An Abiotic Mechanism for the Formation of Atmospheric Nitrous Oxide from Ammonium Nitrate

A. Introduction

Nitrous oxide (N\textsubscript{2}O), presently at 320 parts per billion by volume in the troposphere\textsuperscript{1,2}, is a potent greenhouse gas (GHG) with a long residence time in the atmosphere, ~ 120 yrs, a global warming potential approximately 300 times larger than CO\textsubscript{2} of equal mass\textsuperscript{3}, and is the fourth largest contributor to radiative forcing over the past 250 years\textsuperscript{4}. In addition, N\textsubscript{2}O serves as a major source of stratospheric NO\textsubscript{x} and thus contributes to catalytic ozone destruction. Ravishankara and colleagues found that N\textsubscript{2}O is the single most important ozone depleting substance, and is anticipated to remain the largest throughout the 21\textsuperscript{st} century\textsuperscript{5}. Unlike most other GHGs, the quantification of global nitrous oxide sources is incomplete, with approximately 30% in unidentified sources and mechanisms\textsuperscript{6}.

Soils are estimated to account for ~50 - 60% of global N\textsubscript{2}O emissions\textsuperscript{7}, with high N\textsubscript{2}O production rates reported from agricultural soils\textsuperscript{8}, linked with soil moisture\textsuperscript{9} and O\textsubscript{2} availability\textsuperscript{10}. Most studies to date have focused on biological processes of nitrification, denitrification and nitrate ammonification as the predominant processes for nitrous oxide production in soil\textsuperscript{11}. As 41.8 Tg of solid ammonium nitrate and 13.7 Tg of calcium ammonium nitrate fertilizer are applied to agricultural fields as a N amendment each year (International Fertilizer Association, http://www.fertilizer.org/Home-Page/STATISTICS), it is important to determine if there are other processes leading to N\textsubscript{2}O production from agricultural soils including abiotic processes (vide infra).
Furthermore, ammonium nitrate is also a common component of ambient particles, which can be transported across the globe.\textsuperscript{12,13} It is formed as a secondary species in pure form as a product from gas phase reactions involving nitrogen oxides and ammonia. Nitrate is also formed via reactions of nitrogen oxides on mineral dust and sea salt surfaces, which lead to the formation of adsorbed nitrate, nitrate coatings and deliquesced nitrate layers on the surface of the particles.\textsuperscript{14,15} Gaseous ammonia neutralizes adsorbed nitric acid to yield ammonium nitrate on these particle surfaces.\textsuperscript{16} On agricultural soil, the formation of secondary ammonium nitrate coatings can take place via a similar mechanism on soil particle surfaces. These reservoirs (agricultural soils and atmospheric aerosols) also represent a potential source of nitrous oxide.

**B. Materials and Methods**

*Experimental Methods.* In these experiments, ammonium nitrate coatings on mineral surfaces were prepared by first reacting particle surface with nitric acid to produce a surface layer of adsorbed nitrate. Saturated surfaces of adsorbed nitrate have been previously described in detail.\textsuperscript{17,18} Briefly, aluminum oxide ($\gamma$-Al$_2$O$_3$ – Degussa) was used as a model for mineral surfaces and exposed to nitric acid vapor for 30 minutes at a pressure of approximately 1 Torr at 298 K. Experiments were also done with pure ammonium nitrate and for these experiments, powders of the pure substance was pressed on to one half of the tungsten grid and evacuated over night. These spectroscopic measurements can be done by simply probing each side of the sample grid with the infrared beam. Experiments were carried out using different isotopes of ammonia $^{14}$NH$_3$ (> 99.5 % $^{14}$N) and $^{15}$NH$_3$ (> 98 % $^{15}$N), to better understand the mechanism of formation of N$_2$O. All FTIR spectra were recorded at 298 K. These ammonium nitrate samples, i.e. either the pure sample or the alumina coated sample, were exposed to light ($\lambda$ 300 – 700 nm) using a
broadband Hg light source and a broadband filter as previously described in Driessen et al. Studies of the effect of relative humidity of <1%, 20%, 45%, and 80% were done to assess the importance of ambient moisture on the reaction of ammonium nitrate to yield gas-phase nitric acid. First order empirical rate constants were estimated upon irradiation for the pure ammonium nitrate and the surface coated ammonium nitrate reaction. These data were used in modeling analysis to determine the relative importance of these reactions in the decomposition of ammonium nitrate to yield nitrous oxide (vide infra).

