

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

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As mentioned by referee 2, we presented a modelling study examining whether particle reactions of phenolic compounds with NO₂ can be a significant source of HONO to the gas phase. He stated that the concept behind the work is very interesting, and that we presented some interesting results, but that overall the paper was not developed enough but with a more thorough investigation of the chemistry, and a much more complete examination of the results, this manuscript would be a very good paper, worthy for publication in APC. Accordingly, we considered all his comments and the following are the replies to his general comments. These changes led to an in-depth revision of our manuscript which has now a shorter introduction and a much longer result section highlighting more features from our work than was intended originally.

1.a A table with all initial conditions was added along with following comments:

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"Initial conditions were chosen to be representative of an urban case as listed in Table IV. The initial condensed phase concentrations of aromatics were initially set to 0, but in some case studies described below, their initial concentrations were raised up to 0.1 M arbitrarily. The aerosol considered in that study is assumed to consist of spherical droplets, in a liquid state, monodispersed with a mean radius of 0.1 μm and a liquid content (LC) of 50 $\mu\text{g m}^{-3}$. We simply took local PM10 measurements and transformed that arbitrarily into a spherical liquid droplet to obtain such LC values. This is by no means representative of a tropospheric cloud or of a real aerosol, but it allows use of aqueous phase chemistry, finally the only kind of data available at present time, for this explorative approach. However, one should keep in mind all limitations behind all these extreme simplifications such as ionic strength effects, which were ignored in order to maintain a straightforward simulation of the multiphase processes. Furthermore, at the current state of knowledge, the consideration of activity coefficients for all species would introduce another source of uncertainties to the data set."

1.b Concerning the unrealistic high concentration of aromatics, we added following paragraph:

"However, the situation may be somehow different depending on the source of the droplet being considered. For instance, soot particles are emitted as hydrophobic substrates. However, their aging in the atmosphere gives hygroscopic properties to their surface, and water as well as secondary organic material are condensing on them, leading to a complex aqueous organic system. Such a system is considered here as an aqueous droplet or film containing initially a large fraction of aromatics in various oxidation states. To mimic such conditions, we applied our model to droplets with a variable initial content of aromatics and with their phase exchange being stopped i.e., the high aqueous phase content of aromatics is kept artificially within the particles (again as a proxy for higher non volatile compounds that are in secondary or aged particles and which will not escape from the particulate phase), making sure that the gas phase chemistry is not perturbed by an additional (non-realistic) source for aro-

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matic compounds. Of course we do apply the same reaction scheme, which is a very straightforward simplification and which may eventually not be valid. However, with regard to the lack of knowledge, this is still a working hypothesis that may be considered. As shown in Figure 3, for droplets with a high load of aromatics (i.e., taken as proxies for liquid organic aerosols with a high fraction of WSOC), the model simulates an additional content of day time HONO of about 0.2 nmol/mol i.e., the HONO source is enhanced. The HONO peak occurs subsequent to aerosol injection into the air mass and is not sustained when the aerosol is removed. "

1.c The turning on and off of the aerosols is now introduced in the model description by:

"Our box-model calculations were performed mostly without any aerosol present in our air mass. In fact, fresh aerosol particles were only injected in the air mass once per day between 6.00 and 8.00 or 6.00 and 10.00 am (i.e., with an aerosol lifetime of 2 or 4 hours). During the rest of the time, the air mass was purely homogeneous. The aerosol injection timing was chosen in such a manner that it simulates secondary particle formation resulting from the combined effect of early morning photochemistry and simultaneous high emissions from car traffic in urban environments."

And further underlined in the result section by:

"This "turning on" of aerosol particles for 2 or 4 hours is indeed a very artificial means of probing the chemistry and will of course lead to the wrong diurnal dependence of HONO in the gas phase. However, the initial main idea behind that assumption is to treat the chemistry of secondary or aged particles (resulting from the combined effect of early morning photochemistry and simultaneous high emissions from car traffic in urban environments). It is obvious that the emitted aerosol particles may have longer (or shorter) lifetimes which are not accounted for in this study. On the other hand, for numerical reasons, it is not safe to keep the same droplets for a long period of time as their content may "disappear", at least for compounds having no gas phase

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sources as the aerosol content is not replenished during time, leading to some numerical singularities which may be difficult to be solved. As will be shown below, the impact of the chemistry of the aromatic compounds is mainly observed during the first hour of gas/droplet interaction and reflects the evolution of the pH, which becomes more acidic when the droplet starts to be aged. Accordingly, our simulations will show the main feature of these processes despite that turning on and off of the aerosol."

