

***Interactive comment on* “Evaluation of the pathways of tropospheric nitrophenol formation using a multiphase model” by M. A. J. Harrison et al.**

Anonymous Referee #1

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The manuscript presents a multiphase modeling study that deals with the analysis of nitrophenol formation in both the gas and aqueous phases. Nitrophenols have been identified as toxic species but their formation pathways in the atmosphere are poorly understood. While a few kinetic and product studies on the formation of nitrophenols in the gas phase have been performed, the understanding of aromatic chemistry in the atmospheric aqueous phase is still in its infancy. Even though the study is based on many assumptions and estimates it elucidates the possible role of aqueous phase processes in the formation of these species. It is certainly appropriate for publication in 'Atmospheric Chemistry and Physics' after the consideration of my comments below.

General comments

- It would be useful to add either in the text or in form of an additional table the equilibrium partitioning ratios of the aromatic compounds. This will clarify (i) to what extent both phenols and nitrophenols are close to their equilibrium concentrations in the aqueous phase and (ii) that the dominance of the aqueous phase processes with subsequent evaporation of the nitrophenols is simply based on the uptake of a highly soluble compound which forms a less soluble product. I admit that this information is already somehow included in the text and tables but a brief overview of such values would help to understand the underlying principle.

- In the gas phase it has been shown that ring cleavage products from the reaction of phenols and NO_3 are only a minor pathway. The authors should point out more clearly that the same assumption has been made also for the corresponding aqueous phase processes. Are there any evidences of aromatic reactions in the aqueous phase which yield mainly ring retaining products? I am not saying that it is wrong but the reader should be made aware that a reduced yield of nitrophenols would lead to a minor importance of the aqueous phase processes. In addition, is any rate constant (or estimate) available of the reaction of nitrophenols in the gas or aqueous phase? How would those influence the results?

- The assumed liquid water content (L_c) of $3e-9$ seems unrealistic under the assumption of a droplet diameter of 10 microm. It corresponds to a drop concentration of $< 1 \text{ cm}^{-3}$. The authors should restrict their analysis to a more realistic range of liquid water contents. It does not seem impossible that similar chemical processes might occur in haze particles (for which $L_c = 3e-9$ would be appropriate) but they are even more speculative since ionic strength effects on organic aqueous phase are poorly investigated.

Specific comments

p. 1116, l. 5: 'Relative nitration pathways' sounds odd. Reword 'relative importance of different nitration pathways'.

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- I. 14/15 Not all rate constants in the aqueous phase are faster. Specify.
- I. 25/26 Specify what essential features of multiphase chemistry (e.g., aromatic, nitration)
- p. 1117 Add in the first paragraph of the model description the time range the simulations have been performed for and the procedure how the results in the figures have been derived, i.e., are those integrated formation rates over the whole simulation time or analyzed at one specific time?
- p. 1120, I. 9 What is meant with 'clean' inorganic gas phase?
- p. 1125 Section 3.3. It would be very helpful in order to follow the discussion if the authors would refer here directly to the color coding which has been used in the figures.
- p. 1127, I. 22/23 You refer to species which do not undergo phase transfer but then, in the next sentence, you list OH and NO₃ for which uptake parameters are listed in Table A11. Clarify this (apparent?) contradiction.
- p. 1128, I. 20 Are emission data of nitrophenols available? Is it possible to perform a rough estimate how much nitrophenol can be explained by primary sources and what fraction is obviously of secondary origin (add wither here or in the introduction).
- Table A2 How have the initial concentrations of the radicals been derived?
- Table A10 Add in the caption the reference to Eq.-3
- Table A11 Just as a comment, I would like to draw the authors' attention to a recently published paper by Leyssens et al. (J. Phys. Chem. A, 109, 1864-1872, 2005) who report $\alpha(2\text{-nitrophenol}) = 5.2 \times 10^{-3}$ which is in rough agreement with the estimated value listed here.
- Technical comments
- p. 1117, I. 1 Replace e.g. (Levsen,) by (e.g. Levsen,)

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p. 1129, l. 5 Add a period between 'GDF Considering'

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