Atmos. Chem. Phys. Discuss., 8, S2535–S2538, 2008
www.atmos-chem-phys-discuss.net/8/S2535/2008/

Atmospheric
Chemistry
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Discussions

Interactive comment on “The heterogeneous OH oxidation of palmitic acid in single component and internally mixed aerosol particles: vaporization, secondary chemistry, and the role of particle phase” *by* V. F. McNeill et al.

Anonymous Referee #1

Received and published: 12 May 2008

General Comments:

This manuscript describes results of laboratory studies of the oxidation of pure and mixed palmitic acid (PA) aerosol particles by OH radicals. Reactions were carried out in a flow tube reactor. Reactive uptake coefficients were measured and reactions were monitored using chemical ionization mass spectrometry for gas and particle chemical analysis and an SMPS for particle size distribution measurements. Aerosols included pure PA and PA-coated NaCl particles, and PA-coated aqueous NaCl drops. A model was developed to analyze the results of the pure PA experiments and included surface reactions of PA with OH radicals, secondary reactions between products and PA, product volatilization, and surface renewal of PA.

The reactive uptake coefficients seem to be in agreement with those measured by others, and provide interesting insights into the effects of coatings and water on OH radical reactions. The results indicate significant volatilization of organic reaction products, as also observed by a few other groups, and that secondary reactions of products with PA plays an important role in the chemistry. The manuscript is generally well written and contributes useful new information on the heterogeneous oxidation of organic particles by OH radicals. This is a topic of much current interest and relevance in atmospheric chemistry. The manuscript should be suitable for publication in ACP after issues raised in Comment #3, which may be serious, are incorporated.

Specific Comments:

1. Pages 6044-6045, Section 3.1: I suggest explicity stating the relationship between k'' and k' or the uptake coefficient, and also stating something to the effect that S/So is proportional [PA]/[PA]o, which in turn is proportional to [PA]surf/[PA]surf,o because the surface area/mass is approximately constant.

2. Page 6049, lines 2-4: If the alkoxy radical isomerizes it forms a hydroxylalkyl radical, which then reacts with O2 to form a hydroxyperoxy radical. A stable carbonyl is formed by the reaction of an alkoxy radical with O2.

3. I have one major concern that could unfortunately impact many aspects of the data interpretation. The concern is in regards to the formation (and possible photolysis) of hydroperoxides, which may dominate the chemistry of this system but has not been included in the reaction mechanism, model, or discussion.

It appears that with this OH source significant concentrations of HO2 radicals are formed. In the gas phase, rate constants for RO2 + HO2 reactions are about 10,000 times larger than for RO2 + RO2 reactions between secondary RO2 radicals [Atkin-

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son, J. Phys. Chem. Ref. Data, 26, 215-290 (1997)]. If this holds for the condensed phase, which is likely, then one would expect that in the present system RO2 radicals in the particles will react with HO2 radicals (possibly overwhelmingly) to form hydroperoxides, which are the sole product of the reaction. RO2 + HO2 reactions will also be enhanced for these solids, as compared to liquids, because the RO2 radicals are on the surface where exposure to HO2 radicals is high, and RO2 + RO2 reactions will be slower because of reduced diffusion of RO2 radicals in solids.

Furthermore, for this experimental set-up it appears the entire flow, including reacted particles, is exposed to 254 nm light (If not, then comments below on hydroperoxide photolysis are not relevant.). In the presence of 254 nm light, hydroperoxides are readily photolyzed, forming RO + OH radicals. These RO radicals can react with O2 to form carbonyls, abstract H-atoms from neighboring CH2 groups to form alcohols, or decompose. This is an alternative mechanism to that proposed here and forms all the indicated products. Hydroperoxide photolysis also adds to the pool of OH radicals and so can alter reactive uptake coefficient measurements.

Given the potential importance (and possible dominance) of RO2 + HO2 reactions in this system, and subsequent photolysis of hydroperoxides, more thought needs to be given to the interpretation of these results, their relation to other studies, and their relevance to the atmosphere. RO2 + HO2 reactions are likely to be important in the atmosphere, and might even dominate in low NOx areas. Photolysis of hydroperoxides may also be significant, but certainly not to the degree it would here with 254 nm light [see for example, Gomez et al., J. Phys. Chem. A, 110, 3584-3592 (2006)]. At a minimum, these reactions should be incorporated into the data interpretation and discussion, and I strongly suggest, into the model. The authors may also want to consider a time constant approach [Docherty and Ziemann, J. Phys. Chem. 110, 3567-3577, (2006)]. Perhaps this chemistry is the reason it was necessary to include secondary reactions between oxidation products and PA in the data interpretation.

Technical Comments: None

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