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Possible catalytic effects of ice particles on the production of NO_x by lightning discharges

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Abstract. It is well known that lightning produces NO_x as a result of the high temperatures in discharge channels. Since most viable proposed electrification mechanisms involve ice crystals, it is reasonable to assume that lightning discharge channels frequently pass through fields of ice particles of various kinds. We address the question of whether ice crystals may serve as catalysts for the production of NO_x by lightning discharges. If so, and if the effect is large, it would need to be taken into account in estimates of global NO_x production by lightning. In this theoretical study, we make a series of plausible assumptions about the temperature and concentration of reactant species in the environment of discharges and we postulate a mechanism by which ice crystals are able to adsorb nitrogen atoms. We then compare production rates between uncatalyzed and catalyzed reactions at 2000 K, 3000 K, and 4000 K, which are reasonable temperatures in lightning channels as they cool down. Ice crystal catalysis is expected to produce 2.7 times more NO than if ice crystals were not present. Catalyzed NO production rates are greater at 2000 K, whereas uncatalyzed production rates are greater at 4000 K. Thus, temperatures that favor rapid NO production without ice crystals adsorbing nitrogen atoms are unfavorable for NO production in the presence of ice crystals, and vice versa. The density of atmospheric ice crystals is much larger at 10 km where intracloud (IC) flashes peak than at 5 km where cloud to ground (CG) flashes peak, thus catalytic processes are expected to be more important for IC flashes than CG flashes, perhaps explaining a portion of the discrepancy in IC and CG production rates.

1 Introduction

Though it has been known for a long time that lightning produces oxides of nitrogen (NO_x), serious research on the subject has been undertaken only in the last 30 yr or so. The study of NO_x first achieved prominence when it was found that NO is an important precursor to photochemical smog (Schumann and Huntrieser, 2007). Also, NO and NO_2 have been linked to the destruction of stratospheric ozone (Cohen and Murphy, 2003).

In the atmosphere, NO forms an equilibrium with molecular nitrogen and molecular oxygen at high temperatures, such as those that are generated within the lightning channel (Price et al., 1997). Orville (1968a) found peak temperatures in cloud-to-ground lightning channels between 28 000 and 31 000 K. Rakov et al. (1998) found return-stroke channel peak temperatures exceeded 30 000 K. Recent spectroscopic measurements by Walker et al. (2010) yielded peak temperature estimates of 34 000 K (Fig. 1). Uman and Voshall (1968) found that temperatures in the lightning channel cool at rates depending on channel radius. For a channel of radius 1 cm the central temperature cools to 4000 K in about 7 ms, 3000 K in about 12 ms, and 2000 K in 50 ms. For a channel of radius 8 cm the central temperature has only cooled to about 5700 K in 100 ms, the longest time duration for which the cooling process was modeled. Photographs of lightning have ranged from 5.5 to 11.5 cm in radius (Schonland, 1937) to 1 to 1.5 cm in radius (Idone, 1992), with an intermediate value of 3 cm in radius given by Rakov et al. (1998). Rakov and Uman (2003) estimate the lightning channel to be 1 to 2 cm in radius. The problem is nonlinear as the channel expands until the core temperature has reached 3000 K (Picone et al., 1981). The process is further complicated by the potential for dart leaders to form in the lightning channel between 2000 and 4000 K (Uman, 1984). Finally, the degree of dissociation of nitrogen and oxygen molecules is dependent

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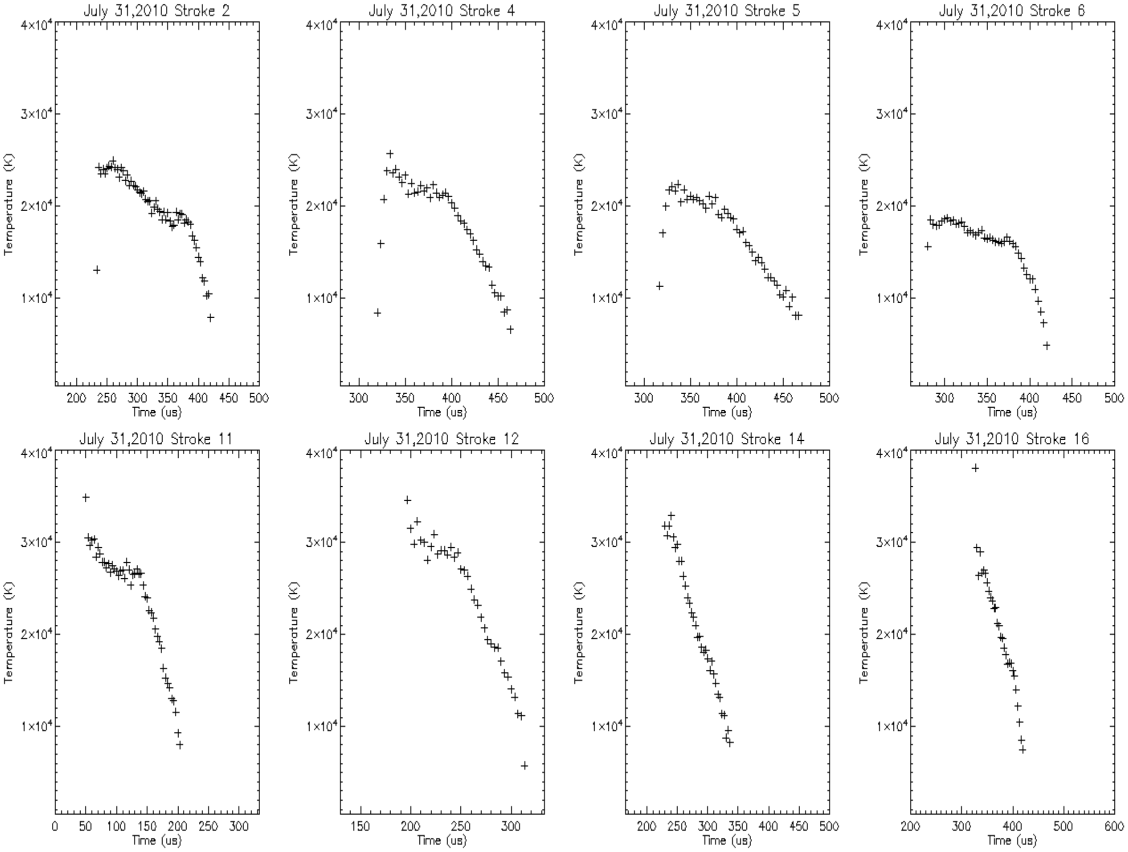

