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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of photo-oxidation products from the reaction of a series of alkyl-benzenes with hydroxyl radicals during EXACT using comprehensive gas chromatography" *by* J. F. Hamilton et al.

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General Comments:

This paper provides important information concerning the products formed in the atmospheric photo-oxidation of aromatic compounds, which is an important and persistent uncertainty in atmospheric chemistry. The chromatographic technique employed represents the state-of-the art, has not to my knowledge been used previously to address this problem, and represents an appropriate approach. A significant problem with identifying and quantifying aromatic ring-opening products is addressed by preparing

authentic samples and using them for calibration and identification.

Unfortunately, the results of the study were mostly negative, with the ring-opening products expected according to current theories (as reflected in the "MCM" detailed mechanism) being much less than expected or absent, and no significant new products in high enough yields to suggest alternative mechanisms or theories. Nevertheless this is an important finding that needs to be published.

Although the GC method represents the state-of-the art, as recognized by the authors there are significant limitations in the sampling approach (involving use of a valve in which "sticky" compounds such as phenols and many multifunctionals tend to hang up) that may prevent detection of important products or cause negative biases in measured yields. The authors are aware of this problem and attempted to address it through comparisons of gas-phase and direct liquid injections. However, as discussed below, it is unclear whether these comparisons were conducted for all the compounds listed on Table 1.

Specific Comments and Substantive Technical Corrections:

The Abstract should state the fact that the yields of the detected ring-opening compounds are much less than expected based on current mechanisms, and some expected compounds were not detected. As indicated above, this is probably the most important result of this work. This is stated in the "Atmospheric Implications" and "Conclusions" sections, but should also be summarized in the abstract.

Structures should be given for all the compounds discussed. Figure 1 gives some of the structures but not all. The nomenclature for such compounds is not obvious to all potentially interested readers, and they should not be made to have to look them up elsewhere to get the full benefit of this work.

More discussion should be given concerning the limitations of the sampling method when the methods are first described.

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Interactive Comment

It should be clarified which of the compounds listed on Table 1 were tested by comparing liquid samples with gas analysis. Is it only the three compounds listed on Table 3 in the "Chamber Calibration" column? Were chamber calibrations attempted for the others or were the results unsatisfactory? If not attempted, why not? This is important because it addresses the issue as to whether the lower-than-expected yields (or negative observations) were due to problems with sampling from the gas phase.

The data from the benzene experiments discussed in the text need to be shown.

Other Technical Corrections:

I could not find Saunders et al, 2002 (Footnote 5 in Table 4) in the reference list. I did not check for all references that may have been cited in footnotes, so there may be other such omissions.

The column headings for types of rate constants on Table 4 are misplaced on the manuscript I printed. Parentheses are missing on some of the J(NO2)Šs on that table.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4359, 2003.