Atmos. Chem. Phys. Discuss., 8, S4394–S4408, 2008
www.atmos-chem-phys-discuss.net/8/S4394/2008/

Atmospheric
Chemistry
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Discussions

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

N. L. Ng et al.

Received and published: 2 July 2008

We thank the reviewers for their comments. We have made changes to the text to address these comments. In particular, we have emphasized more on the uncertainties associated with the quantification of peroxides and that caution must be taken when interpreting experiments with low aerosol yields. In the revised manuscript, we also provide a more accurate estimate of the CIMS sensitivities using quantum calculations of molecular dipole moment and polarity. The concentrations of gas-phase products changed by ˜20% with the new sensitivities. The new sensitivities simply reflect a more accurate estimate of the gas-phase concentrations and they do no affect the conclusions in the manuscript.

Reviewer 1: Response to specific comments:

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

Isoprene is sampled through a 1/4 inch Teflon tubing which is connected to the chamber.

2. Page 3172, lines 23-26: 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?

The largest uncertainty in calculating the SOA yield in the slow isoprene injection experiment probably arises from the isoprene concentration, since it is deduced from a separate calibration experiment and not measured directly. However, we do not expect this uncertainty to be much larger in the calibration experiment (hence the slow isoprene injection experiment) compared to the slow N2O5 injection experiment.

In the calibration experiment (also in the slow isoprene injection experiment) and the slow N2O5 injection experiment, the same amount of isoprene is vaporized, which is then carried into the 65L bag or the 28m3 chamber with an air stream. In the calibration experiment (also in the slow isoprene injection experiment), if the extra step of introducing the isoprene from the 65L bag to the 28m3 chamber does not result in significant loss of isoprene, we would expect the amount of isoprene measured in both experiments to be similar. This is indeed the case, as confirmed by the fact that the amount of isoprene reacted in the slow isoprene injection experiment (inferred from the calibration experiment) is similar to that in the slow N2O5 injection experiment (measured by GC-FID) (Table 1). With a similar amount of isoprene reacted, the amount of aerosol formed in the slow isoprene injection experiment is only about half of that in the slow N2O5 injection experiment, resulting in a much lower SOA yield.

And yes, we did perform another set of experiment (with different initial isoprene concentrations) and we obtained the same result: in Figures 12 and 13, about 200 ppb of isoprene is reacted in both case, but the slow isoprene injection experiment results in

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a much smaller aerosol growth.

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?

The second to last paragraph in the "Implications" section is now modified to include a discussion on the relative importance of other RO2 reactions (RO2+ HO2, RO2+NO) as well. The paragraph now reads, "The extent to which the results from this study can be applied to conditions in the atmosphere depends on the relative importance of the various reaction pathways of peroxy radicals in the nighttime atmosphere: RO2+RO2, RO2+NO3, RO2+NO, and RO2+HO2. However, the fate of peroxy radicals in the atmosphere is uncertain owing to the large uncertainties in the reaction rate constants and ambient concentrations of the radicals (Skov et al., 1992; Kirchner and Stockwell, 1996; Bey et al., 2001ab; Vaughan et al., 2006). For instance, a modeling study by Kirchner and Stockwell (1996) suggests that the RO2+NO3 reaction is the dominant pathway at night; 77% and 90% of the total RO2 at night is predicted to react with NO3 in polluted atmosphere and rural air (mixed with aged air), respectively. The other pathways are not as important; while RO2+RO2 can account for about 8-23% of the total RO2 reaction, RO2+HO2 only accounts for 6-10%, and RO2+NO is minimal (0-1%) (Kirchner and Stockwell, 1996). These results are at odds with the study by Bey et al. (2001ab), which suggests that NO3 radicals are not involved significantly in the propagation of RO2 radicals (<5%). Instead, RO2+NO (77%) and RO2+RO2 (40%) are dominant in the mixed layer in the urban and rural areas, respectively. Although there is no definite conclusion as which reaction pathway dominates in the nighttime atmosphere, both studies seem to suggest that RO2+HO2 is relatively not as important. In this work, we investigated situations in which either RO2+RO2 or RO2+NO3 dominates. In both cases the RO2+HO2 reaction is expected to be a minor channel and thus this is in line with the modeling studies. Although RO2+NO is not considered in this study, this reaction produces the same alkoxy radical as in the RO2+NO3 reaction. It is likely that it would result in similar products as those in the case where the RO2+NO3 reaction dominates. Currently, only the reaction rate constants for small, relatively simple RO2 radicals with NO3 radicals have been reported (e.g. Biggs et al., 1994; Daele et al., 1995; Canosa-Mas et al., 1996; Vaughan et al., 2006) and they are roughly in the range of (1-3) x10-12 cm3 molecule-1 s-1. With the oxidation of various volatile organic compounds by O3 and NO3 under nighttime conditions, it is expected that multi-functional peroxy radicals would be prevalent; the reaction rates of these complex peroxy radicals warrant future study. Furthermore, more field measurements on the concentrations of various radicals would also help to constrain the relative importance of the different reaction pathways."

