotted curve, Figure 3) identical to those observed in previous HNO$_3$ experiments [Vogt and Finlayson-Pitts, 1994].

After reaction, the pellet was dissolved in water and chemically analyzed for both nitrite and nitrate. No nitrite was detected, confirming our assignment of the absorption bands to NO$_3^-$.

In short, the reaction of N$_2$O$_5$ in either the presence or absence of water gives NO$_3^-$ on the salt surface, rather than NO$_2$. The formation of nitrate in the presence of water is slower due to the removal of N$_2$O$_5$ via its heterogeneous hydrolysis to HNO$_3$ on the reaction chamber walls and manifold. Indeed, in the presence of water it is unlikely that significant amounts of N$_2$O$_5$ survive, and HNO$_3$ is likely the actual reactant in this case.

Reaction of HONO with NaCl

In earlier studies, partial support for the assignment of the bands to nitrite rather than nitrate came from the observation that the reaction of HONO with NaCl [Junkermann and Ibusuki, 1992] gave similar IR absorption bands to those produced in the N$_2$O$_5$/H$_2$O/NaCl system. To reproduce these experiments, NaCl was reacted with the gases generated from an NaNO$_2$/H$_2$SO$_4$

mixture. The absorption bands observed are shown in Figure 4 and are indeed the same as those observed in reaction (3) in the presence of water.

The IR spectrum of the reactant gases which had evolved from this NaNO$_2$/H$_2$SO$_4$ mixture (5 Torr in a 10 cm cell) showed bands due to HONO, NO$_2$ and NO consistent with the equilibrium (4):

$$2 \text{ HONO} \longleftrightarrow H_2O + NO + NO_2 \tag{4}$$
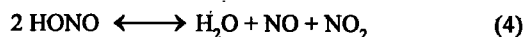
Based on the absorption coefficient of HONO given by Sakamaki et al. [1983] and absorption coefficients for NO and NO$_2$ determined in our laboratory, the concentrations of HONO, NO and NO$_2$ were estimated to be $\approx$ 1x10^{15} molecules cm^{-3} each. The remaining gas (and the major constituent) was water vapor. That significant concentrations of NO, NO$_2$ and H$_2$O coexist with the HONO is expected, based on the equilibrium constant for reaction (4) [Vecera and Dasgupta, 1991].

Given the significant concentrations of NO$_2$ present along with HONO, NO$_2$ could actually have been the reactant. The dashed curve in Figure 4 shows a typical spectrum from the reaction of NaCl with NO$_2$ in the presence of water vapor corresponding to a relative humidity of 15%. Clearly, this reaction shows the same absorption bands as those observed in the HONO experiment, indicating that the reacting species may, in fact, be NO$_2$ rather than HONO.

Subsequent drying of this reacted NaCl by passing dry He through the salt gave the dotted curve in Figure 4, identical to bands shown previously to be due to nitrate ions [Vogt and Finlayson-Pitts, 1994]. This was confirmed by chemical analysis of the reacted NaCl pellet, which showed that the measured nitrate concentration corresponded to 25% replacement of available surface chloride. No nitrite could be detected, indicating that the nitrite must have been smaller than 2% of the total available surface chloride.
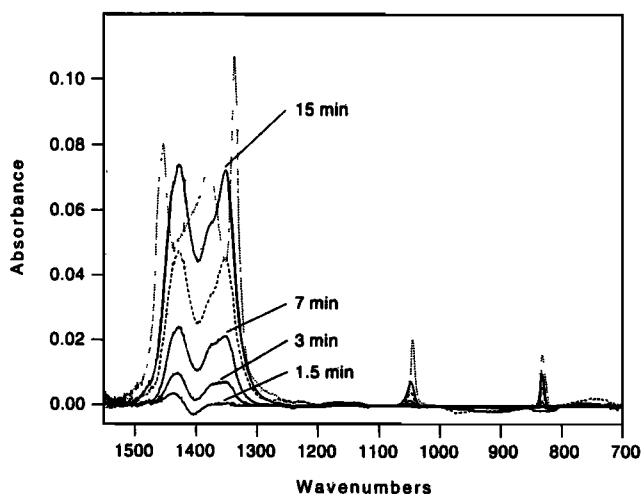

Figure 4. Absorption spectra from the reaction of NaCl with an HONO/NO$_2$/NO/H$_2$O gas mixture (solid lines). The partial pressure of H$_2$O was approximately 4 Torr, determined from the strength of the infrared bands due to water adsorbed on the NaCl. For comparison, a spectrum (dashed line) measured after 8 min from the reaction of NO$_2$ (1.5x10^{15} molecules cm^{-3}) with NaCl in the presence of 3.5 Torr H$_2$O vapor is also shown. After reaction, the adsorbed water was removed by purging with dry helium for 10 min and the spectrum represented by the dotted line was obtained.

Junkermann and Ibusuki [1992] observed low yields (~2-3%) of gas phase nitrite along with chloride ions in the N$_2$O$_5$-O$_3$-H$_2$O-NaCl system. Based on our studies, these nitrite and chloride ions were likely formed by hydrolysis of ClNO which had been formed through reaction (2) with NO$_2$ which is present along with the N$_2$O$_5$.

Conclusions

In summary, while the infrared absorption bands we observe on the salt surface during the reactions of either N$_2$O$_5$/H$_2$O or HONO/NO$_2$/NO/H$_2$O mixtures with NaCl are similar to those reported by Junkermann and Ibusuki [1992], they are clearly due to nitrate ions reversibly associated with water rather than to nitrite. There is no evidence for the formation of nitrite. Hence the reactions of NaCl with N$_2$O$_5$, or indeed with the other oxides of nitrogen we have studied, will not serve as sources of particle nitrite. Unless the nitrate formed on the salt surface photolyzes, it is not expected to be removed at a significant rate by other reactions in the troposphere. Studies are currently underway to investigate the possible role of photochemistry in the tropospheric fate of particle nitrate.

In short, these reactions of the components of sea salt aerosols are not expected to be sources of tropospheric HONO via the initial formation of particulate nitrite.

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