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The impact of multiphase reactions of NO_2 with aromatics: a modelling approach

N. Lahoutifard[1, *], **M. Ammann**[2], **L. Gutzwiller**[2], **B. Ervens**[3], **and Ch. George**[1]

[1]Laboratoire d'Application de la Chimie à l'Environnement (LACE), CNRS-UCBL, 43, Boulevard du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France
[2]Paul Scherrer Institut, Laboratory for Radio- and Environmental Chemistry, CH-5232 Villigen, Switzerland
[3]Institut für Troposphärenforschung Permoserstr. 15, D-04303 Leipzig, Germany
[*]Now at the Department of Chemistry, University of Ottawa, Canada

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Correspondence to: Ch. George (Christian.George@univ-lyon1.fr)

Abstract

The impact of multiphase reactions involving nitrogen dioxide (NO_2) and aromatic compounds was simulated in this study. A mechanism (CAPRAM 2.4, MODAC Mechanism), was applied for the aqueous phase reactions whereas RACM was applied for the gas phase chemistry. Liquid droplets were considered as monodispersed with a mean radius of 0.1 μm and a liquid water content (LWC) of 50 $\mu g\, m^{-3}$. The multiphase mechanism has been further extended to the chemistry of aromatics i.e. reactions involving benzene, toluene, xylene, phenol and cresol have been added. In addition, reaction of NO_2 with dissociated hydroxyl substituted aromatic compounds has also been implemented. These reactions proceed through charge exchange leading to nitrite ions and therefore to nitrous acid formation. The strength of this source was explored under urban polluted conditions. It was shown that it may significantly increase gas phase HONO levels. About one order of magnitude change of HONO concentration was observed with finally, a minor effect on subsequent gas phase daytime photochemistry because of the limited aerosol life time considered.

1. Introduction

Nitrous acid (HONO) may be an important early morning source of hydroxyl radicals in polluted urban atmospheres and may therefore initiate early daytime photochemistry (Lammel and Cape, 1996). The concentration of nitrous acid is observed to gradually increase during night, while after sunrise it is rapidly photolysed leading to OH and NO according to:

$$HONO + h\nu\,(\lambda < 400\,nm) \rightarrow OH + NO \qquad (1)$$

which is believed to be a significant source of OH in polluted atmospheres (Finlayson-Pitts and Pitts, 1997). This may be particularly important in morning hour photochemistry, when OH production rates from other sources such as photolysis of ozone or formaldehyde are slow. It must be underlined that under certain circumstances OH concentrations later in the day may still be influenced by HONO (Staffelbach et al., 1997a; Staffelbach et al., 1997b). Despite its importance and a considerable number of laboratory and field studies, nitrous acid sources are still poorly described.

Direct emissions from vehicle exhaust are contributing to atmospheric HONO concentrations to a small extent. However, emission measurements at different combustion sources (Calvert et al., 1994; Kessler and Platt, 1984; Kirchstetter et al., 1996; Kurtenbach et al., 2001; Pitts et al., 1984a; Pitts et al., 1984b; Sjoedin and Ferm, 1985; Sjoedin et al., 1984) show that HONO emissions comprise typically less than 1% of the total NO_x emitted, whereas atmospheric HONO levels often reach up to 4% of NO_x present (Lammel and Cape, 1996). It is therefore likely that HONO is formed through secondary reactions of nitrogen oxides in the atmosphere. Analysis of field measurements points to NO_2 as a source component with conversion rates inferred of the order of $10^{-6}\ s^{-1}$ (Andres-Hernandez et al., 1996; Harrison et al., 2000). While the known gas-phase reactions leading to HONO are not important under most conditions, NO_2 conversion to HONO seems to be driven heterogeneously. However, it is not clear presently whether the ground surface or aerosol particles form the substrate for such a process. Up to recently, the aqueous phase disproportionation of NO_2 into HONO and HNO_3 in cloud droplets or on other wet surfaces has been invoked as possible heterogeneous process (Ackermann et al., 2001; Kleffmann et al., 1998; Lammel and Cape, 1996). The rates reported for this reaction differ by orders of magnitude, but it seems unlikely that it is fast enough to provide a significant source of HONO in the atmosphere. Recently, the heterogeneous conversion of NO_2 on soot particles emitted from combustion sources has been suggested as more efficient mechanism (Ammann et al., 1998; Gerecke et al., 1998; Kleffmann et al., 1999; Longfellow et al., 1999). It was suggested that NO_2 reacts with an organic reactant on the soot surface leading to HONO. However, more detailed experiments indicated that soot does not contain a sufficient number of these reactants on its surface to provide a significant source of HONO in the polluted troposphere (Arens et al., 2001; Aumont et al., 1999; Kalberer et al., 1999a; 1999b). Nevertheless, the fact that condensed phase organic species seemed to be involved shed a light on possible other sources of such species. For instance, it has been shown very recently, that semi-volatile species from diesel engine exhaust may undergo transfer to the aqueous phase under atmospheric conditions and react there with NO_2 to form nitrite, and consequently HONO if the aqueous phase becomes sufficiently acidic (Gutzwiller et al., 2002). Recently in model studies it was shown that HONO/ NO_2^- can be formed effectively by aqueous phase processes within cloud droplets (Ervens et al., 2002; Williams et al., 2001).