Fig. 1. Decrease in temperature with time following a return stroke, illustrating the variability in temperature decrease over time (Walker, 2010). The rate of temperature decrease varies from 300 K μs^{-1} (lower right image) to just under 100 K μs^{-1} (lower left image).

not only on the central lightning channel temperature, but the radial distribution of temperature away from its center. Figure 1 illustrates this variability in temperature between lightning channels, which would extend to the temperatures invoked in this study. For example, the upper level image depicts a lightning stroke decreasing 15 000 K in 200 µs, while the lower level image depicts a lightning stroke decreasing 20 000 K in 200 µs.

Cook et al. (2000) has proposed three reactions by which NO might be converted into NO_2 in the proximity of a lightning discharge. The first involves combining NO and O_2 to produce NO_2 and O. The second involves NO and O as reactants, with NO_2 as the only product. The third involves NO, O and an additional gas such as N_2, Ar, or O_2, producing NO_2 and leaving the additional gas unchanged. All three of these reactions take place faster than the reaction that produces NO_2 by combining NO and O_3.

A review of recent literature reveals differing estimates of NO_x production per flash in thunderstorms (Table 1). One of the factors affecting these estimates is the relative importance of cloud-to-ground (CG) lightning and in-cloud (IC) lightning in the production of NO_x. For example, Ott et al. (2010) state that IC lightning and CG lightning produce roughly equal amounts of NO_x per flash. Koshak et al. (2010) state that CG lightning produces ten times more NO_x per flash than IC lightning. The Ott et al. (2010) value relies on aircraft measurements obtained post-discharge around a thunderstorm, while the Koshak et al. (2010) model uses production values from laboratory discharges. Augmented production of NO_x as a result of the presence of ice particles at high altitudes could account for the difference in total production estimates.

2 The possible role of ice particles as catalysts for products of NO_x

This paper explores a potential reaction mechanism that invokes adsorption of nitrogen atoms on ice crystals. If this mechanism exists, it could conceivably prolong the availability of nitrogen atoms for reactions within the upper region of thunderstorms, i.e. where ice particles are present. Chemisorption occurring through nitrogen-hydrogen chemical bonding is the most likely adsorption mechanism. Certainly there is a precedent for consideration of these types of chemisorptive catalytic reactions, as it has been found

Table 1. A comparison of estimates of NO_x per flash from several studies. Some values were adapted from Labrador et al. (2005). "Theoretical" includes calculations based on theory as well as modeling studies. For values given in papers as $NO_x\,m^{-1}$, a flash is assumed to be 10 km in length. For DeCaria et al. (2000, 2005) and Ott et al. (2010) the models were constrained by anvil aircraft observations from field studies. For Martini et al. (2011) there were additional model runs conducted using 240 moles/flash.