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

In the revised manuscript, we provide a more accurate estimate of the sensitivities of gas-phase products based on quantum calculations of molecular dipole moment and polarity. The concentrations of the three major products change by +/-20%. While the new sensitivities are more accurate than our previous estimates, these changes do not affect any conclusion made in the original manuscript. All the concentrations of the products measured by CIMS are updated with the newly calculated sensitivities. Unfortunately, currently we cannot estimate the concentrations of individual compounds in the aerosol phase, making it difficult to make specific comments regarding the gas-particle partitioning of these compounds. However, based on the both the gas-phase and aerosol-phase data it appears that the major 1st-generation gas-phase products are being further oxidized to lower volatility compounds which then partition into the aerosol phase.

The sentence on P. 3168, line 28 is changed to "Because authentic standards are not available for the major products, sensitivities are not experimentally determined. We estimate the collision rate of CF3O- with these products (which determines the sensitivity) with the empirical method of Su and Chesnavich (1982), which bases its predictions on an analyte's dipole moment and polarizability. Dipole moments and polarizabilities are calculated with the Spartan06 quantum package, and are based on molecular structures optimized with the B3LYP/6-31G(d) method. Further details on estimating CIMS sensitivities based on quantum calculations are described in Paulot et al. (2008). As isomers would have different polarities and hence different sensitivities, in estimating the concentrations it is assumed that the NO3 attack at C1-position to C4-position is 5.5:1 (See Sect 4.1)."

The sentences on P.3178, line 21 are modified to "Previous studies suggest that NO3 radicals predominantly attack isoprene in the 1-position, with a branching ratio (C1-position/C4-position) varying between 3.5 and 7.4 (Skov et al., 1992; Berndt and Boge, 1997; Suh et al., 2001). As mentioned before, the average branching ratio (5.5:1) is used in estimating the sensitivities of the compounds measured by CIMS."

Reviewer 1: Response to 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-.

Corrected.

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

The reference is added.

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?

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Yes. The sentence now reads ";Based on the observed isoprene decay in these experiments and the isoprene-NO3 rate constant kNO3, the average NO3 concentration in the chamber is estimated to be ˜140 ppt."

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

The phrase "either from RO2+RO2 reaction or RO2+NO3 reaction" is referring to the alkoxy radical formation pathways, not the C5-nitrooxycarbonyl formation pathways. To make it clearer, the sentence is changed to "According to channel (5b), these two products should be formed with a 1:1 ratio; however, C5-nitrooxycarbonyl can also be formed from alkoxy radicals (alkoxy radicals formed through RO2+RO2 reaction or RO2+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".

The sentence is changed to "In Fig. 6, about 49.8 ppb of C5-nitrooxycarbonyl and 26.1 ppb of C5-hydroxynitrate are formed after the addition of the first pulse of N2O5, indicating ˜24 ppb of C5-nitrooxycarbonyl is formed from the reaction of alkoxy radicals." The label of the arrow in Figure 11 referring to the formation of C5-nitrooxycarbonyl is changed from "fragmentation" to "O2/-H2O".