While the identity of these species remained unknown in that study, a few species are known to undergo electron transfer reactions with NO_2 to form nitrite, e.g. hydroxy-substituted aromatics (Alfassi et al., 1986), aromatic amines (Saltzman, 1954) or alcohol amines (Levaggi et al., 1974). It has also been well established that the photochemical degradation of aromatic compounds leads to a number of phenols and cresols (Pan et al., 1993) which may further undergo reaction with OH partially leading to several dihydroxy-substituted derivatives (Olariu et al., 2000). Thus, degradation of aromatics may also lead to species able to undergo reaction with NO_2 in the aqueous phase. In general, the multiphase or heterogeneous chemistry of aromatic compounds is still unclear, i.e. in many cases the source of the large number of polar species identified in aerosols is not really known as they may originate from primary emissions, and both gas and particle phase oxidation processes.

The aim of the present study was to investigate the potential contribution of the multiphase chemistry of aromatics to the HONO sources using the modelling approach. Over the last years, several studies have underlined the influence of the tropospheric liquid phase on the concentration levels of important trace gases (Jacob, 1986; Lelieveld and Crutzen, 1990; Walcek and Stockwell, 1986). For example, Sander and Crutzen (1996) developed a box model (MOCCA) to investigate processes influencing ozone in the marine boundary layer (mbl), and they focused on the potential role of bromine and chlorine compounds on the destruction of ozone. More recently, an aqueous phase chemical model has been developed by Herrmann et al. (2000), CAPRAM, in which organic compounds up to two carbons (including alcohols, aldehydes and acids) are considered. This chemical aqueous phase radical mechanism details both source and of a full set of radicals or radical anions.

For the present study, we modified the CAPRAM mechanism to assess the impact of multiphase reactions of nitrogen dioxide (NO_2) with aromatic compounds of the type mentioned above, e.g. phenol, hydroquinone, resorcinol, *p*-methoxyphenol, *m*-methoxyphenol. Explicitly, the mechanism involves the dissociation of these rather weak acids, followed by electron transfer yielding aqueous nitrite (Alfassi et al., 1986; Ammann et al., 1999a; 1999b; Schall and Heumann, 1993):

$$ArOH \rightarrow ArO^- + H^+ \tag{2}$$

$$ArO^- + NO_2 \rightarrow ArO + NO_2^- \tag{3}$$

$$NO_2^- + H^+ \rightarrow HNO_2 \tag{4}$$

The mechanism above is essentially effective under very high pH values (pK_a(phenol) = 9.8) but in a recent study it was suggested that NO_2 can also react by H abstraction from undissociated phenol leading also finally to NO_2^- (Vione et al., 2001). On the other hand it is well established that the reaction of NO_2 with phenol can lead to nitrophenols (e.g. Dzengel et al., 1999).

In order to test whether these reactions are significant sources of HONO, the fate of aromatics in the condensed phase needed to be described explicitly. This was performed by taking into account all oxidation steps, potentially initiated by radicals or radical anions such as OH, NO_3, SO_4^-, Cl_2^-, Br_2^- or CO_3^-. The model used as well as the scenario considered in this study are described in the next section, whereas model outputs are discussed in the result section.

2. Model description

As our intentions were only to study the influence of given chemical reactions, we performed our simulations using a box model, therefore without any horizontal or vertical transport considerations (i.e. our air mass is considered as instantaneously well mixed). The chemical scheme, we used is derived from "CAPRAM 2.4, MODAC mechanism" (Ervens et al., 2002). This chemical scheme treats in great detail the multiphase chemistry of species with up to two carbons and consider about 440 reactions in the condensed phase. This code was extended in order to simulate the chemistry of few aromatic compounds such as benzene, toluene, ortho-, meta- and para-xylene, ortho- and para- cresol and finally phenol. The phase transfer between aqueous and gas phases of these aromatics and of 34 other species (see Ervens et al., 2002) was described using the methodology derived by Schwartz (1986). For this purpose data on Henry's law constants, gas phase diffusion as well as mass accommodation coefficients were collected or estimated as given in Table 1 (which lists only the data for the aromatics, the whole scheme can be found in the internet under `http://www.tropos.de/CHEMIE/multimod/CAPRAM/capram.html`).

In this reaction scheme, the homogeneous gas phase processes are simulated according to the RACM mechanism i.e. "Regional Atmospheric Chemistry Mechanism" (Stockwell et al., 1997). The RACM mechanism is based upon the earlier Regional Acid Deposition Model, version 2 (RADM2) mechanism (Stockwell et al., 1990) and the more detailed Euro-RADM mechanism (Stockwell and Kley, 1994). The RACM mechanism included, when first published, rate constants and product yields from the most recent laboratory measurements, and it was tested against environmental chamber data. The aromatic chemistry was also revised in RACM. Therefore this code, which treats about 237 reactions and 78 species, is widely used and was applied here without any modification (despite the fact that its NO_x chemistry may not be fully adequate with respect to HONO chemistry) in order to make any comparison with other modelling studies using RACM straightforward.

