

Using GEOS-Chem to Better Understand Isoprene Nighttime Chemistry

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Introduction

Isoprene (C_5H_8) reacts with the nitrate radical (NO_3) during the night to produce a peroxy nitrate radical. As shown below in Figure 1a, peroxy nitrate radicals can react with NO , NO_3 , RO_2 , or HO_2 to form a diverse set of nitrates [1]. The reaction with HO_2 leads to the formation of a nitroxyhydroperoxide (NISOPOOH). NISOPOOH was detected in the field during the 2009 BEARPEX campaign [2] suggesting that its formation may be a dominant pathway for the nighttime chemistry of the peroxy nitrate radicals.

Chamber experiments have shown (Figure 1b) that hydroxyhydroperoxides (ISOPOOH) will react with OH to form dihydroxyepoxides (IEPOX), that have been identified as important precursors to secondary organic aerosol (SOA) formation [3]. We hypothesize that, by analogy, NISOPOOH formed during the night would react with OH at sunrise to generate nitroxyhydroxyepoxide (NIEPOX) (Figure 1c). NIEPOX may thus be another important precursor to SOA formation.

Here, we use GEOS-Chem to evaluate the importance of the nighttime HO_2 pathway and determine how much NISOPOOH remains at the end of the night for it to react with OH at sunrise to form NIEPOX.

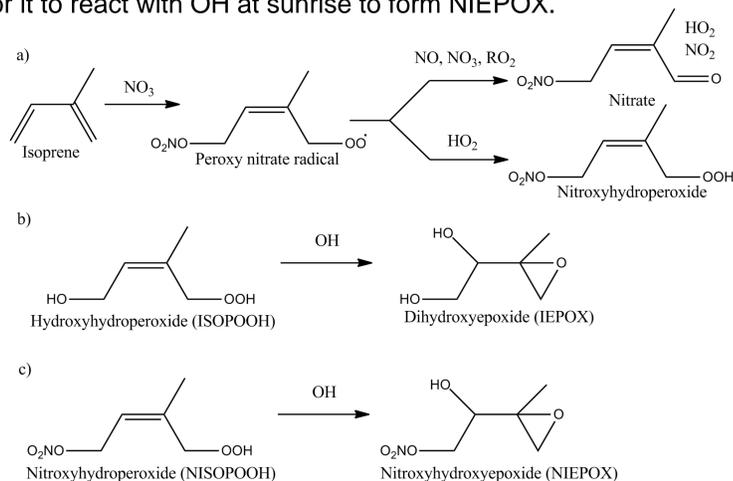


Figure 1: a) General isoprene NO_3 chemistry occurring at night. b) Known daytime formation of IEPOX. c) Proposed sunrise formation of NIEPOX

Methods

All simulations were run using GEOS-5 data, a nested grid (0.5° by 0.667° horizontal resolution and 47 vertical layers), mixing using the VDIFF scheme, isoprene emissions from the Megan inventory, and an adjusted form of the new Caltech isoprene mechanism contained in GEOS-Chem v9-01-03. This mechanism was adjusted in the following ways:

1. All $RO_2 + HO_2$ reaction rates were updated [4].
2. Isoprene NO_3 reactions were updated with a simplified version of the mechanism in the Community Multi-scale Air Quality (CMAQ) model [5].
3. A new species NIEPOX was included into the mechanism with the assumption that NIEPOX will form with similar rates and yields as IEPOX.
4. We understand that there is a diurnal phasing error in the NO_x emissions and this error likely will quantitatively alter the findings of this study.

GEOS-Chem Results

Within the GEOS-Chem framework, we find that the isoprene peroxy nitrate radical reacts dominantly with HO_2 (Fig. 2). Simulations done with CMAQ found a similar result [5]. This confirms that the HO_2 nighttime pathway is important.

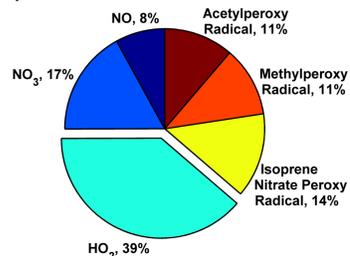


Figure 2. Proportion of the isoprene peroxy nitrate radical that reacts with HO_2 , NO_3 , NO , acetylperoxy radical, methylperoxy radical, and isoprene nitrate peroxy radical calculated from the surface to 2 km altitude during August 2006 over the United States.

GEOS-Chem simulation time traces for isoprene nitrate chemistry were compared with species detected during the BEARPEX field campaign in 2009 at a forested site northeast of Sacramento, CA to evaluate the simulations [2]. Average time profiles for ISOPOOH, IEPOX, NISOPOOH, and NIEPOX look as expected (Fig. 3). The maximum mixing ratio of NISOPOOH at BEARPEX was 44 pptv, which is less than the model predicts. The nested grid may not be providing a strong enough resolution to precisely model isoprene NO_x chemistry at this location or the NO_x emissions phasing may be important.