Reviewer 2: Response to major comments:

My major concern is that the 2-product fit the authors present is completely at odds with their conclusion that a significant fraction of the SOA is made up of C10 peroxides with additional functional groups such as nitrates (and even sulfates). These products would be effectively non volatile, and yet their SOA formation data display the now standard 'Odum-like' increase in aerosol mass yield with increasing organic aerosol loading...Minor pathways could in fact be responsible for SOA formation in the atmosphere as well as in chambers - the ROOR formation proposed here could be one such

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pathway. In fact, a 2% ROOR formation would not be outside the limits suggested by earlier experiments for even light hydrocarbons, and it would help reconcile the product identification with the observed semi-volatile behavior...p 3186 line 27. Can the authors give some bounds for "significantly"? ...This brings me to an analytical question. Is there any way that 2 ROOH could react in the MS to give ROOR?? (Author note: Owing to limited space, please refer to the original reviews for full comments)

The reviewer made an excellent point. We agree with the reviewer on the interpretation of the Odum curve: when plotting SOA yield versus aerosol formed, the "typical" Odum yield curve behavior is observed, implying that the products formed are semivolatile. While there in no doubt that a wide array of ROOR products are identified in the aerosol phase with the UPLC/(-)ESI-TOFMS technique, we acknowledge that there are uncertainties in the quantification of these products. The contributions of peroxides to the total SOA observed are found to be ˜17-32% (Table 3). We can calculate the mass yield of these products using these numbers and the SOA yield in each of the experiments in Table 3. The mass yields for peroxides are calculated to be ˜6-10%. For the two experiments (Table 3, experiments on 8/22 and 10/24) that are performed under similar conditions as those in the yield curve, the mass yield of peroxides is 8% for both experiments. As the reviewer pointed out, if the ROOR mass yield was only ˜2%, this would "match" what we would have expected based on the shape of the Odum yield curve. Owing to the lack of authentic standards, there are indeed large uncertainties associated with the quantification of the contributions of peroxides to total SOA and hence the calculation of their formation yields. It is possible that the contributions of peroxides could have been overestimated. In light of the reviewer's comments, we emphasize more on the uncertainties associated with the quantification of these compounds (Table 3) in the revised manuscript and acknowledge that one needs to be cautious when relating the products inferred from the Odum yield curve to actual products.

The paragraph in Sect. 4.4 is modified, "As discussed earlier, the formation yields of

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ROOR from the reaction of two peroxy radicals is very low for small peroxy radicals (Kan et al., 1980; Niki et al., 1981, 1982; Wallington et al., 1989; Tyndall et al., 1998, 2001). However, according to both gas- phase and aerosol-phase data in this study, it appears that RO2+RO2 reaction (self reaction or cross-reaction) in the gas phase yielding ROOR products is an important SOA formation pathway. Such reaction has been proposed to form low-volatility diacyl peroxides in the SOA formed from cyclohexene ozonolysis (Ziemann, 2002).). In the case of self-reaction of peroxy radicals, the molecular weight of the product is essentially doubled, providing an efficient way to form products of low volatility. Based on the iodiometric spectroscopic method the contributions of peroxides (ROOH + ROOR) to the total SOA formed is 17-32% (Table 3). We can estimate the mass yield of peroxides based on their percentage contribution to total SOA and the SOA yield for each of the experiments in Table 3. It is found that the mass yield of peroxides range from ˜6-10%. For the two experiments (i.e. 8/22/07 and 10/24/07) that are carried out under similar conditions as those in the yield experiments, the mass yield of peroxide is 8%. Based on the shape of the Odum yield curve (Fig. 3), it is expected that the products are semivolatile. Hence, the relatively large contribution of nonvolatile peroxides in the aerosol phase appears to be inconsistent with the observed yield curve behavior. It is evident from the UPLC/(-)ESI-TOFMS data that there exists a wide array of peroxides in the aerosol composition, however, we need to caution that there are large uncertainties associated with the quantification of peroxides owing to the lack of authentic standards. Based on the standard deviations of the measurements, the uncertainty is at least 10%, yet if we take into account of the following factors it is expected that the true uncertainty would be larger. In estimating the percentage contribution of peroxides, an average molecular weight of 433 for peroxides is used. The peroxides formed would largely depend on the branching ratio of various reactions and this number may not reflect the molecular weights of the wide array of peroxides formed. Also, the iodiometric spectroscopic method does not allow the distinction between ROOH and ROOR products. Hence, the contribution of the low volatility ROOR products may not be as high as estimated. ROOH standards were