**Modeling.** Annual photolytic production of N\textsubscript{2}O from atmospheric aerosols over North America was estimated from hourly ammonium and nitrate concentrations from the 2002 CMAQ atmospheric chemical transport simulation described by Spak and Holloway. In order to estimate hourly N\textsubscript{2}O production from fertilizers, monthly ammonium nitrate and calcium ammonium nitrate application rates from Goebes et al. were allocated to the 36 km x 36 km Lambert conformal conic grid used in CMAQ modeling with agricultural spatial surrogates and diurnal temporal profiles from the 2001 National Emissions Inventory. Relative humidity and insolation were taken from the hourly meteorology used as input to the CMAQ simulation.

**C. Results and Discussion**

**Laboratory Measurements.** As shown here, laboratory measurements using FTIR spectroscopy show that N\textsubscript{2}O can be produced via the abiotic decomposition of ammonium nitrate for pure ammonium nitrate samples and for ammonium nitrate coated particles. Figure 1a shows the infrared spectrum of ammonium nitrate at 298 K prior to irradiation. Infrared spectra recorded of the gas phase under different conditions of relative humidity and light (\(\lambda > 300\) nm) are shown in
Figure 1b. The band at 2224 cm\(^{-1}\) shows that nitrous oxide forms under these various conditions but to different extents, with the greatest production in the presence of light and a relative humidity of 45%. Figure 1c shows the data in terms of the relative amounts of \(\text{N}_2\text{O}\) formed under these different conditions with the data normalized to the greatest amount of \(\text{N}_2\text{O}\) formed during photolysis at 45% RH. Under humid conditions, \(\text{N}_2\text{O}\) is the sole gas-phase product, and increases as a function of relative humidity until the deliquescence relative humidity is reached (62% at 298 K\(^{14}\)), after which it decreases. Relative gas-phase concentrations were determined from the integrated absorbances of the nitrous oxide band and experimentally determined conversion factors to take into account different molar absorptivities. Additional control experiments were carried out to compare thermal decomposition of pure \(\text{NH}_4\text{NO}_3\) to yield \(\text{N}_2\text{O}\) under dry condition. Based on the results from these experiments, there was no significant \(\text{N}_2\text{O}\) formation from \(\text{NH}_4\text{NO}_3\) at 298 K in the absence of light.

We also found that \(\text{N}_2\text{O}\) can be produced from reaction of ammonium nitrate coated particles surfaces. Ammonium nitrate coatings were prepared on alumina surfaces as discussed in the Methods section. Figure 2a shows the infrared spectrum of ammonium nitrate coated aluminum oxide particles estimated to be a monolayer coating on the surface.\(^{22}\) This coated surface was used as a model for mineral dust in the atmosphere and for an aluminum silicate soil particle to understand the photochemistry of ammonium nitrate coated particles. Additionally, experiments carried out using different isotopes of ammonia, \(\text{H}^{14}\text{NO}_3\) was adsorbed on the particle surface followed by either \(^{14}\text{NH}_3\) or \(^{15}\text{NH}_3\) to yield different isotopically labeled ammonium nitrate including the mixed labeled coating. The infrared spectra of aluminum oxide coated \(^{14}\text{NH}_4^{14}\text{NO}_3\)
and $^{15}$NH$_4^{14}$NO$_3$ are also shown in Figure 2a following exposure to H$^{14}$NO$_3$/H$^{14}$NH$_3$ and H$^{14}$NO$_3$/H$^{15}$NH$_3$, respectively.

