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Communication

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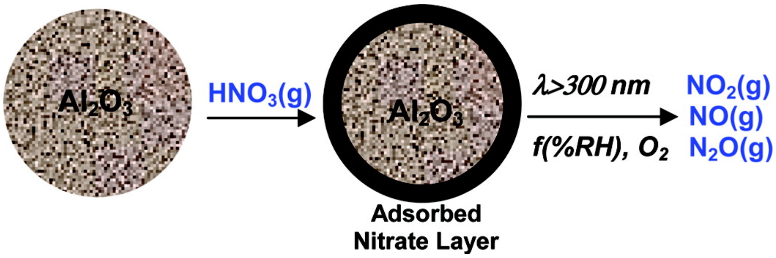

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Photochemistry of Adsorbed Nitrate

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Nitrate ion is an important chromophore in natural water systems.[1,2] In the atmosphere, gas-phase nitrogen oxides readily react with particulate matter (e.g., mineral dust) to yield adsorbed nitrate,[3] yet little is known about the photochemistry of nitrate on the surface of these particles. In this study, the photochemistry of adsorbed nitrate is explored. Because the molecular structure of adsorbed nitrate changes in the presence of coadsorbed water,[4] we have investigated the role of water in the photolysis of adsorbed nitrate. Additionally, the role of molecular oxygen on the gas-phase product distribution is investigated.

The photochemistry of adsorbed nitrate is monitored with transmission FTIR spectroscopy using an experimental apparatus previously described.[5,6] Both the loss of surface nitrate and the formation of surface and gas-phase products are followed. As discussed below, the results presented here show that adsorbed nitrate readily undergoes photochemical reaction to yield several gas-phase products and that coadsorbed water and molecular oxygen alter the product distribution. To the best of our knowledge, this is the first study to investigate (i) the role of solvation in the photochemistry of adsorbates at solid interfaces and (ii) the impact of molecular oxygen, adsorbed water, and relative humidity in photochemical processes on aerosol surfaces that have the potential to alter the chemical balance of the atmosphere.

Nitric acid-reacted alumina (γ-Al_2O_3) is used here as a model for adsorbed nitrate on the surface of atmospherically relevant mineral dust aerosol. Nitrate formation following nitric acid adsorption on alumina surfaces has been previously well characterized with infrared spectroscopy. Recently, quantum chemical calculations of binuclear aluminum cluster models have been used to aid in the assignment of the vibrational spectrum of adsorbed nitrate species following reaction of nitric acid with alumina.[4] In particular, the ν_3 region of the nitrate ion has been carefully assigned and interpreted for nitrate adsorption under dry and humid conditions. It has been shown that under dry conditions, <1% relative humidity (%RH), adsorbed nitrate binds to the oxide surface in several different modes of coordination including monodentate, bidentate, and bridging. Under humid conditions, the infrared spectrum of adsorbed nitrate changes as the nitrate ion becomes solvated by coadsorbed water molecules, forming both inner and outer sphere complexes.

In the current study, the surface was saturated with adsorbed nitrate following nitric acid adsorption (see Supporting Information for experimental details). Following adsorption, the FTIR cell is evacuated to remove all weakly adsorbed products. After introduction of water vapor, molecular oxygen, or both (or neither), the valve between the FTIR cell and the gas handling/vacuum system was closed off to monitor adsorbed and gas-phase products (see Figure 1) formed under different environmental conditions. A 500 W broadband Hg arc lamp (Oriel) is used to irradiate the sample. Both a water filter, to remove infrared radiation, and a filter to remove shorter wavelength radiation ($\lambda > 300$ nm, Oriel filter #59425) are placed at the output of the lamp.

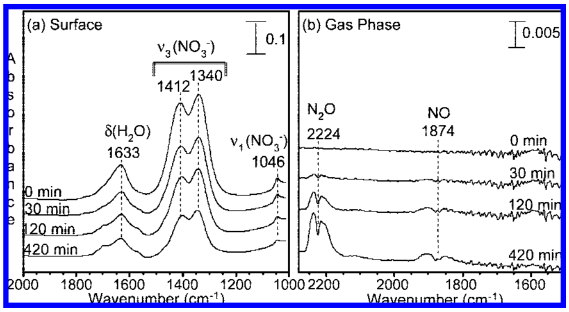

Figure 1. FTIR spectra of (a) surface-adsorbed nitrate at 45 ± 2% RH and 296 K as a function of broadband irradiation and (b) gas-phase products that form upon irradiation. Water absorptions have been subtracted from the spectra.

Figure 1 shows infrared spectra recorded as a function of photolysis time at 45 ± 2% RH. It can be seen from these spectral data that there is a decrease in the intensity of the bands due to adsorbed nitrate at 1046, 1340, and 1412 cm^{-1} as photolysis proceeds (Figure 1a). The formation of gas-phase products is also monitored and, under these conditions, include NO and N_2O (Figure 1b). Vibrational mode assignments of gas-phase products are summarized in Supporting Information Table 1.

Similar spectra were collected for experiments done under dry conditions, < 1% RH. The results of the experiments done under dry conditions show that there is also a decrease in the integrated absorbance of the nitrate absorption bands with irradiation concomitant with the formation of adsorbed products including adsorbed N_2O (see Supporting Information Figure 1). Under dry conditions, there is now the formation of three gas-phase products, N_2O, NO, and NO_2. These same experiments were repeated in the presence of molecular oxygen, and there was a similar decrease in the intensity of the adsorbed nitrate absorption bands upon irradiation. More interestingly, and the focus of this communication, is the change in the gas-phase product distribution under the different environmental conditions, as shown in Figure 2.

