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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Atmospheric pseudohalogen chemistry" *by* D. J. Lary

D. J. Lary

Received and published: 9 November 2004

Thank you for taking the time to read and comment on the paper. I appreciate your time and effort.

Reviewer comment:

> '*The author re-examines the importance of HCN in atmospheric chemistry. I have major concerns with this article. The author lists a number of speculative ideas without providing any convincing support for them or following the arguments through to demonstrate even in a semi-quantitative way that HCN is indeed relevant as a tracer for lightning, sink for NOy (through NCO photolysis) or a potential source of NOy and ozone.*'

Reply: Thanks. Even if it turns out that HCN is not as important as it may first seem, this is still the first time that the atmospheric chemistry of CN and NCO is described. The previous studies have focussed on HCN and the chemistry of the radicals CN and NCO

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have not been to the fore. As for no convincing support I would naturally not agree. I have now added to the paper a vertical profile showing a clear 'C' shaped profile which is a typical signature of the involvement of convection. In addition, the phrasing of the article suggests the possible roles and how this can be tested, for example the 'C' shaped profile. With the recent launch of the Canadian ACE instrument (in the heritage of ATMOS) we should soon see a lot of HCN, NOx and NOy data in the vicinity of tropical convection to further examine this issue. It is therefore timely to have such an article.

Reviewer comment:

> '***1. HCN as a tracer for lightning***
> *The author speculates that HCN might be produced in lightning and that because of its much longer lifetime compared to NOx, it could thus be used as a tracer for lightning. This is an intriguing idea. A lightning source for HCN has been proposed for planetary atmospheres. The question is whether such a source exists and is large enough in the Earth's atmosphere to rival with other known sources of HCN. The main evidence proposed by the author is a scatter plot of NOx and HCN observed by ATMOS. I agree with the second reviewer that Figure 2 is not convincing. Out of 1000 points only 6 points seem to display a positive correlation of high NOx and HCN. This could be a coincidence. If anything, the bulk of the points display a negative correlation between these two species.'*

Reply: Thanks. A more convincing plot has now been added. It is a shame that this discussion forum does not allow the inclusion of figures or i would include it here. It is not really surpassing that only 6 of the ATMOS profiles were near convection as ATMOS did not target the tropics and the missions were each very short. What is interesting is that each of the six profiles with HCN were in costal regions which were cloudy and lightning was a possibility. The various space borne platforms that now

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observe lightning routinely were not available during he ATMOS missions. However, we should soon be able to revisit this as mentioned above with data from the ACE instrument. For the points not associated with lightning one would not expect a positive correlation with HCN and NOx so it is not surprising that the bulk of the points do not display a positive correlation between these two species.

Reviewer comment:

> '*Furthermore the observed NOx mixing ratios are unrealistically high: 10-100 ppbv (Figure 2, second panel). In situ observations close to thunderstorms rarely show mixing ratios larger than a few ppbv [Ridley et al., JGR, 101, 1996; JGR, 109, 2004; Brunner et al., JGR, 106, 2001 - just to cite a few]. It is then hard to believe that ATMOS would be able to observe such large concentrations. In addition, it is unclear what altitude range is used for the data displayed in Figure 2. Are stratospheric observations included, or only upper tropospheric observations? Are there other observations (CO, NMHCs?) that would eliminate other sources of NOx and HCN such as convective transport of surface emissions to the upper troposphere? Looking at the NOy HCN correlation might be a better test of the lightning hypothesis, as NOy has a longer lifetime than NOx (one would expect to find more points with high HCN and NOy in the ATMOS data).*'

Reply: Thanks. You are right the NOx values are high, yet that is what ATMOS reported, you can get the data for yourself and see. Maybe this is a suggestion that another source is involved as well as lightning, or even instead of lightning. For example, maybe biomass burning is producing the NOx and the HCN. However, then why would we get the 'C' shaped profile typical of lightning produced species shown in the new figure now included in the paper? ATMOS does also observe CO, the problem is that not all ATMOS profiles have observations of all constituents, this is another improvement with ACE. Your idea of using CO is a good one and I look forward to being

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able to follow this up with the ACE data when it becomes available. Thanks! The difficulty with the NOy is that not all the nitrogen species are available over all the profile so getting a reliable NOy is not easy.

Reviewer comment:

> '*Even if the author were to use Figure 2 at face value, he could infer a lightning source based on the observed NOx/HCN ratio (about 300) in the supposed lightning plumes. Given a global lightning NOx source of 1-10 TgN/yr, this would imply a lightning HCN source of 0.003-0.03 TgN/yr which is a factor of 20-100 smaller compared to the source from biomass burning. This would suggest that HCN would not be a useful tracer for lightning.*'

Reply: Thanks. The point is that if HCN is produced by lightning it as useful as a local lightning tracer as it is not soluble and long-lived. The shape of its profile can help us examine the vertical distribution of the lightning. This aspect is not affected even if biomass burning is in total much more important for the total amount of HCN. You are probably right that biomass burning produces more HCN in total, however this is a surface source. If lightning is producing HCN it is being produced in the free and upper troposphere as well.