It is seen that nitrous oxide is also produced upon broadband photolysis ($\lambda > 300$ nm) of the ammonium nitrate coated particle under all the conditions studied as shown in Figure 2b. It is notable that upon irradiation of the $^{15}$NH$_4^{14}$NO$_3$ coated aluminum oxide particles, under dry condition (%RH < 1), resulted in one hundred percent formation of the mixed isotope product, with an isotopic shift of the asymmetric stretch to lower frequency (Figure 2c). The connectivity of the atoms was determined from the nitrous oxide absorption frequencies, and the magnitude of shift of 24 cm$^{-1}$ conclusively demonstrates that the product formed is $^{15}$N$^{14}$NO and not $^{14}$N$^{15}$NO, which has a larger isotope shift of 40 cm$^{-1}$.23

The difference between isotopic ratio in the central nitrogen and the terminal nitrogen atoms is defined as the $^{15}$N site preference in N$_2$O.3 This information derived from the distribution of $^{15}$N within the gas phase N$_2$O molecule reflects the possible sources and reaction mechanisms of N$_2$O formation.24 We analyzed the site preference of N$_2$O from adsorbed $^{15}$NH$_4^{14}$NO$_3$ using the N-O stretching frequencies in the IR spectra and found that the abiotic production mechanism of N$_2$O has a very narrow range of isotopic signature and almost one hundred percent of the gas phase N$_2$O is in the form of $^{15}$N$^{14}$NO. These results reveal that gas-phase N$_2$O can be formed under ambient conditions of temperature and relative humidity from ammonium nitrate ion. Focusing on the light initiated reaction pathway, the production of N$_2$O and its isotope signature can be explained in terms of the photoreduction of nitrate coupled to the oxidation of NH$_4^+$.25,26
Furthermore, it can be seen in Figure 2b that under humid conditions, the N\textsubscript{2}O isotope signature becomes more complex as a result of the formation of several isotopic products. The spectral band for N\textsubscript{2}O can be resolved into two components, as a result of the formation of both \textsuperscript{15}N\textsubscript{14}NO and \textsuperscript{14}N\textsubscript{14}NO, suggesting a secondary reaction pathway operating at higher RHs. Heterogeneous formation of N\textsubscript{2}O occurs from the hydrolysis of gas-phase NO\textsubscript{2} via HONO on acidic and oxide surfaces.\textsuperscript{27} The net reaction yields N\textsubscript{2}O and HNO\textsubscript{3} according to:

\[
\begin{align*}
\text{8} \, \text{^{14}NO}_2 + 3\text{H}_2\text{O} &\xrightarrow{H^+} \text{^{14}N}^{14}\text{NO} + 6 \, \text{^{14}HNO}_3 \\
\end{align*}
\]  

The surface mediated secondary reaction of the primary gas phase photoproduct, NO\textsubscript{2}, a product that can be easily seen in the infrared spectra (Figure 2b), may be responsible for the higher N\textsubscript{2}O concentrations observed, and, in particular, accounts for the production of \textsuperscript{14}N\textsuperscript{14}NO following photolysis of \textsuperscript{15}NH\textsubscript{4}\textsuperscript{14}NO\textsubscript{3}, especially at longer photolysis times (Figure 2d).

According to Figure 1, the relative gas phase concentration of N\textsubscript{2}O from pure NH\textsubscript{4}NO\textsubscript{3} decomposition for “%RH< 1, h\nu, O\textsubscript{2}” is \(~0.8\) and it reaches to a maximum (1.0) at %RH 45. Even if we assume that this total increase of \(~0.2\) from %RH < 1 to %RH 45 is only due to heterogeneous hydrolysis of NO\textsubscript{2} then it is only a 25\% increase of the total. Therefore, for pure NH\textsubscript{4}NO\textsubscript{3}, the mechanism shown in reactions 1-5 is the more important one. But, in the case of
adsorbed ammonium nitrate relatively higher amounts of NO₂ is produced from photolysis of nitrate on the surface and this leads to the secondary mechanism enhancing the production of N₂O from adsorbed NH₄NO₃. Higher N₂O concentrations and N₂O fluxes have been observed from the rewetting of agricultural lands, and have been attributed entirely to the biological formation of nitrous oxide.⁹,²⁸ Based on our results, a significant fraction of N₂O formation under those conditions may come from these abiotic process discussed above.

Quantification of N₂O formation shows that the extent of reaction is at least two orders of magnitude greater for the ammonium nitrate coated particle surface than for solid ammonium nitrate as given in Table 1. The percentage yield of N₂O formation during photolysis of adsorbed NH₄NO₃ and the pure salt are calculated from the decrease in absorptions associated with ammonium nitrate as a function of irradiation time. Surface enhanced rate constants (Table 2) were determined by fitting these data to a first order rate expression.

