Atmos. Chem. Phys. Discuss., 13, C8669–C8674, 2013
www.atmos-chem-phys-discuss.net/13/C8669/2013/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozonolysis of surface adsorbed methoxyphenols: kinetics of aromatic ring cleavage vs. alkene side-chain oxidation" *by* E. M. O'Neill et al.

E. M. O'Neill et al.

rhinrich@drew.edu

Received and published: 31 October 2013

We appreciate the time and energy of the two referees. We are confident that our revised manuscript is stronger because of revisions in response to their suggestions and comments. For the sake of clarity, we have reproduced or paraphrased each referee's comments below, follow by our revisions and reply.

Anonymous Referee #1

1. Does the ZnSe crystal in the ATR-FTIR experiments act as a reaction substrate just as Al2O3 and NaCl do?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Author reply: The following text has been added to Section 3.3, paragraph 5. “Control experiments exposing a clean ZnSe crystal to gaseous eugenol showed no significant condensed-phase organic features, indicating that ZnSe did not act as a reactive substrate in these experiments.”

2. How was the spectral irradiance of the xenon lamp measured?

Author reply: Reference to the plot of the spectral irradiance in the Supplemental Material (now Fig. SI-1) is now included in the experimental section along with the following text. “The solar simulator spectral irradiance (Supplemental Material Fig. SI-1) was determined by correlating the total integrated power (λ < 800 nm), measured with an Newport Oriel power meter, and the relative intensity as a function of wavelength, which was measured using an Ocean Optics CCD spectrometer (HR2000).”

3. Do the authors observe any photolysis of ozone?

Author reply: No. We performed additional control experiments where the ozone concentration was measured with the light on and off while flowing through uncoated substrates. This result is now discussed in Section 3.5: “Control experiments flowing O3 through an uncoated NaCl sample showed no changes in measured O3 concentration with the solar simulator on or off, indicating that photolysis of O3 at λ > 300 nm was negligible.”

4. I would recommend additional tests with light irradiation of the organic compounds in the absence of ozone to distinguish between the effect of light itself; the light and ozone; the light, ozone and the substrate; the light and substrate ...

Author reply: We also performed a control experiment where eugenol was exposed to the solar simulator in the absence of ozone. The following text was added to Section 3.5. “Exposing surface adsorbed eugenol to the solar simulator in the absence of ozone showed no discernible changes after several hours.” “Since neither NaCl nor Al2O3 absorb radiation in the region of the solar simulator output, the observed photochemistry

ACPD
13, C8669–C8674, 2013

is likely the result of ozone reacting with photo-excited eugenol." The observation that only the aromatic ring exhibited photoenhanced reactivity while the alkene side-chain remained unchanged are consistent with this conclusion.

5. The changes of the aromatic features could indicate a formation of species with higher molecular weight. Do the authors consider the possibility for formation of high molecular weight compounds during the surface reactions of ozone with methoxyphenols?

Author reply: We are very interested in the potential to form oligomers. Unfortunately, FTIR does not provide distinguishing features for identifying higher molecular weight compounds, and GC-MS extraction of organics is not ideally suited to their detection. The following text has been added to Section 3.3: "No evidence of higher molecular weight products was detected, although admittedly our GC-MS analysis is not ideally suited to their detection due to reversible dissociation during extraction (Jang et al., 2002)." Reference added.

6. It is somewhat strange that the RH does not influence the reaction kinetics. I wouldn't state that the lifetimes of the studied compounds are the same for dry and humid conditions.

Author reply: All observed experimental rate constants measured under humidified conditions agreed, within experimental uncertainty, with the dry rate constants. With that said, we do appreciate the referee's concern regarding atmospheric lifetimes given that partitioning between the gas- and condensed-phase is affected by humidity, and the reaction rate in the gas-phase is likely different. We have revised the final sentence of Section 3.4 to clarify our statement. "These results suggest that the heterogeneous reaction rates listed in Table 2 apply to both dry and humid conditions."

7. It is very surprising that the experiments performed at ozone concentrations of almost 1 ppm do not lead to the plateau in Figure 5b. Also, I don't understand why the x-axis extends to 5 x 10ˆ13 molecules cmˆ-3. Plotting the Eley-Rideal and Langmuir-

ACPD
13, C8669–C8674, 2013

Hinshelwood (LH) mechanism in Figure 5 makes no sense. It is obvious that the obtained results do follow the Eley-Rideal (ER) pattern. Surely, the substrates play an important role with this respect.

