

Interactive comment on “Secondary organic aerosol production from modern diesel engine emissions” by S. Samy and B. Zielinska

Anonymous Referee #2

Received and published: 21 October 2009

Review of Samy and Zielinska “Secondary organic aerosol production from modern diesel engine emissions”

The work presented in this manuscript represents a study of the formation of secondary organic aerosol (SOA) from nitrate radical (dark reaction) and hydroxyl radical (light reaction) initiated oxidations. A study of the reactivity of diesel exhaust in a smog chamber is a very difficult proposition as described by the authors because modern diesel engines produce exhaust that tend to be extremely hydrocarbon poor and NO_x rich. As a result, certain tricks need to be adopted by the experimentalists in order to make the initial mixture sufficiently reactive to see effects of NO reactive loss, ozone formation, or SOA formation. In the present study, the trick employed is to pass the exhaust through a NO_x denuder which captures a high percentage of the NO_x in the

C6120

exhaust stream while passing the diesel VOCs.

Overall, the work is very comprehensive and the manuscript is generally well written. The diesel vehicle selected while light duty is a very realistic source for actual diesel exhaust emitted into an airshed. (For a European scenario this selection is appropriate, while a U.S. scenario would probably have a much greater heavy duty diesel component.) The experimental section gives considerable detail on the analytical techniques. Considerable effort has gone into producing a diesel exhaust mixture which is reactive. This has required the use of a newly designed NO_x denuder. Thus, it is somewhat surprising that for several of the runs without added VOCs (although with formaldehyde as a radical source) the SOA increase was negligible or modest at best. This is unexpected given the recent results of Robinson et al. 2007 Science 315:1259. One shortcoming of the study is a lack of information on the initial VOC composition and levels from the exhaust itself. (This may be too much to ask.) Most of the experimental measurements focus on detailed organic products produced from the emissions and during the photooxidations, mainly alkanic acids, aromatic acids, and diacids (both aliphatic and aromatic). While these products are of interest, the manuscript gives little sense of the fraction of the organic aerosol that these compounds comprise. The discussion appears to be far too focused on the individual products and classes of products and insufficiently focussed on some of the broad (and possibly more important) issues of SOA formation from diesel exhaust. Again this will be considered in more detail below. Overall the manuscript has excellent experimental information and with some minor improvements in the interpretation the manuscript should be published. Comments on the individual sections follow.

Introduction: The strategy for conducting the study should be explained better in terms of why a radical source (HCHO) is needed and the motivation for the experiments with added toluene. This would probably just require abstracting some of the discussion found in Zielinska et al. (2009), as noted by the authors on line 82.

Experimental section: The major missing piece from the experimental section is a con-

C6121

sideration of the procedures for conducting the experiments including the addition of the diesel exhaust to the chamber. (What is found on line 73 should be moved to the experimental section.) How homogeneous mixing of the exhaust in the chamber was achieved and other issues involved in adding all the reactants including the emissions into a large photochemical chamber should also be discussed. How was N₂O₅ generated and added to the chamber in a manner in which it can mix without undergoing too much hydrolysis? At present, some of these procedures are mixed throughout the experimental section. I suggest consolidating them into a single section on procedures right before the Results and Discussion section.

Many of the features of the NO_x rich exhaust from diesel emission described in lines 131-139 is fundamental to the motivation for the study and would be better suited in the introduction where it might have more visibility. Both investigators and readers need to understand these concepts before they can appreciate the difficulty of conducting such experiments with diesel exhaust.

A description of the measurement of glyoxal needs to be provided (values given as yields of reacted toluene in Table 4). Presumably, measurements of glyoxal were made using the DOAS system, but this needs to be stipulated. The values in the table are for gas-phase glyoxal only. Volkamer et al. (2007; GRL, 34, L19807) describe the possibility of the loss of glyoxal to the particle phase which may not be operative here considering the time scales but should be considered nonetheless. The references provided only pertain to glyoxal; what references apply to the determination of the methylglyoxal yield for the same table? Finally, provide the reacted toluene concentrations at the listed aging time which would give the reader the corrected glyoxal and methylglyoxal chamber concentrations based on the yields.

