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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO_3)” *by* N. L. Ng et al.

Anonymous Referee #1

Received and published: 1 April 2008

General Comments:

The paper describes laboratory studies of the chemistry of secondary organic aerosol (SOA) formation and yields from the reactions of isoprene with nitrate radicals. SOA yields are measured and gas-phase and particle-phase products are identified and sometimes quantified using chemical ionization mass spectrometry for real-time analysis of gases, aerosol mass spectrometry for real-time particle analysis, and liquid chromatography with electrospray mass spectrometry for off-line particle analysis. The combination of real-time gas and SOA mass measurements and off-line high-resolution mass spectrometry provides an excellent data set for investigating the detailed chemistry of this system. The data are then used in a global model to estimate the contribution of these reactions for atmospheric SOA.

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Interactive Discussion

Discussion Paper

The experiments are well done and the product analyses are very reasonable. A large variety of multifunctional, low molecular weight products are identified, most for the first time. Both first and higher generation products are observed. Especially interesting and exciting is the identification of organic peroxides of the form ROOR, which are formed in the gas phase from reactions of RO2 radicals. This is a reaction that has been suggested as being possible, but this is the first convincing evidence that it can occur in the gas phase to a significant extent. Because these ROOR products are present in the gas-phase, are formed rapidly, and have low vapor pressures (likely limiting evaporation from walls) there is little doubt they are formed in the gas phase and not through heterogeneous chemistry. This opens up an important new area of gas-phase chemistry for investigation. The mechanisms that are proposed are all very plausible and reflect significant advances in understanding alkene-nitrate radical chemistry. The modeling results indicate that the contributions of these reactions to global SOA are not insignificant. The paper is well written. The figures, tables, and references seem fine. Although there are many figures, this is a very thorough and extensive study. I think the paper is appropriate for Atmospheric Chemistry and Physics and I recommend it be published. I have a few comments.

Specific Comments:

1. Page 3167, lines 10-12: How is isoprene sampled for GC analysis?

2. Page 3172, lines23-26: How certain are you that the yield from the slow isoprene injection experiment is lower? The error bars on the yields include analytical uncertainties but do not represent total uncertainties. Were any replicate experiments performed to determine the reproducibility of yield measurements?

3. Pages 3189-3190, Implications: No mention is made of the potential involvement of HO2 radicals in RO2 chemistry. Is it known that only RO2 and NO3 radicals are important at night? How might this affect the results?

4. Figures 5, 6, 12, and 13: Not much is said about the values of the gas-phase concen-

trations of products measured by the CIMS. Has any thought been given to whether these values make sense for the proposed products? I would think one could learn something about gas-particle partitioning of these compounds given the gas-phase measurements, aerosol mass concentrations, and estimated product vapor pressures. Couldn’t they be related to yield curves?

Technical Comments:

1. Page 3168, line 4 and throughout the manuscript: I think you mean nitrooxy-, which is the term for a -ONO2 group, not nitroxy-.

2. Page 3170, line 1: Surratt et al. (2006) does not describe the iodometric-spectroscopic method; it only refers to the paper by Docherty et al. (2005). I suggest you include the latter reference.

3. Page 3171, lines 21-23: Do you mean the "average NO3 concentration during the experiment is ~140 ppt". Doesn’t it change significantly over time?

4. Page 3179, lines 9-14: It sounds like you meant to write "...radicals (either from RO + O2 reaction or RO + NO3 reaction)."

5. Page 3179, lines 11-12: According to Comment #6, I think you meant to write "formed from the reaction of alkoxy radicals".

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 3163, 2008.