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run in the ESI-TOFMS to examine the possibility of ROOH further reacting in the mass spectrometer to form ROOR and no ROOR products were detected. As mentioned before, it appears that the presence of nitrooxy groups in ROOR products aids their detection in the MS. Since the ROOH standards used do not have a nitrooxy group, unfortunately we cannot rule out the possibility that ROOR products are formed but just not being detected. Finally, it is worth noting that the initial isoprene concentrations in the yield experiments are much lower than those experiments in which SOA composition is measured. In performing the yield experiments, the initial isoprene concentrations are kept relatively low so as to be closer to atmospheric levels. Because of the lower initial isoprene concentration (hence lower aerosol loading), the partitioning of various products would be different and it is likely that level of peroxides would be lower in the yield experiments. Nevertheless, the higher concentration experiments are necessary to produce enough aerosols filter analysis and to map out the complete spectrum of oxidation products. To fully elucidate the relationship between the actual products identified and those inferred from fitting the yield data would require a modeling study that is beyond the scope of this work. However, we emphasize that there are large uncertainties associated with the quantification of peroxides and it is likely that their contributions to total SOA can be overestimated. Indeed, if the mass yield for these nonvolatile peroxides were lower (for instance, ˜2%), this would agree well with the observed yield curve behavior. The measurement of peroxides certainly warrants further study. This work serves as a good example in showing that caution must be taken when interpreting experiments with low aerosol yields, especially when a relatively minor pathway may be responsible for forming the aerosols."

Another are of interest would the daytime NO3 chemistry that Jose Fuentes has been proposing for the sub-canopy of many forests. It seems to me that this could be extremely important because, of course, some of those forests are swimming in isoprene.

The following sentences are added in the "Implications" section, , "It is also worth noting while most NO3 chemistry occurs at night, it can also be important during the day at

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specific locations. Recently, a study by Fuentes et al. (2007) suggested substantial formation of NO3 radicals can take place in forested environments with moderate to high levels of BVOC production, resulting in a significant oxidation of isoprene and terpenes by NO3 radicals. For instance, approximately 60% of the terpenes react with NO3 radicals within the canopy. Clearly, more study is needed to evaluate the importance of NO3 chemistry of biogenic hydrocarbons under different environments and time of the day."

Also, did the authors consider HO2 at night from ozone + alkenes in their model?

In estimating global SOA formation from isoprene+NO3 reaction, only a uniform SOA yield of 10% is applied. We did not consider the reaction mechanisms explicitly (i.e. the various reaction pathways of peroxy radicals, RO2+RO2, RO2+NO3, RO2+NO, and RO2+HO2). We noted in the manuscript that the 10% yield is a ballpark estimate that would be highly sensitive to the nature of the peroxy radical chemistry. However, in the revised manuscript, we include a discussion on the relative importance of RO2+HO2 reaction (please refer to response to review #1 - specific comments #3).

Reviewer 2: Reponses to line-by-line comments:

Fig 2: Can you provide the isoprene mass too? Given the mass yield.

The mass of isoprene reacted is now included in the figure caption.

Fig 6: I don’t think that "evolutions" should be plural. It would be nice to have some information about the likely identity of these masses, either directly on the figure or in the figure caption. That way the casual reader will pick up on what’s going on.

Corrected. It is now mentioned that the likely identities for the intermediate gas-phase products are shown in Fig. 11.

Fig 7: How much processing has gone on developing this AMS spectrum?

The spectra presented in this publication use the standard fragmentation table that has been corrected for contributions of air signal at m/z 18 (water vapor) and m/z 16 (O+). Signal at m/z 18 originates from mainly three sources in these experiments: molecular water in the particle, organic fragmentation into H2O+, and sulfate fragmentation into H2O+. It is unlikely that molecular water makes a large contribution to this signal as the experiments were run under low RH. It is hard to separate the contribution of sulfate and organic species to H2O+ as both increase together during the experiment due to increased collection efficiency. In general, the standard fragmentation table was used for consistency. Changes to the fragmentation table as suggested by Aiken et al. (2008) may not be applicable here as the aerosol formed in the isoprene-NO3 system may have different fragmentation characteristics than the model compounds used in Aiken et al. (2008).

