

Interactive comment on “The formation of SOA and chemical tracer compounds from the photooxidation of naphthalene and its methyl analogs in the presence and absence of nitrogen oxides” by T. E. Kleindienst et al.

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General response to both anonymous reviewers:

The authors wish to thank the two reviewers for their insight and critical thinking in evaluating the manuscript on photooxidation of naphthalene and the evolution of chemical tracers during the formation of secondary organic aerosol. The reviewers' comments have been examined by all five authors and the comments, herein, represents their collaborative response. All comments have been carefully considered and where ap-

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propriate changes and other revisions have been made to the text, tables, and figures. In some cases, the reviewers may have misinterpreted the manner in which experiments or analyses were conducted or how the measurements were made. We have sought to explain these aspects in better detail in the paper and point these out below in our response. By-and-large, virtually all the recommended changes have been implemented, as well as other changes we initiated involving clarifications and additions to the text. (See end of this response for the modifications.) These changes have resulted in a paper that has far more clarity and is also more precise and consistent than the original version and for this we again thank the reviewers.

Comments from Reviewer 1: In this work, the authors study the photooxidation of naphthalene and methylnaphthalenes and its resultant secondary organic aerosol formation in laboratory chambers. They then use phthalic acid as a unique tracer of naphthalene SOA product and estimate the contribution of naphthalene SOA to ambient aerosol at two urban sites in the Los Angeles Basin. This work is consistent with the tracer approach proposed by the same group, and thus adds to the capability of using such approach for SOA source attribution efforts. Publication of this manuscript is recommended after addressing the following comments.

Major comments: - The SOA yields presented here seem much lower than measured by Chan et al., but are closer to those measured by Shakya et al. (ES&T, 2010). These results should be included in the comparisons.

Response: We thank the reviewer for pointing out this publication which should have been included in the original draft. As noted, the SOA yields from this work is lower than those reported in Chan et al. (2009). Some salient points from Shakya and Griffin (2010) are as follows and now included in the text in the Discussion section. One point that is evident from the experimental data of Shakya and Griffin is the fact that for naphthalene, there is relative little change in the yield as a function of organic mass. While these findings might indicate the lack of partitioning behavior, Shakya and Griffin have chosen to interpret the data assuming partitioning. The present Discussion

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Section on p.18 notes the small increase, if any, in yield with increasing organic mass. Table 5 now includes a column with the Shakya and Griffin (2010) SOA yield data included and the discussion considers the comparison.

Reviewer comment: - The NO₂ concentration in the experiments are not shown here. The cyclohexadienyl radical that is formed upon OH addition to the ring can react with NO₂ or O₂, depending on NO₂ concentrations. Nishino et al. (2009) showed that at concentrations above 100ppb, the NO₂ addition dominates. It might therefore be difficult to use the yields measured under unrealistically high (>200 ppb) NO_x concentrations. (Note: this is different from the HO₂/NO competition. Here the competition is between NO₂ and O₂, and since O₂ is constant, it is the absolute concentration of NO₂ that needs to be atmospherically relevant.)

Response: For purposes of the general readership, that might not appreciate the intricacies of the aromatic oxidation mechanisms, here are the two issues the reviewer raises and a third issue relevant to SOA chemistry the reviewer does not mention. (1) Upon reaction with OH in the gas phase, aromatic hydrocarbons and PAHs will form an intermediate adduct which, for a monocyclic aromatic such as toluene, is termed the cyclohexadienyl adduct. (A corresponding adduct for naphthalene would be a bicycloclodecateetraenyl adduct.) Unlike acyclic OH adducts, the aromatic type radical can also react with NO₂ in competition with a normal O₂ addition step immediately following OH addition. For toluene, the reaction pathways are equivalent for NO₂ concentrations of about 3 ppm and thus, not relevant under virtually all atmospheric conditions. Given the broader molecular aromaticity for naphthalene, the NO₂ level required is lower (ca. 0.1 ppm; Nishino et al., 2008) at which point the rate for the competing reactions are nearly equivalent and thus laboratory studies must be carefully considered with respect to atmospheric relevance. (2) The second competition the reviewer refers to is the disposition of the putative peroxy radical formed if in fact O₂ does add to the ring. At sufficiently high NO level (> 100 ppt), NO will be oxidized to NO₂ by the peroxy radical which forms an alkoxy radical. (3) There is a third process, however, which is poten-

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tially relevant to SOA formation under low-NO_x conditions (ca. < 100 ppt) where the competition between RO₂ and HO₂ during the radical-radical recombination processes can change drastically depending the relative rates of these radicals. This can then affect the identity and volatility of condensible oxygenated compounds ultimately forming SOA. We will not go into the details, but this can be an important consideration for laboratory measurements of SOA under low NO_x conditions. The arguments regarding this competition are complex since the RO₂ + RO₂ rate constants can be highly dependent (i.e., by orders of magnitude) on the number of substituent OH groups and their positional relationship to the actual location (that is, β beta, gamma, etc) of the peroxy radical center. Thus, these rates are not well known. The reactions tend to be very difficult to study in the laboratory and thus RO₂ + RO₂ rate constants must be estimated with some caution and could conceivably be high enough to make these reactions competitive under some conditions, especially in the laboratory, and presumably affect measured SOA yields.