Reference	Methodology	Molecules/flash	Moles/flash
Levine et al. (1981)	Laboratory	5.00×10^{24}	8.30
Kumar et al. (1995)	Field study	5.00×10^{24}	8.30
Dawson (1980)	Theoretical	8.00×10^{24}	13.28
Beirle et al. (2010)	Satellite	1.00×10^{25}	16.61
Tuck (1976)	Theoretical	1.10×10^{25}	18.27
Hill et al. (1980)	Theoretical	1.20×10^{25}	19.93
Koshak et al. (2010)	Theoretical	1.41×10^{25}	23.40
Cooray et al. (2009)	Theoretical	2.00×10^{25}	33.21
Lawrence et al. (1995)	Review	2.30×10^{25}	38.19
Nesbitt et al. (2000)	Field study	2.67×10^{25}	44.25
Huntrieser et al. (2002)	Field study	2.70×10^{25}	44.84
Wang et al. (1998)	Laboratory	3.10×10^{25}	51.48
Peyrous and Lapyere (1982)	Laboratory	3.20×10^{25}	53.14
Ridley et al. (2004)	Field study	3.20×10^{25}	53.14
Beirle et al. (2006)	Satellite	5.40×10^{25}	89.67
Koshak et al. (2011)	Theoretical	6.09×10^{25}	101.17
Sisterson and Liaw (1990)	Theoretical	8.20×10^{25}	136.17
Noxon (1976)	Field study	1.00×10^{26}	166.06
Chameides et al.(1977)	Theoretical	1.00×10^{26}	166.06
Kowalczyk and Bauer (1982)	Theoretical	1.00×10^{26}	166.06
Bucsela et al. (2010)	Satellite	1.05×10^{26}	174.36
Schumann and Huntrieser (2007)	Review	1.50×10^{26}	249.09
Huntrieser et al. (2011)	Field study	1.51×10^{26}	250.00
DeCaria et al. (2000)	Theoretical	1.56×10^{26}	258.39
Fehr et al. (2004)	Field study	2.10×10^{26}	348.72
Rahman et al. (2007)	Field study	2.40×10^{26}	398.54
Chameides (1979)	Theoretical	2.50×10^{26}	415.14
DeCaria et al. (2005)	Theoretical	2.77×10^{26}	460.00
Martini et al. (2011)	Theoretical	2.89×10^{26}	480.00
Ott et al. (2010)	Theoretical	3.01×10^{26}	500.00
Jourdain et al. (2010)	Theoretical	3.13×10^{26}	520.00
Drapcho et al. (1983)	Field study	4.00×10^{26}	664.23
Franzblau and Popp (1989)	Field study	3.00×10^{27}	4981.73

that the rate of catalytic ammonia synthesis is primarily determined by nitrogen chemisorption (Klimisch and Larson, 1975); many other reactions are also dictated by nitrogen chemisorption (Shinn, 1990; Wovchko and Yates, 1996; Ertl et al., 1979). The greatest amount of adsorption per unit of ice particles probably occurs with the dendrite crystal habit, since dendrites have the largest specific surface area (Fig. 2). Furthermore, dendrites are formed at a temperature of −18 °C (Bailey and Hallett, 2009), which closely matches the temperature of the negative charge region (N-region) of thunderstorms. According to the results presented in Koshak et al. (2010), this is the region with the greatest amount of lightning NO_x production. Combining the results of Bailey and Hallett (2009) and Koshak et al. (2010), dendrites are expected where lightning NO_x production is greatest.

By the very nature of heterogeneous catalytic reactions, the reaction rates will not be constant, and oscillatory kinetics have been observed in a wide variety of these kinds of reactions (Imbihl and Ertl, 1995). However, assuming only nitrogen atoms are adsorbed, the reaction would be unimolecular. The overall kinetics of adsorption can be modeled by the Langmuir adsorption isotherm (Laidler et al., 2003). The rate constants can be determined using the Eyring equation (Laidler et al., 2003). In using the Langmuir model, it is assumed that all the surface sites are identical and do not react with each other (Boudart, 1995), so that the heat of adsorption doesn't change between surface sites (Seader and Henley, 1998).

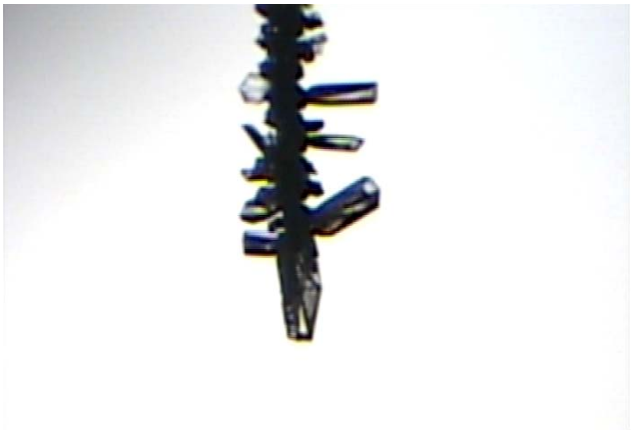

Fig. 2. Sample ice crystals. The bottommost crystal is dendritic. Taken from Peterson et al. (2010).

The Langmuir model is valid in the case of this proposed reaction mechanism. The surface sites participating in this reaction are the hydrogen atoms, which are all identical. While nitrogen atoms can bond with both oxygen atoms and hydrogen atoms on the water molecule, the nitrogen bonded with hydrogen is the most likely to result in the formation of NO_x, since it will have a partial positive charge because of the greater electronegativity of oxygen, with oxygen drawing electrons away from hydrogen on the water molecule (Laidler et al., 2003).

