

Interactive comment on “Atmospheric pseudohalogen chemistry” by D. J. Lary

Anonymous Referee #1

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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 NO_y (through NCO photolysis) or a potential source of NO_y and ozone.

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 NO_x, 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 NO_x and HCN observed by ATMOS. I agree with the second reviewer that Figure 2 is not convincing. Out of 1000 points only 6

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points seem to display a positive correlation of high NO_x and HCN. This could be a coincidence. If anything, the bulk of the points display a negative correlation between these two species.

Furthermore the observed NO_x 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 NO_x and HCN such as convective transport of surface emissions to the upper troposphere? Looking at the NO_y/HCN correlation might be a better test of the lightning hypothesis, as NO_y has a longer lifetime than NO_x (one would expect to find more points with high HCN and NO_y in the ATMOS data).

Even if the author were to use Figure 2 at face value, he could infer a lightning source based on the observed NO_x/HCN ratio (about 300) in the supposed lightning plumes. Given a global lightning NO_x 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.

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).

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.

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On the contrary, the HCN mixing ratios are uniform vertically and decrease near the surface because of ocean uptake.

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 NO_y compared to the main sink for NO_y 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 influence the stratospheric sink of NO_y, but the authors demonstrate that HCN chemistry does not affect N atoms in the stratosphere.

3. Atmospheric CN_x chemistry

Section 3 of the paper is confusing and the relevance of CN_x chemistry is not clearly demonstrated, in my opinion. For example the author suggests that HCN oxidation could be a source of NO_x 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 NO_x and ozone in the troposphere. It seems that this would be a simple exercise.

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 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?

Minor comments

page 5385. line 14. "We suggest that it is timely to compile HCNO emission invento-

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ries". This has been done recently by a number of authors, in particular Li et al. [2003] and Singh et al. [2003].

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

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 would also suggest using the same scale for both NO_y 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.

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

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