Atmos. Chem. Phys. Discuss., 8, S1392–S1394, 2008 www.atmos-chem-phys-discuss.net/8/S1392/2008/ © Author(s) 2008. This work is distributed under the Creative Commons Attribute 3.0 License.



ACPD

8, S1392–S1394, 2008

Interactive Comment

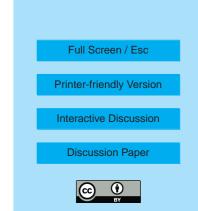
Interactive comment on "Gas/particle partitioning of carbonyls in the photooxidation of isoprene and 1,3,5-trimethylbenzene" by R. M. Healy et al.

Anonymous Referee #3

Received and published: 8 April 2008

Summary:

This paper demonstrates a study on the gas/particle partitioning of carbonyls produced from the photooxidation of isoprene and 1,3,5-trimethylbenzene. The gas and particle phase carbonyls were collected using denuder-filter-denuder sampling system incorporated with PFBHA derivatization of major carbonyls. The quantification of those carbonyls using a GC-MS was used to obtain their experimental partitioning coefficients that were compared against the calculated values based on the conventional gas particle partitioning theory. Although the main idea of this study has been known to the atmospheric community but still limited for understanding of the heterogeneous chemistry in aerosols. The experiments conducted in this paper are well designed. However, some detailed descriptions about the experiments are necessary. The weakness of



this paper is the calculation of the theoretical partitioning coefficients of the carbonyls. It requires the authors to reconsider the assumed parameter values in the standard absorptive gas/particle partitioning equation (see the detail comments below). The reviewer recommended making major revisions on the theoretical partitioning coefficients before publish in this journal.

Reviewer's additional comments:

1. In the experimental section, the reviewer wondered if the authors used any internal standard to track the carbonyl loss during the preparation of the gas and particle samples. From the collection to the injection to the GC-MS, the samples went through several steps such as extraction and concentration etc.. The compounds of interest were volatile or semi-volatile, therefore the loss of these compounds is inevitable and need to be considered for the calculation of experimental partitioning coefficients. Please address this issue in the paper.

2. The compounds shown in Table 2-4 are multi functional. Some have two carbonyls and some have three carbonyls in their molecular structures. Thus derivatization of carbonyls is very complex resulting in various derivatives (e.g., mono, di, tri at different combinations). How do the authors quantify the carbonyls in the gas and the particle phase. How do the authors ensure that the gas phase carbonyls have the exactly same derivatization with the particle phase carbonyls. For example, is the gas phase tricarbonyls have the same fraction of di-derivatives or mono-derivatives with those in the particle phase?

3. Each sampling system (DFD and FDD) has different sampling artifacts. Explain why the DFD system was chosen for the partitioning study? Please explain the potential artifact from the sampling system used by the authors.

4. Page 4742, in the paragraph under the equation 2, the authors assumed the activity coefficients of compound i to be 1 and the MWom 120. How reasonable are these assumptions? Oligomers formed in the particle alter the physical properties and chemiACPD

8, S1392–S1394, 2008

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



cal compositions of SOA, which would influence the activity coefficients of semi-volatile products onto the particle. The reviewer looks forward to seeing authors' effort on finding appropriate activity coefficients. Otherwise, the theoretical partitioning coefficients obtained in the paper are not much meaningful.

5. Page 4730 and Page 4742. On page 4730, the authors mentioned that temperature was 20oC (please use the same unit), while on page 4742 the experimental temperatures were 293K (PSI) and 305K (UCC). Please clarify the experimental temperature. The 12 K difference in temperature is significant enough to change chemical and physical property of aerosol. What is the potential impact of temperature and humidity on measured partitioning coefficient as well as heterogeneous reactions in aerosols?

6. Page 4743, Line 24-26, it stated that "the oligomers can revert to their monomeric form in the solution". How will this influence the quantification of the carbonyls in the filter samples as well as the experimental partitioning coefficients? Please discuss about it in the paper.

7. Figures 2-5, please move the legend to the bottom of the figures.

8. Table 1. Please include the inforamtion of HC (e.g., isoprene or 135-trimethylbenzene). If the authors provide temp and RH information here, this will help the readers.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 4727, 2008.

ACPD

8, S1392-S1394, 2008

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

