Atmos. Chem. Phys. Discuss., 9, S1070–S1073, 2009
www.atmos-chem-phys-discuss.net/9/S1070/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nocturnal isoprene oxidation over the Northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol" *by* S. S. Brown et al.

S. S. Brown et al.

Received and published: 26 March 2009

Reviewer #1

General comments:

1. Omission of descriptions of analytical instruments. The relevant measurements had been listed in Table 1 along with references, stated accuracies and sampling rates. However, the reviewer is correct that certain experimental details, such as sampling issues, are important to the conclusions of the manuscript. A short experimental section has been added to the revised manuscript that explicitly describes these details for the

NO3 and N2O5 instrument and the VOC measurements.

2. Fate of isoprene nitrate derived from NO3: The reviewer's comment is entirely correct. The issue is alluded to in the introduction ("The subsequent fates of such compounds are poorly understood and are an important uncertainty in isoprene oxidation models "), but it was not adequately addressed in section 5 (now section 6) or Figure 8. The following has been added to this section:

"The isoprene nitrate trace is the product of the estimate for total isoprene reacted after dark and the laboratory organic nitrate yield of 80% (Barnes et al., 1990) and includes only production of these nitrates. Potential loss of these nitrates due to further reaction with NO3 or with O3 could reduce the amount of reactive nitrogen stored in this form if it were to result in release of NO2, or increase the amount of organic nitrate if, for example, further reaction with NO3 were to result in the production of di-nitrates."

References to "isoprene nitrates" have been replaced by "isoprene nitrate production" to indicate that the estimate shown in Figure 8 includes only production terms.

Specific comments:

1. Dependence of Phi_Isop on isoprene concentration. Fits of the data in Figure 4, with, for example, polynomial functions do not reproduce the upward curvature well. The reviewer's point is well taken, however, and the following sentence has been added in reference to the value used for Phi_Isop. "This value may be taken as an average above 50 pptv isoprene, since at very large isoprene, the value of Phi_Isop should approach unity (see upward curvature in Figure 4)."

2. Nighttime OH: A qualifying statement has been added to the section on nighttime isoprene loss: "under the assumption that nighttime OH contributes negligibly to isoprene oxidation"

3. The word "chemistry" has been added.

4. The phrase "showed agreement" has been stricken as part of the change that moved

ACPD

9, S1070–S1073, 2009

Interactive Comment

experimental details to a new, separate section.

5. Times for all flights have been added to Table 2.

6. Sunset levels of OH: The reviewer's point is technically correct that all radical sources, OH, NO3 and others, do not start and stop suddenly at sunset or sunrise. However, the period near sunset is one in which all radical sources are small and oxidation tends to be rather slow. The following qualifying statement has been added.

"The choice of sunset as a starting point is arbitrary in that the transition from daytime, photochemical oxidation to nighttime, NO3 oxidation does not occur suddenly, but gradually. However, the period around sunset is one in which previous studies have shown at most very slow oxidative processes (e.g. (Brown et. al., 2004)), such that this time can be taken as the transition point with minimal error."

7. The word "sometimes" has been added.

8. The fraction is a function not of the isoprene emissions themselves, but of their timing. Isoprene emitted late in the day will more likely remain at sunset to be oxidized after dark if there is sufficient NOx. Thus the phrase "late day isoprene emission", as the footprint calculation in Figure 7 indicates.

9. Extent of HNO3 production from N2O5 hydrolysis in the New York City plume in Figure 8. The reviewer is certainly correct that this is an important and related aspect of the NO3-isoprene chemistry described in this paper. This analysis of N2O5 hydrolysis rates from this field campaign has been presented elsewhere (see the preceding references), and an explanation here is beyond the scope of this manuscript. It would require a fairly substantial expansion of the manuscript length. Therefore, the reference to this chemistry is succinct and made in reference to our previous work.

10. Lifetime of isoprene nitrates: The following qualifying sentence has been added at this point: "As noted above, the fate of NO3-derived isoprene nitrates is highly uncertain, and they may be quite reactive."

ACPD

9, S1070–S1073, 2009

11. The isoprene SOA mass is now referred to as "calculated".

12. Other variables the affect SOA yields. The phrase "or the variation in aerosol yields on other variables such as temperature and relative humidity." has been added to qualify the SOA calculation.

13. Justification of comparison to daytime, photochemical SOA production: References from the work of de Gouw et al. have been added at this point to specifically indicate the analysis that shows large, photochemical SOA production in this region.

14. The content of the first paragraph of summary and conclusions has been removed. We thank the reviewer for the suggestion.

Reviewer #2

1. Treatment of NO2 decay in equation (7). The solution in equation 7 does include NO2 loss since it does indeed change quite significantly. The preceding text has been modified to make this clearer: "Because N2O5 hydrolysis is unimportant in comparison to the reaction of NO3 with isoprene for large isoprene levels, the rate of NO2 consumption, which is explicitly incorporated into the expression below, is equal to the rate of reaction (R2)."

2. Isoprene nitrates from NO3 in comparison to long lives organic nitrates, such as PAN. Because of this comment and concern from reviewer #1 regarding the appropriateness of the comparison of the NO3-derived isoprene nitrates to long lives organic nitrates such as PAN, the partitioning relative to PAN has been removed from the abstract.

3. Typographical errors corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 225, 2009.