Atmos. Chem. Phys. Discuss., 11, C7134–C7142, 2011
www.atmos-chem-phys-discuss.net/11/C7134/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Possible catalytic effects of ice particles on the production of NO_x by lightning discharges" *by* H. S. Peterson and W. H. Beasley

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Received and published: 29 July 2011

We would like to thank both reviewers for their efforts in reading our paper and in making suggestions for improvements to the paper's content. Our interpretation of the reviewers' main comments is that they both recommend publication of a revised version of our paper, which we are willing and able to work toward.

Responses to the first reviewer:

Many experiments make use of nitrogen chemisorption- the similarity between ammonia and water made the Klimisch (1975) study the most relevant to our work. Some of the others include Shinn (1990), Wovchko and Yates (1996), and Ertl et al. (1979), the latter also a study of ammonia synthesis.

Regarding comment 12652 L2-4, dendrites have the greatest surface area per unit mass, and therefore are the habit with the greatest potential for surface adsorption. Furthermore, dendrites are formed at a temperature of -18° C, which closely matches the temperature of the N-region of thunderstorms. According to the results presented in Koshak et al. (2010), this is the region with the greatest amount of lightning NOx production.

In comment 12653 L16, the reviewer correctly interprets our conclusion that ice crystals in the hot core of the lightning channel are unlikely to survive. This is the reason for invoking the concentric cylinder model for catalyzed NOx production: a hot, ice-free inner core and a cooler outer core containing ice crystals. In response to the reviewer's question about section 3, there will easily be enough ice crystals in the outer cylinder to catalyze NOx production.

The reviewer requests a plot showing which ice crystal habits are common in regions where lightning is occurring. A comprehensive study of ice crystal habit as a function of temperature, pressure and ice supersaturation may be found in Bailey and Hallett (2009). Similarly, Koshak et al. (2010) shows a frequency plot of lightning segments as a function of altitude. These two plots may be combined to determine where ice crystals occur in relation to lightning-active regions of thunderstorms. As mentioned earlier, dendrites are expected where lightning NOx production is greatest.

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).

Unfortunately, a PDF of ice crystal surface area was not found in the literature. Therefore, Figure 2 is used as a substitute to indicate the reasonableness of our three cylin-

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Interactive Discussion

Discussion Paper

der model of a dendrite.

The reviewer had several questions relating to the change in temperature over time within the lightning channel. A plot of temperature decrease over time in the lightning channel as requested by the reviewer is not easily obtained. Using another person's plot is unavoidable as this research is theoretical in nature and did not involve obtaining direct measurements of lightning. Daniel Walker is working directly with Bill Beasley, so his plot was a natural choice for this paper. Uman and Voshall (1968) modeled the decay of the central temperature for varying channel radii, with an initial central temperature of 8000 K. 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 (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 1969). Finally, the degree of dissociation of nitrogen and oxygen molecules is dependent not only on the central lightning channel temperature, but the radial distribution of temperature away from its center. The purpose of Figure 1 is to illustrate this variability in temperature between lightning channels, which would extend to the temperatures invoked in this study.

Having acknowledged the variability in lightning channel properties, we calculated NO production for a lightning channel 1 cm in radius, with the assumption that temperature was spatially uniform within the channel. Toward this end we employed the hot-channel model of lightning NOx production rather than the shock-wave model, in agreement with Rakov and Uman (2003). Outside the channel the temperature was assumed equal to the ambient atmosphere. 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.

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.

Having established the role of ice crystals in NOx 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 NOx 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 NOx production than CG NOx production.

We are agreeable to adding columns to Table 2 for catalyzed NOx production under differing assumptions, namely the larger ice crystal mass and the presence of hydrogen bonds. This information could also be incorporated into a summary plot with temperature on the x-axis and a measure of production rate on the y-axis.

Finally, the reviewer asks about experiments needed to verify this model. A laboratory study would need 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.

Rather than include a direct reference to the first paper explaining the role of nitric oxide in ozone formation/depletion, the reviewer is encouraged to look up this information in the paper we cited.