3 Stability of ice crystals at high temperatures

Before the production of NO by ice crystal catalysis can be considered, the stability of the ice crystal surfaces must be determined. If the ice crystals sublime in the heat surrounding the lightning channel, there will be no surfaces on which catalytic NO production could take place. Therefore, the rate of decay for ice crystals in high temperature environments must be examined in order for the viability of the proposed reaction to be established.

To model the process, three temperatures were used: 2000, 3000, and 4000 K, since temperatures in this range occur during the cool-down period in a lightning discharge channel. Toward this end we employed the hot-channel model of lightning NO_x production rather than the shock-wave model, in agreement with Rakov and Uman (2003). Capacitances of 0.1 times the radius of the dendrite, equal to the radius of the dendrite, and ten times the radius were used to test the range of possible decay rates for ice crystals in a wide range of possible thunderstorm environments (Rogers and Yau, 1989, pp. 159–160). Kinetic and ventilation effects were neglected. At 2000 K, the decay rate ranges from 4.40×10^{-4} g s^{-1} for the largest capacitance, coefficient of diffusion, and constant of proportionality for the thermal conductivity, to 4.40×10^{-7} g s^{-1} for the lowest of these three values. At 3000 K, the decay rate ranges from 1.63×10^{-3} g s^{-1} to 1.63×10^{-6} g s^{-1}. At 4000 K, the decay rate ranges from 4.97×10^{-3} to 4.97×10^{-6} g s^{-1}. Over the 100 ms interval that temperatures around the lightning channel fall within this temperature range, 5×10^{-4} g ice crystals will survive at 4000 K, while 5×10^{-5} g ice crystals will survive at 2000 K. Ice crystals as small as 5×10^{-8} g may survive at 2000 K if the low end assumptions are valid, but this is an uncertain result.

Since it is unlikely that ice crystals within the hot core of the lightning channel survive, an alternative process must be considered. Air within the hot core mixes with surrounding air (Picone et al., 1981), providing a supply of reactants in the near vicinity. Ice crystals in the surrounding corona sheath would survive, and are still in sufficient proximity to the lightning channel to participate in catalytic reactions. As calculated below, there are more than enough ice crystals in the corona sheath to catalyze nitrogen oxide production. Therefore, only ice crystals within this annulus will be considered.

4 Calculations

First, the Eyring equation ($k = k_B T / h \times \exp[-G_{act}/RT]$, where G_{act} is the Gibbs energy of activation) must be employed to determine the adsorption and desorption rates on the ice crystal surfaces. For this equation three pieces of information are needed. The activation enthalpy and entropy are required to determine the fraction of molecules that can participate in the reaction. Since reaction rates are temperature dependent, the temperature around the ice crystal surface must also be known (Laidler et al., 2003).

For reactions that occur without breaking any chemical bonds, the activation energy is zero. Since atomic nitrogen does not contain any bonds, there will be no activation enthalpy or entropy associated with its adsorption onto an ice crystal surface. Hence, we can assume that the adsorption rate is directly proportional to temperature, with the constant of proportionality equaling the Boltzmann constant (K_b) divided by the Planck constant (h) (Laidler et al., 2003).

For desorption, the process will involve breaking the bond between nitrogen and oxygen. Therefore, there will be a nonzero activation enthalpy and entropy associated with the desorption process. Since the change in enthalpy for adsorption is similar to that of chemical bonds, the nitrogen-hydrogen surface bond should have similar properties to those in ammonia. This gives a bond enthalpy of 390.88 kJ mol^{-1}, and a bond entropy of 101.54 J mol^{-1} K. The bond enthalpy for the nitrogen-hydrogen bond in ammonia is in close agreement with the average bond enthalpy of a nitrogen-hydrogen bond, which is 391 kJ mol^{-1} (Silberberg, 2003).

A temperature for adsorption and desorption must also be determined. Crystal habit diagrams give a temperature range of −10 to −20 degrees Celsius, or 253 to 263 degrees Kelvin, for the formation of dendrites. A value of 260 K will be used, to simplify calculations (Rogers and Yau, 1989, p. 163).

With these values in place, the adsorption and desorption constants may be calculated. The adsorption constant will equal 5.42×10^{12} s^{-1}. Since the Gibbs activation energy associated with desorption leading to the formation of nitrogen molecules and NO is also zero, desorption by these processes also occurs at 5.42×10^{12} s^{-1} (Laidler et al., 2003).

Before the adsorption isotherm can be determined, the concentration of nitrogen atoms must be known. The volume to be considered is a cylinder as tall as the lightning discharge, and encompassing an area in and immediately around the lightning channel. Orville (1968b) found that electron densities were 10^{24} electrons m^{-3} for the first five microseconds, and then decreased to 10^{23} electrons m^{-3} by 20–30 microseconds. It may be assumed as a first approximation that the number of electrons released from atoms equals the number of ions present. While this value is clearly an overestimate given that molecules are also able to ionize, it provides an upper bound for determining whether enough ice crystal surface sites are available to adsorb any and all nitrogen atoms present; this method is also used by Cooray et al. (2007). This approximation would give a total number of nitrogen atoms between 7.808×10^{22} m^{-3} and 7.808×10^{23} m^{-3} (Stull, 2000). By comparison, air at the surface contains 2.55×10^{25} molecules m^{-3}. This means that even at the peak temperature, no more than 12 % of nitrogen molecules are dissociated in the lightning channel, recalling that air is 78 % nitrogen molecules. At a more intermediate height of three kilometers, with density at around 850 g m^{-3}, 5.6 % of nitrogen molecules are dissociated.

