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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.

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We thank Dr. Atkinson for the short comment. We have addressed the issues (see our responses below) and made changes to the manuscript as noted. We acknowledge that the gas-phase mechanism of PAH photooxidation is more complicated than presented and is beyond the scope of this study. In an upcoming study, we will focus on the SOA composition and formation mechanisms.

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

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at an NO2 mixing ratio of ∼60 ppbV (Nishino et al., 2008). Hence in the "high-NOx" 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 OHtoluene 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 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.*

We agree that the complete mechanism is more complicated than presented. Our PTR-MS data are only qualititative, but the products identified are consistent with those identified by other studies in the literature (Sasaki et al., 1997, Wang et al., 2007). The focus of this study is on the aerosol formation from photooxidation of PAH. In our high-NOx experiments, we are concerned with SOA formation under conditions relevant to urban polluted conditions, and thus we have kept NO2 concentrations between 50 and 100 ppb. While the NO2 dependence can be complicated, we are confident that in these experiments the SOA is formed under realistic conditions. In a future study, we will show that the composition of the SOA generated closely resembles that of urban field samples.

We acknowledge that both the yields and the composition of the SOA are closely related to the gas-phase mechanism, but the trend in aerosol yields and volatility under high- and low-NOx is qualititatively consistent with the relative abundance of ring-retaining and ring-opening products. Based on our NO2 measurements and the relative rates measured in Nishino et al. (2008), the OH-naphthalene adduct reacts with O2 and NO2 at approximately equal rates. While reaction of the adduct with NO2 produces 2-formylcinnalmaldehyde at high yields (Nishino et al., 2009), reaction of the adduct with O2 can also produce 2-formylcinnamaldehyde (after formation of alkoxy radical followed by fragmentation). The yield of 2-formylcinnamaldehyde from the O2 route can be high, as our data show little formation of other products (including phthaldialdehyde) in the early stage of oxidation, provided that the NO concentration is high. Therefore from our data we believe that the reaction of the OH-naphthalene adduct with

O2 yields mostly 2-formylcinnamaldehyde, and formation of 1,4-dicarbonyl + glyoxal is likely secondary, as suggested by previous studies. Our ability to quantify the PTR signal would depend on availability of an authentic standard of 2-formylcinnamaldehyde. (See comment on further experiments)

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 APIMS and GC/MS analyses of the naphthalene and naphthalene-d10 reactions (Sasaki et al., 1997; Wang et al., 2007).

While the ring-opening vs ring-retaining pathway explains the overall difference in volatility between high- and low-NOx SOA, not all ring-opening products have higher volatility. However, the products listed in Figs 3 and 4 are the early-generation products observed in the gas phase. As we will show in a subsequent study, the SOA is comprised mainly of highly oxygenated C8 and C10 compounds, which arise from further oxidation of compounds listed in Fig 4. The composition (and volatility) of the SOA will therefore be determined by the branching ratio of ring-opening (which leads to lower MW compounds) versus ring-retaining pathways. While formylcinnamic acid is a ring-opened product with the lowest volatility, this does not affect the general trend of fragmentation dominating under high NOx. To avoid confusion, we state that these compounds *and their oxidation products* likely have a higher MW under low NOx, where decomposition does not dominate. We also acknowledge that owing to the unit mass resolution of the PTR-MS, we cannot distinguish between formylcinnamic acid and epoxide for that mass signal.

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-

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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 $\sim$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" experiments 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.

In our high NOx experiments, HONO is depleted after 2 h, and 2-formylcinnamaldehyde decays slowly (< 0.06 h^{-1}). Aerosol volume was constant, suggesting that photolysis of 2-formylcinnamaldehyde does not contribute to aerosol formation (as photolysis likely leads to formation of more volatile products). It would therefore be interesting to see if the aerosol yields would be different under different photolysis conditions. We agree that the relatively lower 2-formylcinnamaldehyde concentrations (and other ring-opening products) in the low-NOx experiments can also be a result of longer exposure time to UV, since in the high-NOx experiments the observed decay rate (presumably due only to photolysis) of 2-formylcinnamaldehyde is not negligible (about 28% loss over 6 h after HONO is depleted). To address this uncertainty, we have added the following to Section 5.2:

“It is also possible that the relatively lower concentrations of ring-opening products under low-NOx are a result of longer UV exposure time. The OH concentrations are a factor of 5 lower under low-NOx conditions. A longer irradiation time is needed to achieve the same fraction of naphthalene reacted, resulting in greater loss of formylcinnamaldehyde by photolysis, which has been shown to be significant under blacklights (Nishino et al., 2009).”

We agree with Dr. Atkinson that because the fate of the OH-naphthalene adduct under high- and low-NOx conditions might not be as simple as presented, more detailed study is warranted. While Dr. Atkinson suggested running at higher NO2 concentrations, running at lower NO2 concentrations can also provide insight into the fate of the OH-naphthalene adduct reacting with O2. Because 2-formylcinnamaldehyde has been quantified in previous studies (Sasaki et al., 1997), we suggest Dr. Atkinson's group use a dark OH source (alkene + O3) to minimize photolysis of 2-formylcinnamaldehyde. High concentrations of naphthalene can be used to minimize reaction of 2-formylcinnamaldehyde + O3.

References:

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