There are three references to Rogers and Yau (1989) (12653 line 6, 12654 line 17, and 12656 line 8). The first reference points to the discussion on pages 159-160 concerning ice crystal growth rate. The second reference is for Figure 9.6 on page 163. The final reference uses 10-8 g as a starting point for dendritic growth, in text on page 167 and in figure 9.8 on page 168. Figure 9.8 also shows the crystal growing to 10-4 g, prompting this alternate mass as a choice for our sensitivity study. It is not standard practice to

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Interactive Discussion
Discussion Paper

include this information in an article, but we are willing to do so if the editor so wishes.

"No more than 12% of nitrogen" comes from a calculation of the concentration of nitrogen molecules assuming air is 78% nitrogen, and comparing the relative concentration of nitrogen atoms to nitrogen molecules. An equation is unnecessary for conveying this information, but it may be added to the text of the article.

"Figure 13" should be "Figure 2". Other spelling changes by the reviewer are also accepted.

The statement on page 12659 lines 17-19 may be added to the abstract as the second to last sentence.

The equation on page 12659 is derived from equations R1-R6, the Eyring equation, and the adsorption isotherm.

Responses to the second reviewer:

The abstract of our paper suggested, though not explicitly, that our study is theoretical in nature. Certainly it may be revised to add this information.

The nature of the revision requested for 12650 line 21 is unclear. It is already clear from the citation that the review study by Schumann and Huntrieser is being referenced. The same response applies for line 22.

Regarding the comment for 12651, lines 23 and 24, the reviewer has correctly deduced the higher availability of oxygen atoms during the formation of nitrogen oxides. At a first glance one might surmise that nitrogen atoms should be more abundant given the relative abundances of nitrogen and oxygen molecules. However, the stability of the nitrogen- nitrogen triple bond must also be considered. Atomic nitrogen is stable at temperatures well below the peak temperatures in the return stroke. Molecular nitrogen has an enthalpy and entropy of formation of 0 kJ/mol and 191.609 J/mol×K, respectively, with a margin of error in entropy of 0.004. Atomic nitrogen has an enthalpy and entropy of formation of 472.68 kJ/mol and 153.301 J/mol×K, with margins of error of 0.40 kJ/mol and 0.003 J/mol×K, respectively. Recombination of nitrogen atoms is thermodynamically favorable at temperatures below 8221 K. Atomic oxygen is stable at even cooler temperatures than atomic nitrogen. Molecular oxygen has an enthalpy and entropy of formation of 0 kJ/mol and 205.152 J/mol×K, with an uncertainty of 0.005 J/mol×K in the entropy of formation. Atomic oxygen has an enthalpy and entropy of formation of 249.18 kJ/mol and 161.059 J/mol×K, with uncertainties of 0.10 kJ/mol and 0.003 J/mol×K, respectively. While recombination of oxygen atoms is thermodynamically favorable at temperatures below 4260 K. For the range of temperatures considered in this study, oxygen atoms are more plentiful than nitrogen atoms, which may be verified using the numbers given in this paragraph and the equations for Gibbs energy.

It is not clear which thunderstorm variables the reviewer is inquiring about. Diffusion and transport of nitrogen oxides are not considered in this study, only initial production.

As mentioned in the comments to the first reviewer, 10-8 and 10-4 g are taken from a figure in Rogers and Yau (1989) to be a reasonable range of possible dendrite masses within the thunderstorm cloud.

In equation R4, H2O is the ice crystal surface; as a catalyst, hydrogen is not a product of the reaction. The equation stands as is.

The derivation of equation 3 is explained in the comments to the first reviewer (final paragraph of comments), as well as the conclusion on page 12661 lines 26-7, which constitute the large majority of the response to the first reviewer. We were glad for the opportunity to explain this calculation in greater detail, and intend to include this explanation in the final version of the paper.

The changes to Table 1 and other spelling errors/typos are accepted (12651 Section 2 heading, 12656 line 5, and 12657 line 1). Separately, the value for Huntrieser's 2002 study in Table 1 is to be increased by 104. Heidi Huntrieser has also provided results from a more recent study, which we wish to include in the final version of Table 1.

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Interactive Discussion

Discussion Paper

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