These differences in N₂O formation efficiency between the two sources, i.e. the pure ammonium salt and the coated particle, can be attributed to the strength and mode of coordination and the ability of the two chemical species, nitrate and ammonium, to be further reduced or oxidized. Being a polyatomic oxyanion, nitrate is capable of binding in different adsorption modes to the surface, including a bidentate and bridging coordination model,¹⁷ which is not the case in ammonium nitrate salt, restricted to a stable lattice structure. Thus, the observed enhancement in the abiotic N₂O formation in the presence of a surface may be due to the ability of these reactants to form surface complexes with preferred orientation for an effective reaction coordinate to yield
N\textsubscript{2}O production. Additionally, the secondary reaction of nitrogen dioxide (eq. 6) occurs on particle surfaces.

The above laboratory experiments provide strong evidence for the formation of nitrous oxide from ammonium nitrate under ambient conditions, a chemical process that is enhanced in the presence of light, relative humidity and a surface. This source is currently not accounted for in global N\textsubscript{2}O budgets.

**Modeling.** Annual production of N\textsubscript{2}O from atmospheric aerosols and surface fertilizer application over the continental United States from these abiotic pathways can be estimated from results of an annual chemical transport simulation\textsuperscript{20} with the Community Multiscale Air Quality model.\textsuperscript{29} Surface-enhanced photolysis of aerosol ammonium nitrate is estimated to yield 3,964±239/-241 metric tons N\textsubscript{2}O/year, with most production occurring in the free troposphere (Figure 3a), above cloud level. In the absence of a surface, photolysis would yield 2,014±3/-10 tons/year. Annual tropospheric column yields are highest over California—including southern California, the central valley, and offshore plumes—due to elevated ammonium nitrate concentrations and sunny conditions throughout the year (Figure 3b), peaking in summer. Near the surface, urban areas throughout the country produce local hotspots, and the Midwest is a widespread regional source (Figure 3c). The seasonality of N\textsubscript{2}O production over the interior of the continent from this mechanism is consistent with nitrate seasonality, with a maximum in the winter and a summertime minimum.
Estimating photolysis yields from solid pellet ammonium nitrate fertilizers is difficult due to incomplete documentation on their contemporary application in practice. In particular, the percentage of these fertilizers applied to the surface of fields or “side dressed” below the topsoil varies by season and crop in best practices, but actual surface application rates are not reported. We assume that 50% of solid ammonium nitrate fertilizers are applied to the surface, and fertilizer surface area facing the sun is not in contact with a surface. Thus, production from photolysis of “top dressed” solid ammonium nitrate and calcium ammonium nitrate fertilizers applied to the surface of agricultural soils is estimated at $5,322^{+488/-3,328}$ tons N$_2$O/year, with less than 10% due to calcium ammonium nitrate. The spatial distribution of N$_2$O from this source (Figure 3d) is similar to production from atmospheric aerosols, reflecting the common source of ammonia emissions from agriculture. The amount of ammonium nitrate fertilizer used in the U.S. is so large that only one layer of pellets applied to fertilized croplands and photolyzed by catalytic reaction would produce more N$_2$O than the contemporary national emissions inventory for all sources.

Initial N$_2$O production estimates of $9,286^{+726/-5,288}$ tons/year place this mechanism as the 9th-ranked total source and 7th-ranked abiotic source of N$_2$O the in the United States, comparable to adipic acid production, and representing 0.90% of the current estimated national total from all natural and anthropogenic sources. However, much of the estimated production from photolysis of synthetic fertilizers may already be accounted for in field measurements contributing to the highly uncertain estimate for emissions due to nitrogen mineralization from synthetic fertilizers, to which it would contribute 4.04%.
Based on results over North America, N\textsubscript{2}O production by this mechanism is expected globally from both megacities and agricultural areas. Projected changes in anthropogenic emissions suggest that this mechanism may become more important in the future. As NO\textsubscript{x} emissions increase and sulfur dioxide emissions decline, aerosol ammonium nitrate concentrations will rise. However, the continued transition from solid fertilizers to liquid mixes and urea concentrates for many crops suggests that N\textsubscript{2}O production from photolysis of fertilizers may decline as the atmospheric aerosol source increases.