Fig 11: Is it possible to put some rough yields on the arrows in this mechanism figure? It is nice to know what is thought be important and by what margin.

Please refer to response to review #1, specific comments #4. In the revised manuscript the caption of Fig. 11 is changed to "Proposed mechanisms for the formation of various gas-phase intermediate product ions observed by CIMS. Multiple structural isomers are possible. In this figure, RO2' refers to the isoprene peroxy radical (nitrooxyperoxy radical), RO2 refer to a generic peroxy radical. The numbers in the parentheses refer to the molar yields of the products. It is noted that the sensitivity for m/z 393 is not calculated, instead it is assumed to be the same as that for m/z 377)."

p3173 line 10 There is certainly further chemistry going on in the slow isoprene injection case too! It is just rate-limited by the actual injection, not by the chemistry. This statement is misleading in this case.

We agree. The sentences are changed to "The presence of a "hook" at the end of the growth curve for the slow N2O5 injection experiment indicates that further reactions are contributing to aerosol growth after isoprene is consumed (Ng et al., 2006). Higher generation products also contribute to the aerosols formed in the slow isoprene injec-

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tion experiment; however, their contributions are not readily observed in the growth curve owing to the way the experiment is conducted. This is further discussed in Sect. 4.3."

p3174 line 3...Please make some effort to estimate the relative production of first and later generation products with reasonable estimates of the kinetics for NO3 addition to the residual double bond...p 3185. Excess isoprene. We return to the point that a relatively minor amount of 2nd generation chemistry can have a big effect on a 10% yield (5% by carbon, or so). Are the authors certain that HETEROGENEOUS NO3 uptake is not significant here??... (Author note: Owing to limited space, please refer to the original reviews for full comments)

In the excess isoprene experiment, the further oxidation of first-generation products should be suppressed and no aerosol formation is expected. However, a small amount of aerosol is formed instantaneously. Based on the SOA composition data, it appears that the further oxidation of 1st generation products (m/z 232, 377, and 393) is contributing to aerosol growth. The following discussion on the kinetics of formation of 1st and higher generation products is added on P.3185, "...The reaction rate of isoprene and NO3 radicals is kNO3 = 7x10-13 cm3 molecule-1 s-1. To our knowledge, the reaction rate of the 1st generation products and NO3 radicals has not been studied. The structure of m/z 232 (C5-hydroxynitrate) is similar to 3-methyl-2-buten-1-ol (MBO321), except that the gamma-carbon has one nitro group and one methyl group substitution instead of two methyl group substitutions. The reaction rate coefficient of MBO321 and NO3 radicals is kNO3 = 1x10-12 cm3 molecule-1 s-1. It is found that the reaction rate with NO3 radicals increases with increasing number of methyl groups at the gamma-carbon (Noda et al., 2002), which is in accordance with the stabilization theory for leaving groups discussed in Atkinson (1997) and Noda et al. (2000). With reference to this, we would expect the reaction rate of C5-hydroxynitrate and NO3 radicals to be slower than that of MBO321 due to the presence of the electron withdrawing nitro group. Hence, it is likely that the reaction rate of isoprene and NO3 radicals and C5-

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hydroxynitrate and NO3 radicals are roughly in the same range. The relative production rate of first- and second-generation products will then be the ratio of the concentrations of isoprene and first-generation products, and aerosol can be formed either from the condensation of relatively non-volatile first-generation products (e.g. m/z 393) or higher generation products that are formed relatively fast in the gas-phase. [It appears from the UPLC/(-)ESI-TOFMS data that enough RO2+RO2 chemistry to yield many of the products shown in Fig. 14-17.]....."

As mentioned in the manuscript (P. 3186, line 9), we cannot exclude the possibility of heterogeneous reaction. To point this out more explicitly, two references on NO3 uptake are now included: "Studies have shown that NO3 uptake on organic surfaces (even to saturated organic surfaces) be quite rapid (Moise et al., 2002; Knopf et al., 2006; Rudich et al., 2007). Hence, it is also possible that CIMS m/z 393 (a first-generation product according to one of the formation routes) is nonvolatile enough that it partitions into the aerosol phase and its further oxidation proceeds heterogeneously."