As dimensions of the cylinder, a height of 10 000 m is a valid approximation. The radius of the cylinder is taken from the area of high pressure due to thermal expansion. This area only reaches one to two centimeters across, so the radius of the cylinder is set at 0.01 m. A numerical simulation by Wang et al. (1998) gave NO_x production levels similar to experimental results when setting the radius of the leader core equal to this value. $r = 0.01$ m gives a cross-sectional area of 3.14×10^{-4} m^2, and a volume of 3.14 m^3. Using a nitrogen atom density taken from the peak electron density, this gives a total number of nitrogen atoms as 2.45×10^{24} in the lightning channel.

Next, the adsorption isotherm is to be calculated. K, the ratio of the adsorption rate to the desorption rate, is 1. [N], as before, is 1.30 moles of nitrogen atoms m^{-3}. Using these values, the adsorption isotherm is equal to 0.56, meaning just over half of the surface sites will adsorb nitrogen atoms.

The number of ice crystals that are available to adsorb nitrogen atoms is another variable to be considered. In a cylinder immediately surrounding the lightning channel, ice crystals should survive long enough to take part in catalytic reactions. Since the air well away from the channel is too cool to allow nitrogen atoms to survive for a sufficiently long period of time for adsorption, the radius of this larger cylinder is set at 0.1 m, one order of magnitude greater than the thickness of the lightning channel. Removing the volume of the inner cylinder, the outer cylinder has a volume of 311 m^3. Concentrations of ice crystals in clouds have been measured in the range between 0.01 crystals per liter to 100 crystals per liter, or between 10 and 10^5 crystals per cubic meter. This would give a number of adsorbing ice crystals ranging between 3.11×10^3 and 3.11×10^7. The wide variance in ice crystal concentration is needed to account for all possible situations within a thunderstorm. Ice water content varies by two orders of magnitude within stratiform clouds (Vidaurre and Hallett, 2009); the difference is expected to be even larger in thunderstorm clouds. This is partly due to the difference in ice water content in supercooled water-rich updrafts and ice-rich downdrafts (Hallett, 1999). Given the total number of nitrogen atoms formed from dissociating nitrogen molecules in the lightning channel, this gives a number of nitrogen atoms per ice crystal between 7.9×10^{18} and 7.9×10^{22}.

This number needs to be compared to the total number of surface sites available on an ice crystal. The first step in determining the number of surface sites is to calculate the surface area of a dendrite. Rogers and Yau (1989, p. 167), when looking at the growth of a dendrite through the ice-crystal process, start with a crystal mass of 10^{-8} g and show it growing to 10^{-4} g. This gives a radius of 1.62×10^{-3} cm, or 1.62×10^{-5} m, growing to 1.62×10^{-1} cm, or 1.62×10^{-3} m.

However, a dendrite is clearly not a sphere. Based on the picture in Fig. 2, a dendrite can be approximated by three intersecting cylinders, each having a length equal to twice the radius of the circumscribing sphere, or 3.24×10^{-5} m. The radius of each cylinder can be derived from the mass of the ice crystal. Assuming ice-I to have a density of 0.92 g cm^{-3}, the volume of the crystal will be 1.09×10^{-14} m^3. The total surface area of this approximated dendrite will be 3.65×10^{-9} m^2 (de Pater and Lissauer, 2001). Given the more complicated geometry of a dendrite, this is likely an underestimate of dendrite surface area.

Ice-I, the common form of ice that occurs at temperatures and pressures present in Earth's troposphere, has a tetrahedral structure with each oxygen atom surrounded by four other oxygen atoms arranged as the vertices of a tetrahedron (Laidler et al., 2003). Based on this structure, let us assume that the number of water molecules on the outer surface will equal the number of surface sites upon which nitrogen atoms can be adsorbed. With the separation between water molecules equal to 0.276 nm in ice-I, each dendrite will contain 4.74×10^{10} surface sites, far fewer than the number of nitrogen atoms available for adsorption. Since a smaller dendrite radius was chosen, the upper estimate of ice crystal density, 3.11×10^7 crystals will be used. This results in an estimate of 1.47×10^{18} surface sites, or 2.45×10^{-6} moles of surface sites, available around the lightning channel for adsorption of nitrogen atoms, as compared to 7.9×10^{18} nitrogen atoms available for adsorption (Laidler et al., 2003). The total number of surface sites containing nitrogen atoms will be given by the concentration of nitrogen atoms at that temperature.