Author reply: Although these results cannot distinguish between the two mechanisms, we believe it is relevant to keep this discussion given its prominence in similar heterogeneous ozonolysis investigations. The choice to expand the x-axis to 5 x 10ˆ13 molecules cmˆ-3 was simply to show where the ER and LH fits begin to deviate, but we would be fine adjusting this axis if the referees and editor insist. It is worth noting that LH saturation often does not occur till higher O3 concentrations are studied. For example, pseudo-first-order rate coefficients for the ozonolysis of benzo[a]pyrene appear linear up to 2 x 10ˆ14 molecules cmˆ-3 (Kwamena et al., 2004; Zhou et al., 2012), initial reaction probabilities for the ozonolysis of terminal alkene SAMs appear constant until 2 x 10ˆ13 molecules cmˆ-3 (Dubowski et al., 2004), and oleic acid bound to polar and non-polar particles exhibit near-linear pseudo-first-order rate constants up to 2 x 10ˆ14 and 4 x 10ˆ14 molecules cmˆ-3 for polystyrene and silica particles, respectively (Rosen et al., 2008). Based on these prior results, it does seem possible that a LH type mechanism might be operative, which is why we've decided to not identify the ozonolysis of adsorbed methoxyphenols as conclusively following an ER mechanism. We have, however, tried to make this discussion more concise and have deleted sentences repeating this comparison in Section 3.3 (see referee 2, comment # 13).

8. In the future, theoretical studies on a molecular level would reveal more details about the interactions between ozone and the reactions substrates, hence, they are highly recommended.

Author reply: We agree and would be eager to collaborate with theoretical chemists with expertise in modeling these systems.

Anonymous Referee #2.

9.Please describe in detail the 10m transmission cell, especially the volume, material,

ACPD
13, C8669–C8674, 2013

duration of dwell of the gases.

Author reply: The following text has been added to Section 2.1. “Gas phase spectra were recorded by directing this flow through a 2 L transmission gas cell, which uses White cell multi-bounce optics to achieve a 10-meter pathlength (Thermo Antaris), housed in a Thermo Nicolet 6700 FTIR ...”

10. The authors should also mention the method of determining the relative humidity as well as the dew point of what they call 0% RH. The residual content of water of dry air is important related to heterogeneous reactions involving monolayers. The authors should discuss the influence of the remaining water molecules on the molecules adsorbed on the inorganic substrates.

Author reply: The Methods text has been revised to read, “The relative humidity (RH) was controlled by adjusting the relative flow rates of dry and humidified streams of purified air using two mass flow controllers. RH was measured upstream of the DRIFTS reaction chamber using a Vaisala HMT338 gauge. It should be noted that even for “dry conditions” (referred to as 0% RH hereafter) the DRIFTS substrates contain residual surface adsorbed water (Ghosal et al., 2004).” Reference added.

11. If the xenon lamp mentioned on page 19976, line 18, which was used as solar simulator is the same as in the supplemental section, the authors should refer to the figure in the supplement. Further the method of determining the spectral irradiance of the xenon lamp should be mentioned.

Author reply: Please see response to referee comment #2.

12. While dealing with monolayers, it is applicable to refer to parts of a monolayer like 0.9 monolayers than reporting the ‘exact’ number of molecules per square meter.

Author reply: The method of quantifying extracted organics (in molecules per gram NaCl) combined with the BET surface area (mˆ2 per gram) results in the molecules per m2 surface concentration. Calculating the fraction of a monolayer from this value

ACPD
13, C8669–C8674, 2013

requires that we know the area per adsorbed molecule, which will depend on the exact geometry of adsorption and is therefore very difficult to estimate. To clarify this issue, the following text was added to Section 3.1. “Since it is difficult to estimate the effective area of an individual adsorbed methoxyphenol, we cannot accurately calculate the fraction of a monolayer. Nonetheless, based on our prior work with surface adsorbed catechol, we believe these surface concentrations correspond to near monolayers (Woodill et al., 2013).”

13. The detailed discussion of the entire heterogeneous mechanism is hampered by the impossibility to clearly distinguish between ER or LH type mechanisms. This discussion is done twice (section 3.2 and 3.3). I suggest shifting both discussions to a separate section, dealing only once with this topic and problem.

Author reply: We have decided to keep the ER vs. LH discussion in Section 3.2 for the ozonolysis of 4-propylguaiacol. As mentioned in our reply to comment # 7, we have decided to eliminate the repeated discussion in Section 3.3 (ozonolysis of eugenol) and believe this does not detract from our discussion.

14. The authors should check the paper for missing units like table 1: missing unit cmˆ-1. Further, the authors could think about presenting difference spectra I1/I2 to indicate spectral changes or differences instead of laying infrared spectra on top of each other.

Author reply: Units have been added to Table 1. We did consider difference spectra but decided that showing the initial and final reaction spectra presented similar information, although admittedly, our overlayed spectra do require two colors for clarity.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 19971, 2013.