

Interactive comment on “Observation of isoprene hydroxynitrates in the Southeastern United States and implications for the fate of NO_x” by F. Xiong et al.

Anonymous Referee #1

Received and published: 28 July 2015

General comments

This manuscript describes environmental chamber experiments and field measurements aimed at determining the role of hydroxynitrates (INs) in the photooxidation of isoprene. Despite intense effort over the years to determine the extent of IN formation from isoprene, significant uncertainty in the branching ratio remains to be resolved. The authors use a GC-ECD/CIMS combined method, which allows for a method to estimate the isomer-specific yields even in the absence of authentic standards for some of the isomers. One of the main findings of the work is that the dominant isomer, 1,2-IN, is susceptible to hydrolysis in the presence of water, which affects the detection sen-

C5313

sitivity, and thus may bias some previous measurements towards an erroneously low overall branching ratio. Because the overall branching ratio is determined to be larger than previous GC-based measurements, the authors also speculate that GC sensitivity for 1,2-IN may have been overestimated. These are significant new insights into the problem of inconsistent branching ratio reports in the literature. The authors then go on to analyze the diurnal cycle observed during the SOAS field campaign and find that the isoprene oxidation was NO-limited, and that the oxidation could be described as being in the “high NO” limit during the morning and the “low NO” regime during the afternoon. Interesting conclusions about the diurnal interplay of IN production and loss processes, including the effects of transport, add value to the significance of the work. The work has been carefully planned and executed, and the manuscript is clearly written. For these reasons, this study is quite appropriate for Atmospheric Chemistry and Physics.

Specific comments

The iterative method to determine the isomer-specific branching ratios is quite critical to the accuracy of the overall analysis. While I am comfortable with the description of the very careful efforts to understand the sources of calibration errors, the manuscript would be improved with a more extended discussion of this method and the results. In particular, I am intrigued by Supplement Figure S8, which shows the model-determined isomer-specific branching ratios. While it seems to me that this figure contains very important results, I could not find a reference to this figure in the main manuscript. In particular, Figure S8 shows that there are only two significant isomers formed (1,2-IN and 4,3-IN), which is quite a different result than that reported by both the CIMS-based (Paulot et al. 2009) and GC-based (Lockwood et al. 2010) previous laboratory studies. The new finding suggests that the OH-initiated oxidation of isoprene is more regiospecific than these previous studies indicated, which is interesting (and simplifying with respect to modeling isoprene oxidation). In particular, both of the previous studies identified the various 1,4- and 4,1-HNI isomer-producing reaction pathways as having minor, yet significant, branching ratios, but Figure S8 indicates that they are very minor

C5314

products. It would be helpful to explain what part(s) of the analysis are responsible for the difference as compared to the two previous laboratory studies.

p. 17851 line 25: I'm not familiar with the scrubbing technique described here. Please provide a reference to the method and indicate what species are being removed.

p. 17853 line 3: Since the relative quantity $[IN]/([MVK]+[MACR])$ is the critical quantity being analyzed, it would be helpful to know how much the absolute quantity ($[MVK]+[MACR]$) varied in the SOAS data being analyzed here, as larger variations in the absolute value would have the potential to cause more uncertainty in the relative value. Additionally, can the absolute variations in $[MVK]+[MACR]$ be qualitatively explained according to expected changes in transport and boundary height?

p. 17863 line 4: Is the 13% branching ratio OH + HNI pathway to IEPOX under the low NO conditions a significant source of IEPOX in the afternoon, or does the modeling indicate that ISOPOOH is still the dominant precursor of IEPOX?

Technical corrections

p. 17848 line 14: What is the solvent used in the IN solutions?

p. 17851 line 14: change to "... , so wall loss correction was not applied to the IN measurements."

p. 17856 equation 2: the alpha term in this equation should be defined immediately as the nitrate branching ratio.

p. 17859 line 24: typo: "efficiency"

p. 17862 line 9: typo: "different"

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 17843, 2015.