P 3174 line 21. The 393 ion only appears slowly during the first injection. This is presumably because its precursor has reached some sort of steady state before the second injection?

It is possible that the product ion at m/z 393 shows a slower rate of formation (Fig. 6) compared to other product ions because it is formed from the further oxidation of a first-generation product. It is proposed that there are two formation pathways for m/z 393 (Section 4.1 and Figure 11): Firstly, the hydroxynitroxy alkyl radical formed can react with O2 to form a peroxy radical, which then reacts with the isoprene peroxy radical to form the product ion m/z at 393. Secondly, m/z 393 can be formed from the further oxidation of 2-methyl-2-vinyl-oxirane. If this second oxidation step is slower, it will result in a relatively slower increase in the amount of m/z 393 observed. Also, we cannot exclude the possibility of m/z 393 interacting with the tubing due to its relatively low vapor pressure - if some of the initial m/z 393 formed sticks to the tubing, it would appear to form slowly.

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p 3180... the RO2+RO2 reaction is presumed to proceed via a common tetroxide intermediate, ROOOOR...this evidence for ROOR formation seems to me to suggest a direct pathway out of a 4-member transition state RO[OO]OR -> ROOR + O2. (Author note: Owing to limited space, please refer to the original reviews for full comments)

This work shows that the RO2+RO2 reaction can be an effective way in forming SOA. However, we do not think that we can go far as to infer how the reaction proceeds based on our data. Nevertheless, given the potential importance of this reaction, the following sentences are added to the last paragraph of the "Implications" section to discuss the possible mechanisms of ROOR formation, "Ghigo et al. (2003) ruled out the direct formation of products (RO, ROH, RCHO) from the tetroxide intermediate ROOOOR. Instead, they proposed that the tetroxide breaks up into a weakly bound complex of two RO radicals and O2, which then fall apart or undergoes intersystem crossing to form the corresponding alcohol and carbonyl products. The formation of ROOR was not discussed in Ghigo et al. (2003) owing to little experimental evidence for the production of ROOR. However, the observation of ROOR formation in this study suggests that this reaction does occur and is potentially important for aerosol formation. As pointed out by Dibble (2008), the mechanism proposed by Ghigo (2003) would seem to allow for easy production of ROOR from the RO-RO-O2 complex. Therefore, it appears that there are at least two possible pathways for ROOR formation: it can either be formed through the RO-RO-O2 complex as suggested by Dibble (2008), or there may exist a direct pathway for ROOR formation from ROO + ROO. Certainly more work is needed regarding the formation, detection, and quantification of ROOR products."

p 3188 line 26. .. please dont quote the SOA production from his model as if it were a fact. It is a model result. You should also quote Goldstein et al, who suggest that SOA production is somewhere between 150 and 400 Tg/yr...(Author note: Owing to limited space, please refer to the original reviews for full comments)

There may be a typo in the review - when citing the SOA production from Goldstein et al. (2007), probably the reviewer meant to say "150 and 400 Tg C yr-1, instead of

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150 and 400 Tg yr-1". The sentences are changed to "If we take as a rough estimate a 10% SOA yield from the isoprene + NO3 pathway from the results in Table 4, 2 to 3 Tg yr-1 of SOA results from isoprene + NO3. This rate of production would make SOA from isoprene + NO3 as significant as that from sesquiterpenes, biogenic alcohols, and aromatics, each of which is estimated to produce about 2 to 4 Tg yr-1 of SOA based on yields measured in chamber studies (Henze et al., 2007). As a reference, the global SOA production is estimated to be 10-70 Tg yr-1 (Kanakidou et al., 2005). Recently, Goldstein et al. (2007) provided several alternative approaches to estimate global SOA production: 510-910 Tg C yr-1 based on the global mass balance of VOC removal, 225-575 Tg C yr-1 based on SOA deposition plus oxidation, 140-540 Tg C yr-1 based on comparison with the sulfate budget, and 223-615 Tg C yr-1 required to maintain the assumed global mean vertical SOA distribution. If we assume mass carbon/mass organics = 0.5, the lower limit for SOA production from these estimates would be 280 Tg yr-1, which is much larger than that estimated from chamber SOA yields. Still, the 3 Tg yr-1of SOA estimated for the isoprene + NO3 system is worth noticing."

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