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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Enhanced SOA formation from mixed anthropogenic and biogenic emissions during the CARES campaign" *by* J. E. Shilling et al.

Anonymous Referee #2

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Overall Comment:

This is an interesting and well-written manuscript that will likely motivate a lot of needed discussion on the role of anthropogenic emissions on biogenic SOA formation. The authors do an incredible job in trying to bridge their aircraft measurements to prior laboratory studies on biogenic SOA formation (particularly those studies on isoprene SOA formation). After carefully reading this manuscript a few times, I have a few questions remaining about the interpretation of the results in relation to the exact chemical mechanism likely producing isoprene SOA in this region. I should note that I agree based on their BVOC measurements that isoprene oxidation likely explains the observed en-

hancements in OA mass observed when biogenic VOCs mixed with the urban plume. The authors argue that the enhancements in isoprene SOA might occur due to changes in the VOC:NOx ratio. Although this may be partially true, I think the authors need to be more specific than this. As an aid in describing this chemistry in more detail, I have attached a rough schematic in Figure 1 attached here that outlines what is currently thought to occur in the gas phase to yield isoprene SOA formation. Specifically, I've outlined this according to high-NOx and low-NOx (or NOx-free) regimes. What I would argue is the most important aspect to understand is how the RO2 radicals further react once they are initially formed from isoprene OH-iniitated oxidation. As this figure shows, understanding the relative ratios of RO2 + HO2 versus RO2 + NO versus RO2 + NO2 are important. Related to this mechanism, does your NOx data indicate when NO2/NO ratios were at their highest, did you see the most OA formation? During the day one would expect the NO to get photochemically converted to NO2. Thus, when isoprene is oxidized in the presence of a higher NO2/NO condition, you will likely have MACR form that then further reacts via the H-abstraction channel from the aldehydic H to yield the acyl peroxy radical that combines with NO2 to form MPAN. Studies by Surratt et al. (2010, PNAS) and Chan et al. (2010, ACP) showed that increasing initial NO2/NO ratios in their photooxidation experiments of isoprene lead to the highest SOA yields likely to the favored formation of MPAN. By favoring MPAN formation, Surratt et al. (2010) and Chan et al. (2010) showed that the OH-initiated oxidation of synthetic MPAN yielded the same types of SOA constituents formed when starting with the photooxidation of isoprene under high-NO2/NO ratios. Before these studies, the work of Kroll et al. (2005, 2006) only examined isoprene SOA formation from the perspective of high-NO or NO-free experiments. Thus, in those initial experiments by Kroll et al. (2005, 2006), they generally found that SOA was at its highest when NO was very low. It was argued in those experiments that RO2 + NO favored the formation of RO radicals that then fragmented into volatile products that would not form SOA from isoprene oxidation. The issue with the low-NO pathway is that aerosol acidity has been demonstrated as a requirement to yield SOA from the reactive uptake of isoprene epoxydiols

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(IEPOX) (Paulot et al., 2009, Science; Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T). Considering that sulfate aerosol loadings are low during this campaign, which has been demonstrated to provide the necessary surface for reactive uptake of IEPOX, I think the authors have a good case that NOx is playing some role in enhancing isoprene SOA formation. I wonder if there can be any correlation found between NO2/NO ratios and the OA observed in the field study here? My group has been working further on the high-NOx mechanism to understand how we exactly get SOA from isoprene under these conditions. I wonder, do the authors have any particle data showing any nucleation events associated with the urban plume mixing with the biogenic emissions? In short, it seems that the authors argue correctly that there seems to be some non-linear NOx-dependent pathway to SOA formation from isoprene. However, based on the new lab studies, we now know that increasing NO2/NO ratios enhance the SOA mass from isoprene under high-NOx regimes.

In addition to above, a few specific/technical comments outlined below that need to be addressed before publication in Atmospheric Chemistry and Physics can be considered. As a result of my remaining questions/suggestions, I recommend this manuscript be accepted with major revisions noted.

Specific/Technical Comments:

1.) Positive Matrix Factorization (PMF): I'm just curious, why wasn't PMF used for the AMS dataset? I'm assuming this is due to the nature of how the data is collected (i.e., aircraft measurements). Studies by Slowik et al. (2010, ACP) and Robinson et al. (2010) have showed that a factor could be resolved from the organic fraction that was likely associated to isoprene SOA. Lin et al. (2012, ES&T) showed that these prior studies by Slowik et al. (2010, ACP) and Robinson et al. (2010, ACP) was likely due to reactive uptake of gaseous IEPOX onto pre-existing sulfate aerosols. The unique fragment ion that appeared in the mass spectra associated with these PMF factors was m/z 82. Did the authors confirm that m/z 82 with the same elemental composition was or was not observed in their AMS data set? I ask this since the authors used a

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HR-TOFMS.

