

## ***Interactive comment on “Isoprene oxidation by nitrate radical: alkyl nitrate and secondary organic aerosol yields” by A. W. Rollins et al.***

**Anonymous Referee #1**

Received and published: 3 May 2009

This article provides new insights into the complex NO<sub>3</sub>-initiated chemistry of isoprene, which could as the authors state in the introduction be important under ambient conditions even during daytime.

My comments mainly relate to the SOA chemical composition (section 4.1). It is clear that the dinitrate-diol structure (MW 226) does not allow to explain the nitrate/organic mass ratio of 0.18 observed with the AMS technique. The authors have provided several reasonable explanations for this discrepancy and conclude (section 6) that either some additional chemistry was responsible for the chemical content of the SOA, or the aerosol nitrogen content is higher than measured. In this respect, I like to point out that there is evidence that the MW 226 dinitrate-diol isoprene product is indeed formed under ambient conditions; more specifically it has recently been detected and

C482

characterized in the organosulfate form (MW 306) (Surratt et al. 2008). In addition, there is evidence that MW 197 mononitrate-triol isomeric products are formed under ambient conditions; these products have been detected as major products, have been characterized in the organosulfate form (MW 261), and appear to be together with the 2-methyltetrol organosulfates major tracers for isoprene SOA formed under acidic conditions (i.e. in the presence of sulfuric acid) (Surratt et al., 2007; Gómez-González et al., 2008).

It appears that under ambient (polluted) conditions mixed oxidation of isoprene involving the participation of both NO<sub>3</sub> and OH radicals is important. Laboratory studies in which isoprene SOA tracers were measured in ambient fine aerosol (PM<sub>2.5</sub>) by liquid chromatography/negative ion electrospray mass spectrometry indicate that the two most abundant isoprene SOA tracers are (Gómez-González et al., 2008): - tetrol structures (or the 2-methyltetrols) [MW 136; MW(sulfate form) 216] and - triol/mononitrate structures [MW 197; MW(sulfate form) 261]. It is interesting to note that if these SOA tracers would be taken into account with a ratio 1:1 one would arrive at nitrate/organic mass ratios of 0.23, much closer to the value of 0.18 observed in the current study.

Additional comment: page 8876 – line 26: some cited studies do not deal with isoprene SOA.

References cited:

Gómez-González, Y., Surratt, J. D., Cuyckens, F., Szmigielski, R., Vermeylen, R., Jaoui, M., Lewandowski, M., Offenberg, J. H., Kleindienst, T. E., Edney, E. O., Blockhuys, F., Van Alsenoy, C., Maenhaut, W., and Claeys, M.: Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(-) electrospray ionization mass spectrometry, *J. Mass Spectrom.*, 43, 371-382, 2008.

Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J.

C483

H.: Evidence for organosulfates in secondary organic aerosol, *Environ. Sci. Technol.*, 41, 517–527, 2007.

Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, *J. Phys. Chem. A*, 112, 8345–8378, 2008.

---

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 8857, 2009.