Reviewer comment:

> '*The author uses figure 1 as another piece of evidence that there might be a lightning source of HCN in the upper troposphere. Some of the HCN data for 1993 looks somewhat strange with large levels in the lower stratosphere (1 ppbv, factors of 2-5 larger compared to other years) and very low levels in the upper troposphere (50 pptv).*'

Reply: Thanks. You are right those points do look strange. I did not use those in any

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of the conclusions drawn in the paper. I guess that is a question for the ATMOS team not me!

Reviewer comment:

> '*Finally, in situ observations of HCN (Singh et al. 2003, Li et al. 2003) do not show a "C" shaped profile for HCN, which would be expected if lightning were a significant source. On the contrary, the HCN mixing ratios are uniform vertically and decrease near the surface because of ocean uptake.*'

Reply: Thanks. If the Singh et al. profiles are not near currently active convection/lightning there will not be a C shaped profile. However, Figure 2 of Singh et al., In situ measurements of HCN and CH3CN over the Pacific Ocean: Sources, sinks, and budgets, JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES 108 (D20), 2003 (the reference I assume you mean) does show several high values of HCN around 8 to 10 km. The ratio of high HCN values to low HCN values shown by Singh et al. is very similar to that observed by ATMOS. So I can not see how this undermines what is presented in our paper. In fact, a charitable eye may see a 'C' shaped profile in Singh et al.'s figure 2. The top of the C at around 8 km the bottom of the C around 3 km.

Reviewer comment:

> '***2.HCN as a source of N atoms***
> *I fail to see the relevance of increased N production in the troposphere when considering the photolysis of NCO (section 2.3 and figure 4b.). How important would this be as a sink for NOy compared to the main sink for NOy in the troposphere: formation of HNO3 and followed by rainout/deposition? I suspect that it would be very small and thus of no significance for the troposphere. Increased N atom concentration could in- fluence the strato-*

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spheric sink of NOy, but the authors demonstrate that HCN chemistry does not affect N atoms in the stratosphere.'

Reply: Thanks. It probably is a small contribution. However, it was presented as an interesting fact as other than NO photolysis this is the only source of N atoms that I know of. There is surely a value in presenting new information even if it is not the most stunning. May I please suggest that your generally caustic tone was perhaps rather unnecessary.

Reviewer comment:

'***3. Atmospheric CNx chemistry***
Section 3 of the paper is confusing and the relevance of CNx chemistry is not clearly demonstrated, in my opinion. For example the author suggests that HCN oxidation could be a source of NOx and ozone in the troposphere, but he does not quantify this source using the known (or estimated) rate constants and compare them to the other known sources of NOx and ozone in the troposhere. It seems that this would be a simple exercise.'

Reply: Thanks. The aim of the paper was to give an overview of pseudo halogen chemistry and not as the final word in quantifying every aspect of the chemistry and its impact. I do not really see anything unclear at all in pointing out that the slow oxidation of HCN leads to NOx production. The quantification of the NOx source would be an interesting avenue of further study. However, I must say I do think that you have been over critical as this paper was not a paper on NOx sources.

Reviewer comment:

'*Section 3.1. is repetitive and confusing: the author mentions the fact that Cicerone and Zellner (1983) and Brasseur et al. (1985) failed to reproduce*

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observed stratospheric HCN profiles, without saying the sign of the discrepancy. This is repeated twice in the same section (page 5390 and 5391). If I follow the argument, it seems that the author argues that HCN does not photolyze in the lower stratosphere and thus these previous studies (which did assume HCN photolysis) were underestimating the observations because of this. What would be the quantitative effect of excluding photolysis? Would models be able to reproduce the observations in the stratosphere?'

Reply: Thanks. The repetition has been edited. My model seemed able to reproduce the stratospheric observations.

Reviewer comment:

'*page 5385. line 14. "We suggest that it is timely to compile HCNO emission inventories". This has been done recently by a number of authors, in particular Li et al. [2003] and Singh et al. [2003].'*

Reply: Thanks. You are right, I prepared the text of this section a while back before the Singh paper came out. The sentence has been deleted.

Reviewer comment:

'*page 5386. line 18. "... exactly what ATMOS observed (ATMOS)". Is there a typo or missing reference?'*

Reply: Thanks. It is neither, the reference is given in the bibliography on page 5395 it is the ATMOS web site where the data can be downloaded http://remus.jpl.nasa.gov.

Reviewer comment:

'*Figure 1. Why does the author use a log scale for HCN on Figure 1? Given the range of HCN mixing ratios, a linear scale might be more appropriate. I*

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would also suggest using the same scale for both NOy and HCN in order to allow a comparison of the values - which is what the author seems to want the reader to do, but is difficult to do right now.'

Reply: Thanks. The top axis accidently had the wrong range. This has now been fixed. Both HCN and NOy are plotted on the same log scale shown at the bottom.

Thank you for taking the time to read and comment on the paper. I appreciate your time and effort.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5381, 2004.

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