This section has a considerable inconsistency in the introduction and use of acronyms. For example line 109 mentions fluorine-ethene-propene (FEP) foil while line 167 talks about another type of Teflon, PTFE, without saying what it means. (In both cases, only the acronym is needed.) Similarly, OH is introduced as hydroxyl radical while N₂O₅

C6122

has no analogous description. Dichloromethane is introduced three times in lines 188, 194, and 199 twice as CH₂Cl₂ and once as DCM. Methanol is mentioned in lines 189, 192, and 199 only the last time with an acronym. One acronym that does need an explanation at first use is DPM (diesel particulate matter). Thus, Section 2.2 requires considerable editing to make it presentable. The authors should consider putting some of the material into the already existing supplemental information section. As a final note, spaces are needed in many of the units used, such as on line 248, gcm⁻³ should be g cm⁻³ and many similar instances.

For the final paragraph of the current experimental section (line 250-259), some context needs to be provided before a discussion of toluene addition experiments can be understood, especially in light of the dramatic changes in SOA formation upon its addition.

Results and Discussion:

In my opinion, the major finding in this study is the relatively low yields of SOA formation found for the irradiated diesel emissions according to Table 2 (and S3). Experiments L-1a and L-1b (added VOC mixture 2) essentially give no change in SOA formation upon irradiation even at presumably moderate to high VOC-to-NO_x ratios. As noted above, this appears to be contrast to the findings of Robinson et al. (2007). The dilution ratios appeared to be sufficiently high in these experiments that any intermediate or semivolatile VOCs initially in the particle phase would have partitioned into the gas phase upon dilution. In the present experiments, the only conditions under which SOA was formed was through the addition of an exogenous radical source (photolysis of added HCHO) or the addition of the VOC mixtures including toluene which were found to considerably increase SOA levels. Thus, some comparison of the present work with that of Robinson et al. (2007) is warranted.

Some consideration should be given to the possibility that some of the VOC components of the diesel exhaust might be lost in the denuder. This might explain some of

C6123

the differences between this work and Robinson et al., if such constituents were highly reactive SOA producers.

In terms of organization, I suggest moving section 3.3 to follow 3.1. The argument then would be better structured.

Section 3.2 is at the heart of the interpretation. Some context for this section needs to be placed in the introduction given its length and importance. Thus, the sentence starting on line 321 would be better suited for the introduction. At present, this section comes across as an ad hoc collection of individual compounds or compound classes. This section needs to be better tied into the discussion of the bulk properties of the aerosol.

Line 347 mentions particle size profiles. I had expected to see one or more SMPS profiles in the paper and believe it would be a valuable addition to get a better sense of the particle number, surface, or volume distribution before and at the maximum aging time in Expt 2b. At a minimum, such distributions could be placed in the supplemental information.

The paragraph starting on line 355 belongs near the beginning of the section. It represents a significant limitation in interpreting irradiations from complex sources.

For the paragraph beginning on line 386, to what degree might reactions of N₂O₅ with the PAHs be important?

It is not clear what the authors are trying to state in the sentences between lines 401 and 405. It would be helpful to restate this in clearer terms.

Just to be clear, is 1,12-dodecanedicarboxylic acid the same as n-tetradecanedioic acid?

Some expanded discussion of the significance of pyrolyzed organic carbon and the associated sentences (line 490) need to be made even if it requires a few sentences from Zielinska et al. (2009).

C6124

In lines 476-478, is the implication that the partitioning scaling factors are somehow EUPHORE specific. If it is not, it certainly comes across that way.

Darnall et al. (1979; JPC 83:1943) originally proposed the dicarbonyl route for aromatics.

The authors need to be clearer in what is being communicated in the sentence starting on line 495.

Two references have incorrect last names – line 613: Alvarez should be Gomez Alvarez; line 692: Cauwenberghe should be Van Cauwenberghe, V is not his middle initial, although it has been written as such in numerous publications. Also, some of the references have incorrect capitalization. On line 861, the name of the journal is missing.

Table 1 and Figures 1 and 5 might be placed in supplemental information.

In Table 3, it is surprising that nonanoic acid would be found in both gas and particle phases with the implication that heptanoic acid is solely in the particle phase.

An absolute start time for the irradiations would be valuable for understanding Tables 2 and 4.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 17665, 2009.

C6125