2.) On p. 26325, line 20, the authors state: "Signal intensity at m/z 82 is an AMS marker for isoprene epoxydiols (Lin et al., 2012; Robinson et al., 2011); we observe relatively small but significant signal intensity at m/z 82 in nearly all mass spectra, regardless of the dominant emission sources."

It would be better to say m/z 82 is a marker for isoprene epoxydiols-derived SOA, instead of IEPOX itself, since IEPOX is the gas phase precursor that would not be measured AMS.

3.) PTR-MS data: Did they observe ions at m/z 119 or m/z 101? If so, did these correlate or anti-correlate with isoprene, MVK, or MACR signals? These ions might indicate the [M + H]+ ion for gaseous IEPOX (MW 118) or the [M - H2O]+ ion.

4.) Abstract, p.26298, line 24: Did the authors mean to say: "A strong, non-linear NOx dependence" It seemed maybe the word NOx was missing here.

5.) Section 3.2, p. 26310, line 1: Change "show" to the word "shown"

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 26297, 2012.

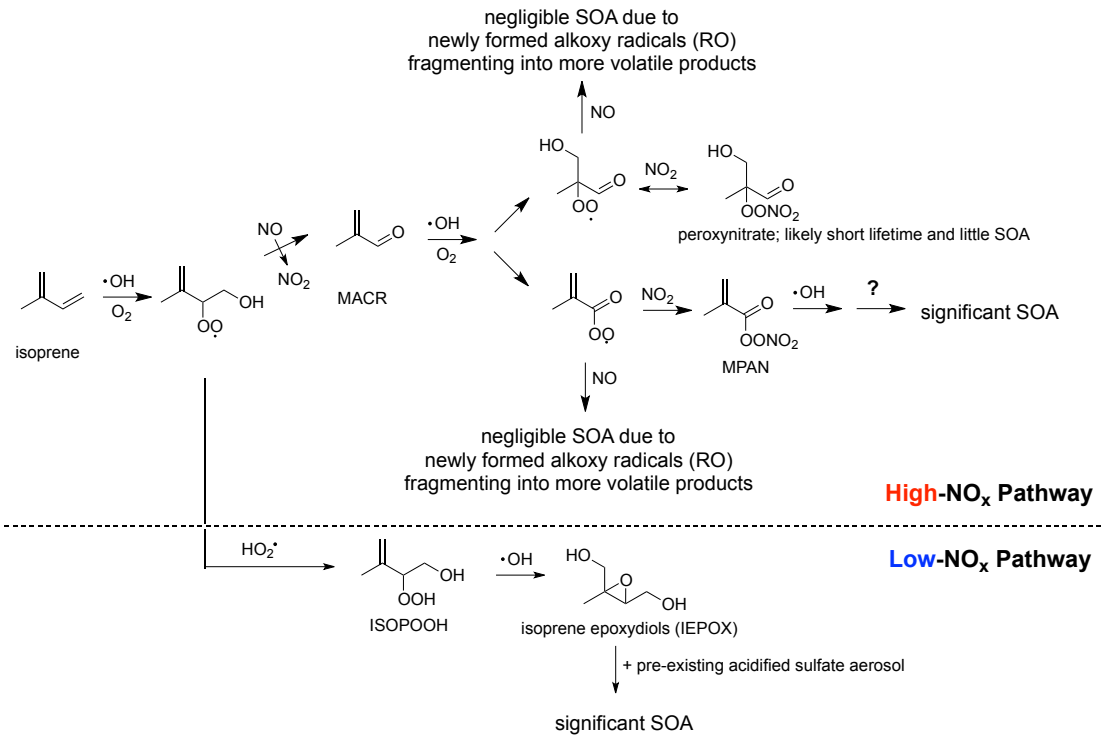

Fig. 1. Tentatively proposed mechanism from the literature (Chan et al., 2010; Surratt et al., 2010) that yields SOA from the OH-initiated oxidation from isoprene under high- or low-NOx conditions.

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