

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

A. Rollins

ice@berkeley.edu

Received and published: 24 June 2009

Reviewer comment: This article provides new insights into the complex NO₃-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

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formed under ambient conditions; more specifically it has recently been detected and 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 NO₃ and OH radicals is important. Laboratory studies in which isoprene SOA tracers were measured in ambient fine aerosol (PM_{2.5}) 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.

Response: We thank the reviewer for these insightful comments and references. These other studies provide evidence that SOA in our experiment was likely formed primarily from the condensation of the dinitrate-diol (MW 226), since as the reviewer points out the organosulfate form of this molecule has been found to be among the most important tracers for isoprene SOA. While it may be the case that under ambient conditions isoprene SOA is mostly formed from mixed OH and NO₃ chemistry, we believe that OH chemistry could not have played a significant role in the gas phase mechanism in this study. A high (500 ppm) level of CO was used in the chamber to ensure that OH concentration was kept low enough to account for a negligible fraction of the isoprene oxidation. We calculate that < 0.1% of the isoprene would have

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reacted with OH. This being the case we are not aware of mechanisms that could form tetrols, or triol/mononitrates and thus presume that the dinitrate-diol would have been the primary product here.

We will add to the discussion the evidence from Surratt (2008) that SOA from these dinitrate-diol molecules is formed in the atmosphere from isoprene oxidation.

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

Response: This sentence was worded poorly. We meant only to use these references as examples that oligomers of carbonyls in SOA with varying carbon backbones has been observed in many studies. We will reword this section.

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