Atmos. Chem. Phys. Discuss., 9, S865–S869, 2009
www.atmos-chem-phys-discuss.net/9/S865/2009/

Atmospheric
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Discussions

Interactive comment on “Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs)” *by* A. W. H. Chan et al.

R. Atkinson

Roger.Atkinson@ucr.edu

Received and published: 18 March 2009

Comment from Janet Arey, Noriko Nishino and Roger Atkinson, Air Pollution Research Center, University of California, Riverside, CA 92521, USA

This is a very interesting study; however, we believe that the interpretation of the results and reaction mechanism may be more complicated than discussed. As noted by the authors, the OH-naphthalene adducts react with O2 and NO2 at equal rates in air at an NO2 mixing ratio of ~60 ppbV (Nishino et al., 2008). Hence in the "high-NOx"

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experiments, ˜50-60% of the OH-naphthalene adducts would react with NO2 and the remainder with O2. 2-Formylcinnamaldehyde has been observed as a major product of the OH + naphthalene reaction under conditions where the OH-naphthalene adducts reacted dominantly with NO2, and the recent re-evaluation of the Sasaki et al. (1997) data by Nishino et al. (2009a) results in a 2-formylcinnamaldehyde yield from the OH-naphthalene adducts + NO2 reaction of ˜56%. The mechanism for formation of 2-formylcinnamaldehyde from the OH-naphthalene adducts + NO2 reaction is not clear; assuming that 2-formylcinnamaldehyde arises from decomposition of an alkoxy radical (as shown in Figure 6) would mean that the NO2 + OH-naphthalene adducts reaction leads to alkoxy radical + NO. While calculations by Andino et al. (1996) showed the OH-toluene adduct reaction with NO2 to form alkoxy + NO to be significantly endothermic, this may not be the case for the corresponding OH-naphthalene adduct reactions. Note that the present study shows for the first time (from the "low-NOx" experiments) the formation of 2-formylcinnamaldehyde from the OH + naphthalene reaction in the absence of NO2.

The available data suggest that the OH-monocyclic aromatic adducts react with O2 and NO2 at equal rates in air at NO2 mixing ratios of ˜1-10 ppmV (˜3.3 ppmV for the OH-toluene adduct), and that the OH-monocyclic aromatic adduct + O2 reaction proceeds in large part by formation of a bicyclic radical which (after addition of O2 and reaction with NO) results in formation of sets of 1,2-dicarbonyl + unsaturated 1,4-dicarbonyl products (Arey et al., 2009). The yields of 1,2-dicarbonyls from the OH-monocyclic aromatic adduct + NO2 reactions appears to be much lower than from the O2 reactions (both reactions being under conditions where organic peroxy radicals would react with NO to form alkoxy radicals) (Atkinson and Aschmann, 1994; Bethel et al., 2000; Nishino et al., unpublished data, 2009). In contrast, the OH-naphthalene adducts react with O2 and NO2 at equal rates in air at an NO2 mixing ratio of ˜60 ppbV, and the OH-naphthalene and OH-alkylnaphthalene adduct + NO2 reactions lead to dominant formation of 2-formylcinnamaldehyde and its homologs (Wang et al., 2007; Nishino et al., 2009a), with low (<5%) yields of glyoxal from naphthalene, 1-methylnaphthalene

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and 1,4-dimethylnaphthalene (Nishino et al., 2009b). In other words, under atmospheric NOx conditions the major expected products from the monocyclic aromatics are 1,2-dicarbonyls + unsaturated 1,4-dicarbonyls, while those from the naphthalene and alkylnaphthalene reactions are expected to be ring-opened dicarbonyls without loss of carbons.

The authors should be cautious about stating that the higher SOA yields from the "low-NOx" reactions were due to increased "ring-retaining" products. The lowest volatility compound listed in Figure 4 is formylcinnamic acid, a "ring-opened" compound identified only by LC/MS analysis by Bunce et al. (1997). The proposed epoxide structure for the isomeric compound listed under "ring-retaining" is for a product observed by API-MS and GC/MS analyses of the naphthalene and naphthalene-d10 reactions (Sasaki et al., 1997; Wang et al., 2007).

Comparison of the reaction products under "high-NOx" vs "low-NOx" conditions shown in Figure 3 is complicated by the fact that, as shown by Nishino et al. (2009a), 2-formylcinnamaldehyde photolyzes rapidly. The photolysis rate of 2-formylcinnamaldehyde is approximately that of NO2 for blacklamp irradiation, and Nishino et al. (2009a) observed that photolysis was the dominant loss process for 2-formylcinnamaldehyde in CH3ONO - NO - air irradiations of naphthalene. For the "high-NOx" conditions, the OH-naphthalene adducts would react roughly equally with NO2 and O2 and in the presence of NO the OH-naphthalene adducts + NO2 reaction leads to ˜56% 2-formylcinnamaldehyde via an as yet unknown mechanism. In the absence of NOx the OH-naphthalene adducts will react totally with O2, with the 2-formylcinnamaldehyde yield not being known. Since the OH radical concentrations were a factor of 5 lower in the experiments carried out in the absence of NOx, then assuming the same light intensity, photolysis of 2-formylcinnamaldehyde in the "low-NOx" experiments would be a factor of 5 more important than in the "high-NOx" experiments. Because it is likely that photolysis of 2-formylcinnamaldehyde was its dominant loss process, the concentrations of 2-formylcinnamaldehyde in the "low-NOx" exper-

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iments would be significantly lower than in the "high-NOx" experiments even if the 2-formylcinnamaldehyde formation yield is the same at low- and high-NOx.

It would be interesting if the authors would carry out future experiments at higher NO2 concentrations (say $>$500 ppbV) such that the OH-naphthalene adducts react dominantly with NO2.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1873, 2009.

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