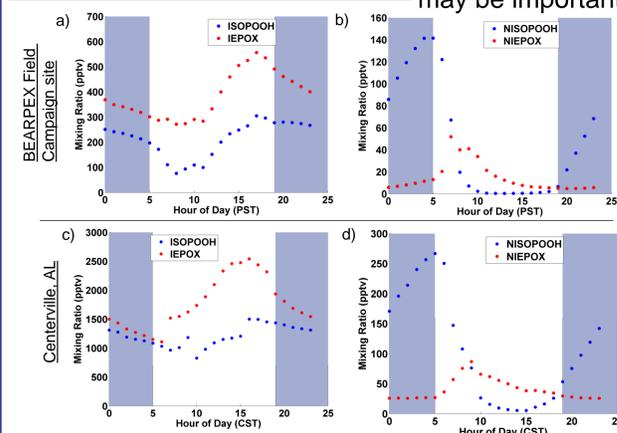


Figure 3. Simulated average daily time traces during August 2006 of ISOPOOH, IEPOX, NISOPOOH, and NIEPOX in the planetary boundary layer at the BEARPEX field campaign site (a and b) and in Centerville, Alabama where NO_3 at night is not over-predicted in the simulation (c and d).

As shown in Figure 3, GEOS-Chem simulations suggests that NISOPOOH remains at the end of the night to react with OH to form NIEPOX after sunrise. Much of the NISOPOOH seems to be lost via photolysis. The photolysis rate used now is a generic peroxide rate constant. As shown in Figure 3 and 4, the mixing ratio of NIEPOX is much lower than IEPOX. It is currently unclear, however, what the yield of SOA from these epoxides are, so it is not possible to directly compare the SOA source from the concentrations alone.

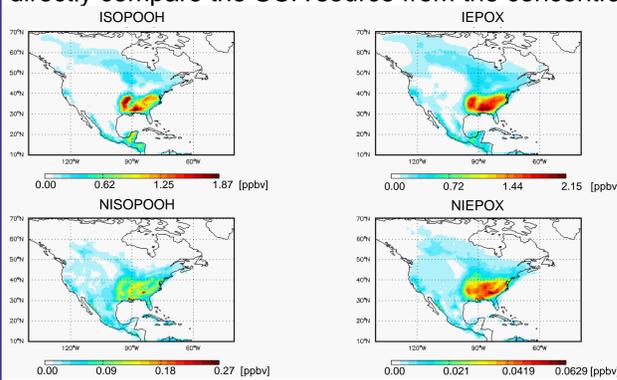


Figure 4. Simulated average mixing ratios of ISOPOOH, IEPOX, NISOPOOH, and NIEPOX at the surface during August 2006. As shown this isoprene chemistry is most important in the southeast of the United States.

Preliminary Chamber Results

Previous chamber studies conducted on isoprene nighttime chemistry had been run under high NO_3 and RO_2 conditions that do not mimic the formation of NISOPOOH in the environment [1]. We have performed preliminary chamber experiments under conditions where $[HO_2] > [RO_2]$ or $[NO_3]$ leading to the formation of NISOPOOH. We subsequently oxidized NISOPOOH by OH demonstrating the formation of NIEPOX in large yield. Further, NIEPOX (like IEPOX) is taken up on acidified seed.

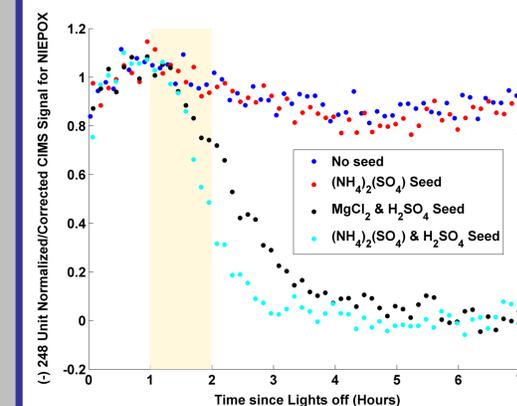


Figure 5. NIEPOX uptake onto neutral and acidic seed aerosol. The gas phase concentration of NIEPOX was monitored using a triple quadrupole chemical ionization mass spectrometer (CIMS). MS/MS data illustrated that the signal for (-) 248 arises from both NIEPOX and NISOPOOH. The (-) 63 daughter mass of (-) 248, however, appears to be produced only by NISOPOOH, allowing us to separate these two isobaric compounds. The tan region indicates when seed was injected.

Conclusions/Future Work

- 1) Preliminary chamber studies confirm that NIEPOX will form through the proposed pathway and will deposit onto acidic seed. More chamber studies will be conducted to better constrain the chemical mechanism, reaction rates, and deposition rates of NIEPOX to include into GEOS-Chem.
- 2) Initial GEOS-Chem simulations confirm that it is possible to form NIEPOX at sunrise. As shown by Figure 4, isoprene chemistry is much more important in the southeast of the US than at the BEARPEX site. Comparing the model results with field studies that will be conducted during the Southern Oxidant and Aerosol study in Alabama this summer (2013) will better confirm the legitimacy of the model.
- 3) The same analysis will be rerun with v9-02 of GEOS-Chem once it is released because a new more complete isoprene mechanism will be incorporated and the anthropogenic emission rate factors including those for NO_x will be updated up to 2010 rather than only 2006.

References

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