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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The impact of multiphase reactions of NO_2 with aromatics: a modelling approach" *by* N. Lahoutifard et al.

Anonymous Referee #1

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The study of Lahoutifard et al. concerns the impact which heterogeneous reactions involving $NO_{2(g)}$ and hydroxy substituted aromatics in liquid droplets have on the tropospheric HONO budget under urban conditions. Although this study is novel in that it incorporates a direct route for the interaction of NO_x with organics in the aqueous phase the findings have not been presented in any significant depth for the reader to assess what causes this route to be relatively insignificant to $HONO_g$ levels. Moreover, some of the most important details regarding the model parameters used and the additional chemistry supplemented into the chemical mechanism are either missing or much too obscure. A limiting factor should be the low solubility of $NO_{2(g)}$ but no mention is made of this in the entire text. Therefore I suggest that before this manuscript proceeds to the next stage of publication the following points are addressed :

(i) The entire text should be checked extensively for grammatical errors.

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(ii) The model description section should be subdivided into three subsections dealing with model parameters, the gas phase mechanism and the aqueous phase mechanism to improve clarity for the reader.

(iii) An additional table should be added which summarises the most important model parameters (e.g SZA, Lat., Long., Date, etc).

(iv) A clear description of which heterogeneous processes are being considered should be given (i.e.) gas/droplet or gas/aerosol/droplet. The authors constantly refer to aerosol whereas the reaction mechanism used has been constructed for use in dilute solution.

(v) The aromatic reaction set should be made available as either an appendix or at the CAPRAM website.

(vi) No mention is made regarding the relatively low solubility of NO_2 compared to other gaseous species, which will be a limiting factor to the importance of this HONO route.

(vii) A wintertime simulation should be performed to examine whether the efficiency of $HONO_g$ release increases as a consequence of lower $NO_{2(g)}$ photolysis and enhanced uptake due to lower temperatures.

(viii) A source/sink analysis should be performed for NO_2^- so that the reader can determine which formation route is the most important.

Specific comments :

p149, ln5 : Quantify the percentage contribution vehicle exhausts make to the total $HONO_g$ concentration under urban conditions.

p150, ln9 : Which previous study does the comment regarding the identity of the species relate to ??

p150, ln 28 : It is more relevant to discuss the version of CAPRAM which is used in this study rather than the predecessor (i.e) that of Ervens et al, (2002) not Herrmann et al,

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(2001).

p151, ln2 : Please re-phrase the sentence concerning the details of CAPRAM to improve the clarity of the text.

p151, ln 13 : Here it should be stated that reactions 2-4 will be rather trivial under typical atmospheric conditions (i.e. droplet pH < 6.0).

p151, ln 14 : The two reactions discussed in the text should be provided as chemical equations. Some additional comment regarding the rapidity of the processes is also needed.

p151, ln21 : The sentence regarding the layout of the paper should be re-written to provide more clarity.

p152, ln 5 : The number of extra reactions with which the mechanism of Ervens et al, (2002) was supplemented with should be quantified.

p152, ln 22 : Give an example of where RACM has been used under urban conditions to support this statement.

p155, ln 21 : pKa values should be provided for the hydroxy substituted aromatics given in Table II to allow the reader to estimate the fraction of each compound which exists in both the dissociated and undissociated forms. Furthermore, it should be made clear whether the reaction of $NO_{2(aq)}$ with the undissociated form of the aromatics are accounted for in the study. If not, some reason should be given why these reactions are neglected considering the discussion on P151, ln 14.

p156, ln 15 : More detail is needed concerning the initial concentrations used for both gaseous and aqueous phase species, especially concerning the hydroxy substituted aromatics (i.e.) provide a link to the appropriate source.

p156, ln 17 : No information is provided for the latitude, longitude and time of year for which the simulations have been performed. Moreover, some details regarding the

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software with which the modelling was performed maybe of interest to some readers.

p156, ln18 : Are these conditions representative of a typical tropospheric cloud?? The small droplet radius means that the uptake of $NO_{2(g)}$ maybe over-estimated.

p158, ln4 : As soot is not considered in the present study all discussion concerning this aspect of heterogeneous HONO formation should be limited to the introduction, as it is irrelevant to the findings presented here.

p159, ln1 : Some comment should be made regarding the efficiency of reactions(12) and (13) under the conditions chosen for this study. Reaction (14) should be removed if it is insignificant in Urban scenarios.

p159, ln 14 : If the aqueous phase becomes more acidic reactions (15) to (20) could become rather negligible in terms of nitrite formation due to protonation of the reactant(i.e the aromatic). Are the dissociation equilibria incorporated into the mechanism ??

p160 : A source/sink analysis for NO_2^- should be provided as chemical fluxes for the case where the total aromatic content equals 0.01M. This could be performed at, say, 1 hr after heterogeneous chemistry is turned 'on'. Such an analysis would enable the reader to assess which of the reactions (15) to (20) is most important in terms of HONO formation.

p161 : A wintertime simulation should be performed to investigate the efficiency of this route at lower temperatures and when the photolysis of $NO_{2(g)}$ is minimal.

p161 : The conclusions section should be updated to account for the modifications made to the paper (e.g.) the source/sink analysis.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 147, 2002.