Figure 2 displays the relative gas-phase product distribution following broadband irradiation ($\lambda > 300$ nm) of adsorbed nitrate under different environmental conditions. The error bars represent the standard deviation from triplicate measurements. Relative product yields were determined by converting integrated infrared absorbances into gas-phase concentrations. The calibration factor for each gas-phase species is provided in Supporting Information Table 2. Concentrations are then normalized to the largest amount of gas-phase product species, which is NO in the absence of molecular oxygen and NO_2 in the presence of molecular oxygen. The data are plotted this way so that changes in the product distribution under different environmental conditions can be easily compared. It is estimated that the absolute total gas-phase nitrogen content is within 25% under the different environmental conditions.

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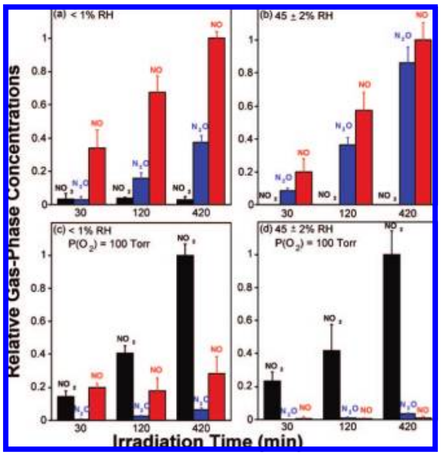

Figure 2. Relative gas-phase concentrations obtained from FTIR spectra following irradiation of adsorbed nitrate under different environmental conditions, <1% RH, and at 45 ± 2% RH, in the presence and absence of oxygen at $T = 298$ K after 30, 120, and 420 min.

The results presented here clearly show that adsorbed nitrate undergoes photochemistry upon irradiation with light ($\lambda > 300$ nm). Loss of adsorbed nitrate is estimated to be between 20% and 30% under the different environmental conditions after 30 min of photolysis, and there are clear differences in the gas-phase product distribution under different environmental conditions of %RH, i.e., when the nitrate ion is coordinated to the oxide surface or solvated by water molecules, and in the presence of molecular oxygen.

In solution and snow packs, nitrate ions undergo the following reactions upon photolysis at 305 nm under acidic conditions:[1,8−11]

$$NO_3^- + H^+ \xrightarrow{h\nu} NO_2 + OH^\bullet \tag{1}$$

$$NO_3^- \xrightarrow{h\nu} NO_2^- + O(^3P) \tag{2}$$

The nitrite ion formed in reaction 2 can then undergo further photolysis ($\lambda_{max} = 354$ nm) to yield

$$NO_2^- + H^+ \xrightarrow{h\nu} NO + OH^\bullet \tag{3}$$

These reaction mechanisms can begin to explain many of the results described here in that the dominant nitrogen-containing, gas-phase products include NO_2 and NO. Molecular oxygen enhances NO_2 formation under dry conditions with formation of some but much less NO and N_2O. However, as shown here, NO_2 is the major product under the most atmospherically relevant conditions, i.e., under humid conditions and in the presence of molecular oxygen. These changes in the gas-phase product distribution are most likely related to a number of factors that depend on environmental conditions and thus impact the formation of photoproducts. These factors include primary and secondary photoprocesses, quantum yields, and subsequent surface reactions, all issues that warrant further investigations.

The formation of nitrous oxide, N_2O, is of interest, as it is a well-known greenhouse gas.[12] Several studies have shown that N_2O_3 and other dinitrogen complexes can form in the presence of NO and NO_2 on alumina as well as silica surfaces.[13,14] In addition, as discussed by Trogler, surface-catalyzed reactions of NO can lead to the formation of N_2O, and this heterogeneous mechanism is poisoned in the presence of even small amounts of molecular oxygen.[12]

Recent studies by Yu et al. have shown that irradiated sodium nitrate solutions can yield hydroxyl radicals that readily oxidize α-pinene.[15] Furthermore, there is now evidence that surface reactions of nitrogen dioxide to yield gas-phase nitrous acid, HONO, are enhanced in the presence of light.[16−20] Given the importance of heterogeneous chemistry and the association of secondary species such as nitrate, sulfate, and organics with aerosols such as mineral dust and sea salt, there is the question as to whether there could be continued reactions involving these adsorbed species. Some of these continued reactions could be initiated by sunlight when secondary species contain chromophores that absorb light in the solar spectral region, such as nitrate ions at interfaces.[21]

The potential importance of heterogeneous photochemical reactions involving particulate nitrate is discussed here. The results shown here suggest that the photolysis of adsorbed nitrate on mineral dust aerosol, as nitrate in organic thin films,[22] may play a role in the chemistry of the atmosphere through renoxification, i.e., the conversion of particulate nitrate to NO_2 and NO. Furthermore, these results suggest that there will be a relative humidity dependence on this heterogeneous photochemical reaction due to the role of coadsorbed water in these reactions. Most importantly, in the presence of molecular oxygen and water, the conversion of nitric acid to nitrogen dioxide through an adsorbed particulate nitrate intermediate could potentially be a significant, yet previously unknown, renoxification mechanism in the atmosphere.

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Supporting Information Available: Additional experimental methods, table of gas-phase products, calibration table, and FTIR spectra as a function of irradiation time under dry conditions, <1% RH, in the absence of oxygen. This material is available free of charge via the Internet at http://pubs.acs.org.

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