The initial concentration of oxygen atoms is another variable affecting NO production rates. The fraction of oxygen molecules in a lightning discharge channel dissociated into oxygen atoms will be temperature dependent. Similarly, the fraction of the nitrogen molecules will also be temperature dependent. Let us assume that at $t = 0$ s, all initial dissociation of nitrogen and oxygen molecules has already taken place.

With this in mind, the concentration of NO depends on the rate of dissociation and recombination of oxygen between molecules and atoms, given by k_2 and k_{-2}, and on two more sets of reaction steps, which are different for the catalyzed and uncatalyzed reaction mechanisms. For the uncatalyzed reaction, the other reaction steps are the dissociation and recombination of nitrogen between molecules and atoms, with rates k_1 and k_{-1}, the combination of nitrogen and oxygen atoms into NO with rate k_3, and the reverse reaction which is the breaking up of NO into nitrogen and oxygen atoms with rate k_{-3}. For the catalyzed reaction, the second reaction step involves free nitrogen atoms striking the adsorbed nitrogen atoms to form nitrogen molecules, with rate k_4, and the dissociation of nitrogen molecules to form adsorbed nitrogen atoms, with rate k_{-4}. The third reaction step will involve the combination of adsorbed nitrogen atoms with free oxygen atoms to form NO, with rate k_5, and the breaking up of NO to form free oxygen atoms and adsorbed nitrogen atoms, with rate k_{-5}. Further, the reactions for uncatalyzed NO production as well as the adsorption and desorption rates, given by k_6 and k_{-6}, must be considered. To simplify the equations dictating the kinetics of these reactions, the steady state approximation is employed. For both the uncatalyzed and catalyzed reaction, $d[\mathrm{N}]/dt = 0$ for temperatures below 5000 K is the approximation used.

$$N_2 \rightarrow 2N \tag{R1}$$

$$O_2 \rightarrow 2O \tag{R2}$$

$$N + O \rightarrow NO \tag{R3}$$

$$H_2ON + N \rightarrow N_2O + N_2 \tag{R4}$$

$$H_2ON + O \rightarrow H_2O + NO \tag{R5}$$

$$H_2O + N \rightarrow H_2ON \tag{R6}$$

To account for the variability in NO production rates due to temperature, temperatures of 2000 K, 3000 K, and 4000 K were used, all within the temperature range for which the steady state assumption is valid. The surface of the ice crystal was assumed to remain at 260 K, since any heat released by adsorbing nitrogen atoms would be spread throughout the crystal. At this temperature adsorbed nitrogen is continuously being removed as N_2 and NO, while new nitrogen atoms are continuously being adsorbed (Silberberg, 2003).

5 Results and discussion

For the uncatalyzed reaction, the rate of NO production is given by

$$d[\mathrm{NO}]/dt = k_1[\mathrm{N_2}] - k_{-1}[\mathrm{N}]^2 \tag{1}$$

It might seem counterintuitive at first that the rate of NO production doesn't depend on the concentration of oxygen atoms. However, the concentration of oxygen atoms far exceeds the concentration of nitrogen atoms over the temperature range in consideration. Therefore, nitrogen atoms are the limiting reagent. Direct integration gives

$$[\mathrm{NO}] = (k_1[\mathrm{N_2}] - k_{-1}[\mathrm{N}]^2) \times t \tag{2}$$

assuming zero production of NO at $t = 0$ s. This equation is limited by not taking into account the limited availability of nitrogen atoms, but gives useful information about NO production. For a time interval of 50 ms, a constant temperature of 2000 K gives a total NO concentration of 9.92×10^{-6} mol m^{-3}. Increasing the temperature to 3000 K increases the production rate of NO such that the total number of available nitrogen atoms is converted to NO in 2.60×10^{-6} s. At 4000 K, NO production rates are the greatest (Table 2 and Fig. 3), in agreement with Picone et al. (1981). It should again be noted that total conversion of nitrogen atoms does not imply total conversion of all nitrogen to NO; the quantity of NO produced is limited by the dissociation of nitrogen molecules.

For the catalyzed reaction, the rate of NO production is given by an exponential relationship:

$$\begin{aligned}[\mathrm{NO}] = {} & \exp[-((k_{-5}-k_5)\times[\mathrm{H_2O}]\times t)] + \Big(k_1[\mathrm{N_2}] - k_{-1}[\mathrm{N}]^2 \\ & + k_{-4}[\mathrm{H_2O}][\mathrm{N_2}] - k_4[\mathrm{HOH-N}][\mathrm{N}]) + k_{-6}[\mathrm{HOH-N}] \\ & - k_6[\mathrm{H_2O}][\mathrm{N}]/(-((k_{-5}-k_5)\times[\mathrm{H_2O}]))\end{aligned}$$

At a constant temperature of 2000 K, all the available nitrogen in the cylinder around the lightning channel is converted to NO in 3.77×10^{-7} s. Thus, catalytic production of NO is significantly greater than uncatalyzed production at this temperature (Table 2). At 3000 K, all the nitrogen atoms are converted to NO in 2.81×10^{-7} s, also indicating more rapid NO production from the catalyzed reaction steps at this temperature. At 4000 K, consumption of NO occurs, and in fact any NO existing at 4000 K will be consumed; as a result, the concentration of NO will drop to zero. Thus, temperatures that favor rapid NO production without ice crystals adsorbing nitrogen atoms are unfavorable for NO production in the presence of ice crystals.

