

Interactive comment on “The impact of multiphase reactions of NO₂ with aromatics: a modelling approach” by N. Lahoutifard et al.

Anonymous Referee #2

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Overview

The authors present a modeling study examining whether particle reactions of phenolic compounds with NO₂ can be a significant source of HONO to the gas phase. The concept behind the work is very interesting, and the authors present some interesting results, but overall the paper is not currently developed enough to warrant publication. With a more thorough investigation of the chemistry, and a much more complete examination of the results, this would be a very good paper, worthy for publication in APC.

General Comments

1. Concentrations/speciation of aromatics and phenolics.

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a. It would be useful to know the initial concentrations of the dominant/important gas-phase and condensed-phase aromatic compounds under at least two specified "high" and "low" concentration conditions (e.g., in a table of initial conditions).

b. Given the very low Henry's law constants for the aromatic compounds, and the very low liquid water content of the assumed aerosol, I am guessing that under the "high" condensed phase aromatic concentrations (e.g., 0.01 M) there are unrealistically high gas-phase mixing ratios of the aromatic compounds. If so, this likely alters the gas phase chemistry in an unrealistic way which might affect overall chemistry, and suggests this scenario is unrealistic.

c. The "turning on" of aerosols for 2 or 4 hours in the morning is a very artificial means of probing the chemistry and, of course, leads to the "wrong" diurnal dependence of HONO(g) (i.e., highest values during daytime). What happens if particles are allowed to be present throughout a model day?

d. I would like to suggest an alternative, complementary approach to the current scheme of having to make phenolic compounds by reactions of OH and other radicals with aromatics: include primary emissions of phenolic-containing particles. A number of papers have shown that wood combustion releases very high concentrations of gas- and condensed-phase phenols (e.g., Hawthorne et al., 1992; Anastasio et al., 1997). Although not completely characterized, this group of compounds includes a number of large phenols of low volatility that will exist primarily in the particles. Instead of relying on having to form phenols by the radical reactions in the current model, the authors could allow nighttime emissions of phenolic-compound-containing particles, with simultaneous and subsequent reactions of NO₂. This should reduce the problems described above in b. and c.

2. Results

a. Approximately a third of the current Results section belongs either in the Introduction or Methods sections: namely, from line 4 on p. 158 ("Aerosol particles might be a

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source...") to line 14 on p. 159. In fact, much of this material could be deleted as it repeats information presented earlier (e.g., why list reactions (15) - (20) when they are all in Table 2?).

b. The results section is far too short, especially given the suggestion above that approximately 1/3 of it is not actually "results". There needs to be a more detailed description of what occurs in the model and why. For example, what are the most important pathways for HONO(g) formation? What phenolic compounds are most important? What is the gas-particle partitioning of the phenols?

c. On a related note, Figures 1 and 2 are, together, described in only one paragraph (p. 159-160). More explanation is required for a reader to follow what is important. On page 159 (starting at line 27) results from a model run are discussed in detail, but this model run is not included as a figure. Why not describe Fig. 2 here? (Or replace Fig. 2 with the run that is described in the text?)

d. The authors need to run sensitivity studies on important factors in the model (in addition to the initial aromatic concentration in the condensed phase). For example, what about the influence of pH? The initial pH assumed in the particles (pH 4.5) is probably higher than is realistic for urban particles; what happens to the chemistry if the initial pH is lower (or higher)?

Specific Comments

1. Part of title should be changed to "...Reactions of NO₂ with Phenols..." or something similar since according to their scheme it is only the phenolic compounds, and not aromatics in general, which are responsible for the reduction of NO₂.

2. Pages 156-157. Description of past measurements of particulate OC is too long and somewhat confusing. For example, all measurements should be expressed in the same units where possible.

3. Figure 1. a. Is this figure needed? Could it be explained very simply in a sentence

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or two in the text instead? Would a different aromatic concentration be more useful to show? b. In any case, it would be useful to plot the total aqueous phase concentration of aqueous N(III) (i.e., HONO(aq) and NO₂-(aq), in gas phase equivalent units) on the same graph (or at least mention it in the figure caption if it is much smaller than the gas phase values).

4. Figure 2. a. Both runs (base case and NO₂/phenolic reactions) should be plotted on the same scale for clarity. b. As described for Fig. 1, it would be interesting to have the total aqueous phase N(III) plotted on the same graph.

References

Anastasio, C., B. C. Faust and C. J. Rao, Environ. Sci. Technol. 31, 218-232, 1997.

Hawthorne, S. B., D. J. Miller, J. J. Langenfeld, and M. S. Krieger, Environ. Sci. Technol. 26, 2251-2262, 1992.

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