The first of the processes, that is Process (1), is the one the reviewer is asking about. This first process is relevant gas-phase chemistry but it is an open question as to how relevant it is to SOA formation and represent a possible confounding aspect of hydrocarbon chemistry. These processes might be thought to be more relevant to ozone chemistry than SOA chemistry, although the two are coupled. At this stage understanding, both types of experiments are difficult to study in the laboratory, especially in a batch mode, since processing times for OH reactions in a chamber must necessarily be much faster than in the atmosphere, given the necessity of higher radical concentrations and limited lifetimes due to wall loss considerations, thus requiring chamber NO_x levels to be higher than typically found under ambient conditions.

We appreciate the distinction that the reviewer is making with respect to the competition for the initial naphthalene adduct that is formed immediately after reactions with hydroxyl radicals. While the experiments in the presence of NO_x, were necessarily performed at modest to high ppb levels, simply because of chamber constraints and

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to produce enough OH for reasonable conversions of naphthalene for tracer analysis, this may leave the competition favored in reaction with NO₂. The question of course is what, in fact, the NO₂ concentration is during the chamber processing period. In this work, we have no true NO₂ measurement and it must be inferred from the NO_x measurement. Thus, with respect to naphthalene yields, a statement has now been added to the text, to reflect the changes in chemistry as a function of NO₂, although their effect on SOA formation in naphthalene is unknown.

In the text on p.19, we discuss uncertainties in SOA formation related to the NO₂/O₂ ratio in the laboratory system. We have also referenced and mentioned the Nishino et al. (2008) paper. However, the more novel aspect of this paper has more to do with the formation of atmospheric tracers and in this case, the mass fractions for the tracers appear largely to be independent of the NO_x concentration in the chamber and thus the NO₂ concentrations appear to have little bearing on the results. To summarize, SOA formation yields can be dependent on the exact chamber conditions but these are extremely difficult to resolve experimentally given the precision of SOA measurements and the unconstrained nature of the system. To convince the reviewer that we appreciate the competitive factors involved for various branching ratios in aromatic and PAH chemistry, we would like to summarize them as follows: (1) the disposition of the initial carbon-ring radical from the addition reaction of OH in the presence of NO_x (i.e., the NO₂/O₂ ratio); (2) under intermediate NO levels, the disposition of the subsequent peroxy radical with respect to the NO-to-RO₂ (or HO₂)- ratio; (3) and finally under low NO_x conditions the formation of highly condensable organic peroxides which depend on the RO₂/HO₂ ratio. Thus, the reactant ratios that can influence SOA formation are the NO₂/O₂ ratio, the NO/RO₂ ratio, and the RO₂/HO₂ ratio. Resolving these effects for modeling purpose are expected to require substantial experimental effort. A highly abbreviated version of these points, so as not to detract too much from the main subject matter under consideration, is now given in the text at the bottom of p.16.

In one final point on this matter, it should be noted that the processes above influence

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the gas-phase chemistry and the present paper considers aerosol formation. Thus, gas-particle partitioning might be different for different product distributions. However, this does not appear to be a major factor based on the work of Shakya and Griffin (2010) who saw very little dependence of SOA yield with organic mass, suggesting that partitioning might be less a factor than Chan et al. (2009) had suggested. Moreover, many of the measurements in both studies were probably also prone to NO₂ levels higher than 100 ppb during the oxidation, even though only the initial chamber NO₂ concentrations shown in their tables were below 100 ppb. In our own study, Table 5 shows yields for experiments with and without NO_x being virtually identical. Nonetheless, in the Discussion Section, we mentioned the possibility that NO₂ reaction with the initial adduct can affect the gas-phase product distributions and their possible effect on reported the organic aerosol yields, although we believe this does not play an important role in the SOA yields for naphthalene. This has been stated in the manuscript at the bottom of p.19, "For PAHs and monoaromatic hydrocarbons, the initial OH-addition adduct can react with NO₂ to form nitro compounds as early reaction products, which are detected in the gas phase (Nishino et al., 2008). The extent to which such compounds partition to form SOA could be a consideration in this work but has not been explored. However, as seen in Table 5, the yields determined in this study at high organic loading suggest that while the gas-phase product distribution may differ with NO₂ levels, the SOA formation yields appear to be insensitive to this, as seen by the NO_x-free initial conditions."

