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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.

Anonymous Referee #1

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In the manuscript O'Neill et al. the ozonolysis of selected methoxyphenols coated on two substrates i.e. NaCl and α-Al2O3 was studied under dark conditions and in the presence of light. The effect of relative humidity was evaluated as well. The studied compounds eugenol, isoeugenol and 4-propylguaiacol which emerge from the biomass combustion processes are of atmospheric relevance. Concerning the reaction products various analytical techniques such as GC-MS, 1H-NMR, DRIFTS and ATR-FTIR have been employed and a number of reaction products were conclusively identified. I recommend publication of this article in Atmospheric chemistry and Physics and I strongly encourage the authors to continue their research on this topic. However, I have few

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comments and/or suggestions which should be considered before publication.

Regarding the infrared spectroscopy do the authors considered the influence of ZnSe crystal on the surface reactions? ZnSe represents a reaction substrate just as Al2O3 and NaCl do.

How was measured the spectral irradiance of the xenon lamp presented in Figure 5 of Supplementary material? Do the authors observe any photolysis of ozone?

The experiments performed in presence of light give some additional information about the compounds under study. However, the experiments were done in a not conventional way so to say. The xenon lamp was repeatedly turned on and off to follow the changes on the spectroscopic features. In reality such a scenario is impossible and it can't be appreciated what do induce the changes in the bends in Figure 9; is it the effect of light itself, the light and ozone, the light, ozone and the substrate, the light and the substrate. . .. .

I would recommend additional tests with light irradiation of the organic compounds in absence of ozone. This could be easily done by UV-VIS spectroscopic measurements in aqueous solution or other solvents depending of the solubility of the compounds. Then, the solvent effects have to be also taken into consideration. It is interesting to see how the UV-VIS spectra change with the time exposure. Only in this way we can get a clearer picture about the reaction mechanisms.

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? See for instance Duarte et al., Anal. Chim. Acta, 2005, Nieto-Gligorovski et al., Atmos. Environ., 2010.

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 con-

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ditions.

It is very surprising that the experiments performed at ozone concentrations of almost 1 ppm do not lead to the plateaux in Figure 5b. Also, I don't understand why the x-axis extends to 5x 1013 molecules cm-3. Plotting together Eley-Rideal and Langmuir-Hinsshelwood mechanism in Figure 5 makes no sense. It is obvious that the obtained results do follow the Eley-Rideal pattern. Surely, the substrates play an important role with this respect.

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

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