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Atmospheric
Chemistry
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Discussions

Interactive comment on “Consecutive reactions of aromatic–OH adducts with NO, NO_2 and O_2: benzene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresoland aniline” *by* R. Koch et al.

Anonymous Referee #4

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This manuscript reports on experimental kinetic study of the consecutive reaction of a series of aromatic-OH adducts with various atmospheric scavengers using flash photolysis/resonance fluorescence technique. Aromatic hydrocarbons emitted from anthropogenic sources play important roles in ozone production and secondary organic aerosol formation. However, their oxidation mechanisms are still poorly understood. The results from this study provide useful kinetic data (e.g. the rate constants) on the consecutive reaction of the aromatic-OH adducts with the relevant atmospheric scavengers, which are still rare in the literature. The paper may be publishable after the

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following issues are addressed:

My main concern with their technique lies in that their approach neglects the isomeric reaction pathways for the non-benzene OH-adducts, which may incur additional multi-exponential kinetic behaviors. For example, OH addition to toluene leads to formation of four possible adducts and each adduct has distinct kinetics with respect to the reaction with O2 (I. Suh et al., Chem. Phys. Lett. 364, 454, 2002; J. Am. Chem. Soc. 125, 12655, 2003). The kinetics of the O2 addition to the four OH-toluene adduct isomers is complex and the adduct radical curve will exhibit multi-exponential behavior. Each of the four OH-toluene adduct is formed with a single time constant given by the sum of the individual rate constants. The isomeric branching ratios are given by relative rate constants which have been calculated by previous work. The four OH-toluene adduct isomers react with O2, each with its own characteristic rate constant. As a consequence, the kinetics of adduct may appear intractable. Such a complexity should be addressed and evaluated.

The paper was rather poorly referenced. There have been several important experimental and theoretical studies on the aromatics-OH reactions, which are relevant to the present work. For example, a recent study has performed experimental studies to identify and quantify the products from OH-initiated m-xylene oxidation (J. Photochem & Photobio A: Chemisty. 176, 199-207 (2005). The products quantified in that study accounted for about 47% of the carbon balance of m-xylene.

In the discussion section, the authors seem to only discuss the case of benzene (pages 9-11).The discussion should cover all title compounds, including the comparison between the current study and the available literature data.

The authors draw a conclusion that the only relevant atmospheric scavenger for aromatic-OH adducts is O2 (on page 11). In order for the readers to better understand this point, the authors should provide explicit explanation. For example, why can the reactions of the title aromatic-OH adducts with the other atmospheric scavengers (e.g. NO and NO2) be neglected in the atmosphere?

Minor comments:

The authors should avoid writing complex sentences, which may cause ambiguity. For example, on page 5, “ Note that the formal reaction (2), which represents the part of a-c which is proportional to [A], contains the abstraction channel as well as the reaction of OH with possible impurities of the aromatic”.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7623, 2006.

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