Reviewer minor comments:

-pg. 12176 ln 5: "... conducted in the either the presence..." Remove the first "the".

Response: Changed as recommended.

- pg. 12177 ln 7: The base ion should be M+89, not M-89

Response: The mass spectra shown are those of the phthalic acid trimethylsilyl (TMS)-derivatives (MW 310). As noted in p.12177, m/z 89 ion loss, resulting in an observed

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ion fragment at m/z 221 (m/z 310-89=221), comes from loss of the [O-Si-(CH₃)₃] group. Thus, M-89 is the correct base ion.

- pg. 12177 ln 7: It is unclear to me why there would be a fragment resulting from a loss of methyl group [M-CH₃]⁺. There are no methyl groups in phthalic acid.

Response: The mass spectra is that from the TMS-derivative and not the parent compound itself. The methyl losses come from the trimethylsilyl groups.

- pg. 12178 ln 11: Instead of "worse-case scenario", I suggesting rewording it to "upper bound estimate of gas-phase artifact".

Response: Changed as recommended in the third paragraph on p.15. By convention here and throughout, an initial incomplete paragraph at the top of a page will be considered Paragraph 1.

- pg. 12180 ln 15-29: Should include a reaction scheme that will describe the mechanisms more clearly.

Response: Such reaction mechanisms for SOA formation for naphthalene photooxidation are highly uncertain and proposed gas-phase mechanisms have already been presented in multiple publications including Nishino et al. (2008) and Kautzman et al. (2010) for naphthalene and are probably analogous to the methylnaphthalenes and now referenced as such and given at the end of the first paragraph on p.18.

- pg. 12180 ln 15-22: Is there any evidence for naphthoic acid formation? Abstraction of H atom is quite slow compared to OH addition to the ring. In toluene, for example, the abstraction route is only 10%. The increase in reaction rate by methyl substitution is likely due to stabilization of the radical by the methyl group after OH addition to the ring.

Response: During the course of this study, we sought to examine additional compounds that could be used as tracers, such as naphthoic acid. With respect to 1-, 2-naphthoic acid, MW 172 dal, silylation gives derivatives of MW 244 dal. An examina-

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tion of the selected ion chromatograms from ER469 for 2-methylnaphthalene indicated that three of the ions m/z 229, 245, 273 (ordered from most intense to least intense) due to (M-15), (M+1), and (M+29), respectively, could be detected at a retention time (RT) of 21.08 min under chromatographic conditions described in the paper. No other fragments could be detected above the noise in particular there was no evidence for (M-89) and (M-117). The most intense ion is 2-3 orders of magnitude lower in intensity than the strongest ions for phthalic acid. Estimated concentrations of 2-naphthoic acid, based on phthalic acid, are on the order of 1-10 pg m⁻¹, what we would consider negligible. 1-Naphthoic acid levels in ER470 are even lower. Thus, we would consider both naphthoic acid isomer levels to be negligible in the chamber during the 2-, 1-methylnaphthalene chamber irradiations which is discussed in the middle of the final paragraph of p.17.

We also examined the selected ion chromatograms from the naphthalene photooxidations for 1-, 2-naphthol and again saw very weak evidence for the derivative above the limit of detection in the particle phase. Naphthol has a MW of 144 dal and forms a single TMS derivative with a MW of 216 dal. We examined the selected ion (M+1), (M+29), (M-15), (M-89), and (M-105) chromatograms for coincident peaks. Perhaps the weak nature of the signal was due to a lack of instrumental sensitivity, insufficient organic mass collection, or the fact that the compound remains in the gas phase. Having seen little unambiguous evidence for 1-, 2-naphthol in the particle phase in laboratory experiments we did not pursue the matter further. It is also possible that our experimental conditions were not ideal for its formation and subsequent partitioning into the particle phase.

- pg. 12182 ln 8-11: The sentence "Moreover, the SOA formation profiles..." is very vague. What does SOA formation profile mean? Is this referring to the time profile? If so, is there a figure that shows the claimed consistency? Or does the consistency lie in the chemical composition?

Response: The observations were based on data that is yet to be published and since

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the sentence was purely supplemental, we have chosen to eliminate the sentence from the manuscript. The reference, Robinson et al. (2007) remains, since it was used earlier.

Additions to text and references.

The following text was added: "These trends are similar to the findings of Stone et al. (2009) for composite SOA." This sentence refers to the observation by Stone et al. (2009) that weekend SOA attribution masses were higher than weekday mass and is also seen in this work as shown in Figure 4. The sentence appears toward the end of the second paragraph on p.16. The Stone et al. (2000) reference has been added.

Hu et al. (2008) was missing as noted by Reviewer 2 and has now been added.

Shakya and Griffin (2010) has now been added.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 12163, 2012.