1.d Referee 2 made a very interesting suggestion for an alternative, complementary approach to the current scheme of having to make phenolic compounds by OH reactions: include primary emissions of phenolic-containing particles. This idea was underlying under our variable initial concentration of aromatics but was not expressed as mentioned by referee 2. We now added following comment:

"However, the situation may be somehow different depending on the source of the droplet being considered. For instance, soot particles are emitted as hydrophobic substrates. However, their aging in the atmosphere gives hygroscopic properties to their surface, and water as well as secondary organic material are condensing on them, leading to a complex aqueous organic system. Such a system is considered here as an aqueous droplet or film containing initially a large fraction of aromatics in various oxidation states."

2.a-c The results section has been deeply revised to match referee 2 comments about its length to content ratio. We added new figures (giving more information about other species than those initially considered), discuss in more detail the effect of pH and concentration. All together, these new comments more than doubled the length of the results section.

2.d A source sink analysis is now presented in Figure 4 with following comments:

"Figure 4 shows the instantaneous reaction rates of the system $\text{NO}_2 / \text{NO}_2^- / \text{HONO}$ (in M s^{-1}) at 07:00 am on the 7th day of simulation which corresponds to one hour interaction time between the gas phase and the droplets. The figure shows the sink

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and source rates at high aromatic levels (i.e., initial condensed phase concentrations were initialised at 10⁻² M, which are levels found in field campaigns, (Fraser et al., 1998; Fraser et al., 2000; Hawthorne et al., 1992)) because it better illustrates the competition between all pathways. In fact, under such conditions, the pH is about 5 where the reaction chain (12) to (17) is most effective. It can be seen that the sum of the contributions of reactions (8-10) have very high rates exceeded by the rates of reactions (12) to (17). While in Figure 4, this is not the case for the individual reactions as all of them are competing directly with reactions (9-10), but their sum (with respect to nitrite formation) starts to exceed the rate of that reaction meaning that additional HONO is formed. It must be underlined from Figure 4 that when comparing loss and source processes for HONO, that the latter is more or less always produced from a liquid droplet and that reactions (12) to (17) are just an additional source that may become important under some particular conditions. However such conditions, may be readily be observed in urban environment under wood smoke influence but also and more generally under combustion emission influence which produce large concentrations of phenolic type compounds i.e., reactants that may initiate reactions (12) to (17)."

Specific comments.

1. We kept the title unchanged simply because the NO₂ reaction with aromatics may not be limited only to phenolic type compounds. Of course the present study focuses somehow on such compounds simply because there is currently a lack of knowledge for the other family, but certainly such reactions will occur also with other aromatic compounds.

2. This part has been removed to get a better focused manuscript.

3. Figure 1 has been replaced by a new one having following caption:

"Diurnal behaviour of gas phase HONO, O₃ and NO₂ and liquid phase pH, NO₂, NO₂⁻, phenol and phenolate during the exposure of monodispersed droplets (with a radius of 0.1 μm and LC = 50 μg m⁻³), initially free of aromatics. The multiphase chemistry was

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activated between 6:00 and 10:00 am."

4. Figure 1 has been replaced by a new one having following caption:

"Diurnal behaviour and pH dependence of gas phase HONO or condensed phase nitrite ions formed through reactions (12) to (17) during the exposure of monodispersed droplets (with a radius of $0.1 \mu\text{m}$ and $L = 50 \mu\text{g m}^{-3}$) initially free aromatics with varying constant pH. The multiphase chemistry was activated between 6:00 and 10:00 am, starting on the 5th day. The lower panel shows the behaviour of both HONO and NO_2 concentrations as a function of pH."

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