**Conclusions and Environmental Implications**

These findings add to the body of evidence that abiotic mechanisms for N\textsubscript{2}O production from ammonium nitrate and nitrate are important and estimated to produce approximately 5\% of total U.S. anthropogenic N\textsubscript{2}O emissions. A recent study by Samarkin et al. has also shown that nitrate in soil pore spaces is reduced by minerals containing Fe(II).\textsuperscript{31} Based on the mechanism discussed here, we predict that the amount of N\textsubscript{2}O would be seasonal and follow an isotope signature similar to the biotic mechanism, making it difficult to distinguish between the two. However, since the abiotic mechanism is sunlight initiated, its correlation with diurnal and seasonal patterns of solar irradiance allows it to be distinguished from N\textsubscript{2}O produced from biota. This would require routine measurements of atmospheric N\textsubscript{2}O at a higher temporal resolution than the current daily and monthly monitoring regimes.
Figures

Figure 1: a. Surface spectrum of $^{14}$NH$_4$NO$_3$ salt collected under dry (%RH < 1) condition. The spectrum was referenced to the clean grid and gas-phase subtracted. b. FTIR spectra of gas phase products formed during the photolysis of $^{14}$NH$_4$NO$_3$ salt under different experimental conditions. c. Relative gas-phase concentrations from $^{14}$NH$_4$NO$_3$ photolysis under different conditions.

Figure 2: a. FTIR spectra obtained after exposing $\gamma$-Al$_2$O$_3$ to gas phase nitric acid (1.77 Torr) followed by the exposure to gas phase $^{14}$N or $^{15}$N-labelled ammonia (1.65 Torr) under dry (%RH < 1) condition to produce an ammonium nitrate coating. Each spectrum was referenced to the clean oxide spectrum prior to exposure to nitric acid. b. FTIR spectra of gas phase products formed during the photolysis of adsorbed $^{14}$NH$_4$$^{14}$NO$_3$ under dry (%RH < 1) and wet (45% RH) conditions. c. FTIR spectra of gas phase products showing the isotopic shifts with adsorbed $^{15}$NH$_4$$^{14}$NO$_3$ under dry (%RH < 1) and wet (45% RH) conditions. Inset shows the peak fitting for the different nitrous oxide isotopes formed ($^{15}$N$^{14}$NO and $^{14}$N$^{14}$NO) in the mixed labeled experiments at 45% RH. d. Relative gas-phase contributions of $^{15}$N$^{14}$NO (orange) and $^{14}$N$^{14}$NO (green) as a function of irradiation time.
Table 1 Percent yield of N$_2$O formation following broadband irradiation of thin NH$_4$NO$_3$ surface coatings and pure NH$_4$NO$_3$ for ninety minutes

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>% Yield</th>
<th>( k_{\text{min}} )</th>
<th>( k_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis of NH$_4$NO$_3$ salt</td>
<td>( 2.26 (\pm 0.15) \times 10^{-3} )</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>Photolysis of adsorbed NH$_4$NO$_3$</td>
<td>( 2.54 (\pm 0.12) \times 10^{-3} )</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>%RH &lt; 1, O$_2$, hv</td>
<td>( 2.90 (\pm 0.16) \times 10^{-3} )</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>%RH 20, O$_2$, hv</td>
<td>( 2.20 (\pm 0.20) \times 10^{-3} )</td>
<td>2.93</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. First order rate constants for N$_2$O formation following broadband irradiation of thin NH$_4$NO$_3$ surface coatings and pure NH$_4$NO$_3$ under different relative humidity conditions.

<table>
<thead>
<tr>
<th>%Relative Humidity</th>
<th>First order rate constants x ( 10^5 ) s$^{-1}$</th>
<th>First order rate constants x ( 10^5 ) s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(in the presence of surface (adsorbed NH$_4$NO$_3$))</td>
<td>(in the absence of surface (pure NH$_4$NO$_3$))</td>
</tr>
<tr>
<td>( k )</td>
<td>( k_{\text{min}} )</td>
<td>( k_{\text{max}} )</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>20</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>45</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>80</td>
<td>0.8</td>
<td>0.7</td>
</tr>
</tbody>
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Figure 3. Annual N$_2$O production over the continental United States from ammonium nitrate (metric tons): a. Vertical profile over study domain from atmospheric aerosols. b. Integrated vertical column. c. Surface-level production from atmospheric aerosols. d. From solid ammonium nitrate and calcium ammonium nitrate fertilizers.
References