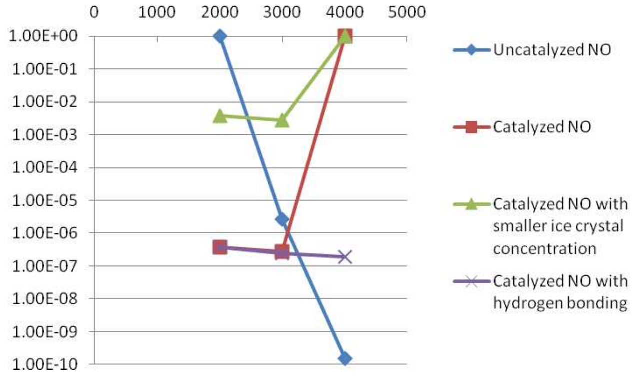

Fig. 3. Same as Table 2, but plotted on a logarithmic scale. Temperature is the independent variable and time the dependent variable. For simplicity temperatures consuming NO are depicted as taking a large amount of time to produce NO.

This consumption by the catalytic reaction steps at 4000 K occurs as a consequence of Le Chatelier's principle. At temperatures above 3290 K, N + O is favored over NO in reaction three. As a result, the adsorption of nitrogen atoms onto ice crystals shifts the equilibrium position toward the reactants, consuming NO. At 2000 K NO is thermodynamically favored over N + O, and this effect is small.

As shown by Uman (1984), on average, temperatures fall to 4000 K in 10 ms, to 3000 K in 20 ms, and to 2000 K in 50 ms, assuming a channel radius of 1 cm. It should be noted that recent results of Walker (2010) indicate that every lightning channel has a unique temperature profile. Setting the lightning channel temperature equal to the values in the graph shown in Uman and Voshall (1968) for a channel radius of 1 cm, the channel spends about 3 ms at 4000 ± 200 K, about 8 ms at 3000 ± 200 K, and about 15 ms at 2000–2200 K. Extrapolating the graph one might assume up to 10 ms are spent in the range 1800–2000 K. Since uncatalyzed NO production at 4000 K is 1000 times faster than catalyzed production at 2000 K, one might assume that ice crystals actually serve to reduce the amount of NO produced. However, both uncatalyzed production at 4000 K and catalyzed production at 2000 K are converting all the available nitrogen atoms in the cylinder to nitric oxide, which would imply equal NO production from the catalyzed and uncatalyzed processes. This is true within the range of ice parameters (concentration, mass, capacitance) that converts all available nitrogen atoms to nitric oxide.

Table 2. Time for NO to be produced from all available nitrogen atoms for catalyzed and uncatalyzed reaction mechanisms at 2000, 3000 and 4000 K. Numbers indicate how quickly equilibrium NO concentration is obtained.

Temperature	Uncatalyzed NO	Catalyzed NO	Catalyzed NO with smaller ice crystal concentration	Catalyzed NO with hydrogen bonding
2000 K	Limited production	3.77×10^{-7} s	3.76×10^{-3} s	3.76×10^{-7} s
3000 K	2.60×10^{-6} s	2.81×10^{-7} s	2.81×10^{-3} s	2.50×10^{-7} s
4000 K	1.49×10^{-10} s	NO consumption	NO consumption	1.9×10^{-7} s

This is where the long residence time at 2000 K becomes important. Bhetanabhotla et al. (1985) proposed a mixing time of 10 ms in the lightning channel. At 4000 ± 200 K there is insufficient time to mix fresh air into the cylinder, and NO production is roughly limited to the available nitrogen in the cylinder. At 2000 ± 200 K the channel has 2.5 mixing times to bring in fresh air. With the continued consumption of all available nitrogen, catalyzed NO production is expected to be 3.5 times the amount we calculated in the cylinder (from the original nitrogen atoms available plus the extra nitrogen molecules mixed in and dissociated), while uncatalyzed NO production at 4000 K would only be 1.3 times the amount calculated for the cylinder. Both catalyzed and uncatalyzed production at 3000 K consumes all available nitrogen atoms, so there would not be a difference in NO produced from the processes at this temperature. Therefore, using the temperatures 2000, 3000, and 4000 K, ice crystal catalysis is expected to produce $3.5/1.3 = 2.7$ times more NO than if ice crystals were not present.

Using the smaller ice crystal density of 10 crystals per cubic meter dramatically reduces the catalyzed production of NO at 2000 K and 3000 K. At 2000 K, the catalyzed NO production consumes all the available nitrogen in 3.76×10^{-3} s, four orders of magnitude more slowly than with a higher ice crystal density. At 3000 K, catalyzed NO production consumes all available nitrogen in 2.81×10^{-3} s, also four orders of magnitude more slowly than with the higher ice crystal density. In fact, uncatalyzed production of NO will occur more quickly than catalyzed production at 3000 K, due to the lower temperature of adsorbed nitrogen atoms (260 K). At 4000 K, the catalyzed consumption rate decreases by four orders of magnitude.

