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

N. Lahoutifard et al.

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Interactive comment on " The impact of multiphase reactions of NO2 with aromatics: A modelling approach" By N. Lahoutifard, M. Ammann, L. Gutzwiller, B. Ervens and Ch. George

As mentioned by reviewer 1, this study is novel in that it incorporates a direct route for the interaction of NOx with organics in the aqueous phase. He however felt that: "the description of our work was not presented in any significant depth for the reader to assess what causes this route to be relatively insignificant to HONO levels". This remark arises from the fact that our initial intention was only to produce a short notice about that study. Nevertheless, we did take care about all remarks of referee 1; the following are replies to his numbered specific comments.

(i) The manuscript was deeply revised and hopefully grammatical errors removed from

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the text. This in in-depth revision led to a shorter introduction and a much longer result section highlighting more features from our work then was intended originally.

(ii) The model description section was subdivided as requested.

(iii) The additional table was not added (as we preferred adding on with other initial conditions) but requested parameters are listed in the following paragraph:

"Simulations were carried out for a total duration of 10 simulated days, the first five days being considered as an initializing period. The parameters such as temperature and pressure were kept constant during the simulation (T = 291 K, p = 1 atm, rh = 76 %), such model parameters are identical to those described by Ervens et al. (2002). Especially, the simulations were made for a sunny period of the year, starting the 21st of June at latitude of 51°N. The corresponding photolysis rates at ground level, which can be found on the internet at http://www.tropos.de/CHEMIE/ multimod/CAPRAM/capram.html, are listed at their maximum value (i.e., at a solar zenith angle of 0°). Sunrise and sunset are at 04:00 am and 08:00 pm respectively and the photolysis rates follow a semi-sinusoidal diurnal cycle with a maximum at noon."

(iv) The heterogeneous processes being considered have been clarified by adding in the "Model description / gas phase and uptake processes" section following sentences:

"Our reaction scheme does not have any heterogeneous reactions (i.e., gas-solid interactions such as soot reactions) as it is a purely multiphase model meaning that trace gases are transferred into the aerosol, assumed to be liquid, and react only in the bulk of the droplet."

(v) The aromatic reaction set was not added in this manuscript as it will be published by its authors i.e., H. Herrmann and B. Ervens, but it will be downloadable soon from the CAPRAM web site (as the latter is currently undergoing a full updating process).

(vi) "A limiting factor should be the solubility of NO2(g)Ě", to answer that criticism we add following text:

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"Nitrogen dioxide has a very low physical solubility in water; its Henry's law constant is as low as 0.013 Matm-1 at 291 K (Schwartz and White, 1981) meaning the Henry's law equilibrium will be reached very rapidly for small droplets as those considered in this study. Accordingly, the condensed phase NO2 concentration is small and proportional to the gas phase density with a net flux of NO2 into the droplet being very small after a few minutes of simulation. This is mainly valid for a gas having a low solubility and which does not undergo fast chemical reactions, which is the case of NO2 taken up by pure water. However, this is completely changed if some reactions are added (as those considered here involving aromatic compounds). In such a case, the uptake of NO2 is not driven by its solubility but by the kinetics of the chemical processes in the condensed phase. Accordingly, despite a low solubility the conversion of NO2 into NO2- may become important depending on the characteristics of the chemical transformation as it will allow a significant (at least compared to the pure water case) net flux of NO2 into the droplet."

(vii) The reason having not considered a wintertime simulation has been added:

"The temperature was not varied in our study simply because many temperature dependences of the rate constants are not known which prohibits any simulation at lower temperature as those encountered during winter time. It may be argued that at lower temperature the solubility of NO2 becomes higher therefore allowing a stronger impact of the reactions described above. However, this would be too simple. First of all, solubility and chemical kinetics have different temperature trends. While the first physical parameter (through the Henry's law constant) increases with decreasing temperature, rate constants (for elementary reactions) decrease. Therefore lowering the temperature has two opposite effects that may cancel each other, so that in the absence of appropriate experimental values, we cannot arrive at a firm conclusion with regard to this aspect. An additional effect is that reaction products (i.e., HONO) have also a higher solubility leading to a lower out-gassing and therefore a smaller impact. Keeping in mind all these arguments, we believe that temperature effects may not be so large, at least over the conditions encountered at ground level over Europe, which correspond to our case study. Accordingly, to have a consistent data set for the studies performed here we kept the temperature constant."

(viii) A source sink analysis is now presented in Figure 4 with following comments:

"Figure 4 shows the instantaneous reaction rates of the system NO2 / NO2- / 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 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)."

Referee 1 also listed a number of very specific points which were all taken into account and the text modified accordingly. Below we just underline some of these changes:

* The introduction was sharply reduced in length; by this process the discussion on direct emissions was removed. * The reference on the compound identity was added.

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* The Ervens et al. (2002) paper is now thoroughly used as the reference for the CAPRAM mechanism. * pKa values are now provided in a Table and the reactions being considered clearly identified by the following statement:

"Additionally, we also include the following reaction scheme in the liquid droplet:

C6H5O- + NO2 –> C6H5O + NO2- (12)

p-C6H4OHO- + NO2 –> p-C6H4OHO + NO2- (13)

o-C6H4OHO- + NO2 –> o-C6H4OHO + NO2- (14)

p-C6H4OCH3O- + NO2 –> p-C6H4OCH3O + NO2- (15)

m-C6H4OCH3O- + NO2 –> m-C6H4OCH3O + NO2- (16)

C6H4CH3O- + NO2 –> C6H4CH3O + NO2- (17)"

* Initial conditions are now listed in an additional Table with following comments

"ĚInitial 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 μg 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."

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* A discussion on the effect of pH was added:

"The more obvious parameter is the acidity of the droplet as it controls the levels of dissociated aromatics Ű or, more generally, the fraction of dissociation. To test this parameter, we made some simulations during which the pH was fixed at a constant value in the range from 3 to 7. The corresponding results are depicted in Figure 2. Of course, fixing the pH has a very strong influence on many processes within the droplet that are far beyond just reactions (12) to (17). Nevertheless, such simulations may correspond to droplets transferred to other air masses where either acid levels are lower or in which alkaline species (such as ammonia, or particulate buffers arising from the aerosol source, e.g., combustion, erosion, Ě) are more abundant. From Figure 2, it can be seen that this additional source of HONO is only active at higher pH but not necessarily alkaline ones. In fact additional HONO (and therefore nitrite ions) is already formed when the pH is higher than 4, which is still a reasonable value for droplets under many atmospheric conditions. Therefore, a small contribution to the HONO budget may be expected from this chemistry involving aromatics at moderate acidity. Note however that such a pH may be more representative of remote conditions than those encountered in an urban atmosphere (which was the main objective of the present case study). It must also be underlined that increasing the pH will, on one hand, increase the amount of aromatics being dissociated so that they may act as reactants in the reaction sequence from (12) to (17). On the other hand, the increasing pH will trap an increasing fraction of HONO within the droplet as nitrite ions. This means that this source of gaseous HONO may only be very important if the droplets become more acidic after the reactions (12) to (17) were initiated at higher pH."

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