Using Roger and Yau's (1989, p. 168) upper limit ice crystal of mass of 10^{-4} g, an increase in mass of four orders of magnitude increases the dendrite surface area by three orders of magnitude. This will have the same effect as increasing the ice crystal density by three orders of magnitude. Setting the crystal density as a constant, catalyzed NO production rates are three orders of magnitude higher for the larger dendrites than for the smaller dendrite size, at both 2000 K and 3000 K. At 4000 K, the rate of consumption by the catalytic reaction mechanisms will increase by four orders of magnitude.

Yet another uncertain assumption concerns the nature of the nitrogen-hydrogen surface bond. Let us assume a hydrogen bond instead of a chemical bond. The enthalpy and entropy of breaking this bond can be calculated from the properties of vaporization of ammonia. At 260 K only about three of every seven surface sites will contain adsorbed nitrogen, at equilibrium (Shriver and Atkins, 1999).

Using a hydrogen bond model does not significantly affect catalytic NO production at 2000 K, with all available nitrogen atoms consumed in 3.76×10^{-7} s. At 3000 K, NO production consumes all available nitrogen atoms in 2.50×10^{-7} s, also roughly the same as for a chemical bond. The most significant difference occurs at 4000 K. Instead of NO consumption, all the available nitrogen atoms are consumed for NO production in 1.9×10^{-7} s. This production rate is still slower than for uncatalyzed NO production. It is assumed that the equilibrium shift for NO is still hindering the catalytic reaction mechanisms at 4000 K.

Having established the role of ice crystals in NO_x production, the next step is to determine the relative effect of this process on cloud to ground (CG) versus intracloud (IC) lightning. In Koshak et al. (2010) the region of greatest NO_x production in CG lightning is around 5 km above the surface, while in IC lightning it is 10 km above the ground. Vidaurre and Hallett (2009) note that a mix of supercooled water and ice may exist in clouds with temperatures down to −40 °C. Since 5 km is much warmer than −40 °C in the standard atmosphere, while 10 km is cooler than −40 °C, it is expected that ice plays a greater role in IC NO_x production than CG NO_x production.

If experiments were to confirm the catalytic reaction steps outlined above, then it would be clear that theories of NO production based solely on the presence of nitrogen and oxygen molecules would result in underestimates of total NO production. A laboratory study would need to simultaneously grow ice in a confined chamber and produce electrical discharges in the near vicinity of the chamber-grown ice. Current methods of growing ice crystals in the laboratory involve a glass thread as a growth substrate suspended vertically (Peterson et al., 2010) or horizontally (Petersen et al., 2006). Both are incompatible with the method used for creating discharges in a confined chamber (Peterson et al., 2009); the shock wave is expected to destroy the glass thread, thus removing ice crystals from the region of interest. Experimental verification must therefore wait for new methods of growing laboratory ice.

6 Conclusions

It is reasonable to conclude that NO_x may be produced in the atmosphere through a wide variety of reaction mechanisms. High temperatures, such as those present in lightning, may dissociate N_2 and start the process of NO_x formation. It is hypothesized that ice crystals, if present in the region of a lightning discharge channel, could play a catalytic role in the formation of NO_x, and so would increase the production of NO_x species. Rates of production for NO, both with and without ice crystal catalysis, are compared for constant temperatures of 2000 K, 3000 K, and 4000 K over 50 ms. Ice crystal catalysis is expected to produce 2.7 times more NO than if ice crystals were not present.

At 2000 K ice crystals play a catalytic role, increasing NO production many times over rates seen in the absence of catalysis. At 3000 K ice crystals also catalyze NO production, but by only one order of magnitude above the uncatalyzed NO production. At 4000 K NO is consumed in the catalyzed reaction, while it is produced at a rapid rate by the uncatalyzed reaction steps. The production rates are strongly dependent on both the ice crystal mass and number density. The nature of the nitrogen-hydrogen bond does not significantly affect catalyzed NO production at 2000 or 3000 K, but assuming a hydrogen bond rather than a chemical bond results in production rather than consumption of NO at 4000 K.

Since the lightning channel spends more time at lower temperatures, it is reasonable to speculate that the catalytic production mechanisms win out, producing more NO than the uncatalyzed reaction. However, it appears that the difference in total production is not enough to account for the differences in CG and IC lightning NO_x production ratios reported in previous studies. It may be that additional ice crystal mechanisms affect lightning NO_x production or that more detailed modeling of the processes than attempted here might yield different results.

As future spectroscopic measurements of lightning temperature are gathered, an average channel temperature as a function of time will be obtained. With this information, the total NO production over the duration of the lightning event may be determined, so that better estimates of the total increase in catalyzed NO production over uncatalyzed production per flash may be possible.

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