However, in order to reduce the size of the RACM scheme, a lumping procedure was used which resulted, for the aromatics, in three compound families. The latter are TOL (for toluene and less reactive aromatics), XYL (for xylene and more reactive aromatics) and CSL (for cresol and other hydroxy substituted aromatics). While for any gas phase reactions, we kept the lumped compounds, the condensed phase scheme of “CAPRAM 2.4, MODAC mechanism” treats every reaction explicitly. We therefore had to detail the aromatic compounds once transferred into the aerosol. This has been done considering following assumptions (taken from Ferrari et al., 1998):

$$TOL_g \rightarrow , 0.5\,C_6H_{6\,aq} + 0.5\,C_7H_{8\,aq} \tag{5}$$

(i.e. 50% benzene + 50% toluene)

$$CSL_g \rightarrow 0.6\,C_6H_6O_{aq} + 0.2\,C_7H_8O_{aq} + 0.1\,C_6H_6O_{2\,aq} + 0.1\,C_7H_8O_{2\,aq} \tag{6}$$

(i.e. 60% phenol + 20% cresol + (5% hydroquinone + 5% resorcinol) + (5% meta methoxyphenol and 5% para methoxyphenol))

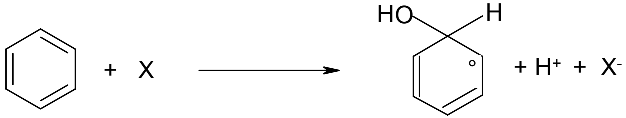
$$XYL_g \rightarrow C_8H_{10\,aq} \tag{7}$$

(i.e. 100% xylene, no differences in reactivity of *o*-, *m*-, *p*-xylene assumed)

where the subscripts *g* and *aq* refer respectively to the gas and aqueous phases. It is obvious that this splitting into these explicit compounds is somewhat arbitrary and limited by nature since it cannot reflect the full nature of the chemistry of aromatics. In fact, the aromatic content of polluted urban air masses is highly variable due to the influence of local or regional emissions which can only be partially captured by a code as RACM due to the lumping procedure. It must also be underlined that the above splitting into “real” compounds may not be fully coherent with the initial lumping in RACM. But nevertheless, we believe that our approach is still justified within the case studies reported in the result section.

All of the above detailed aromatics undergo condensed phase oxidation via the primary attack of radicals or radical anions such as Cl_2^-, Br_2^-, CO_3^-, NO_3, OH or SO_4^- leading to different pathways including H-atom abstraction (at side-chains or at the aromatic ring), addition or electron transfer. Several investigators (Herrmann et al., 1995; Merga et al., 1994; O’Neill et al., 1975; Steenken et al., 1990) reported possible pathway for the reactions of free radicals with aromatic compounds in aqueous solutions. Electron transfer was assigned, for NO_3 and SO_4^-, to be the predominant pathway (Herrmann et al., 1995). However, for the purpose of the present study details of the reaction mechanism are not a central issue as all reactions were expressed as “simple reactions” for which the products are identical from either electron transfer reaction or adduct build-up. For sake of simplicity, we assumed that all radicals will lead to the same mechanism (with still different kinetics) and that all reactions are directly occurring at the aromatic ring (i.e. side-chain reactions are omitted). It is obvious that these assumptions do highly simplify the oxidation mechanism of aromatics but still we believe that this approach retains the main fate of these oxidation processes. It must also be underlined that the knowledge on the aqueous chemistry of aromatics is scarce which does not enable, at the present time, a realistic detailed mechanism to be laid out and used.

The general aromatic oxidation mechanism starts with the formation of a primary HCHD (‘hydroxy cyclohexadienyl’) radical identical for each initial attack on the aromatic ring (therefore, this radical is called “derivative” and numbered according to its parent aromatic), i.e.:



benzene	derivative (1)
xylene	derivative (2)
toluene	derivative (3)
cresol	derivative (4)
phenol	derivative (5)

$$X = OH, NO_3, SO_4^-, Br_2^-, Cl_2^-, CO_3^- \quad (8)$$

This radical derivative then reacts with oxygen according to (Ervens, 2001; Pan et al., 1993)

$$\text{Derivative(i)} + O_2 \longrightarrow 0.4\,\text{ArOH} + 0.4\,HO_2 + 0.6\,\text{derivative(ox)(i)} \quad (9)$$

where ArOH is a hydroxy substituted aromatic based on the chemical structure of the initial aromatic being oxidised (i.e. toluene will lead to cresol while benzene's oxidation will result in phenol). As already explained, the radical derivatives (1 to 5) may be formed from the addition of X, followed by reaction with water and the elimination of HX, or they arise from a direct electron transfer from the aromatic ring to the oxidant X. Such radical derivatives were experimentally observed to decay with a half-life time of about 1 ms (Herrmann et al., 1995). Such a decay is mainly due to three pathways which are: (a) formation of hydroxy substituted aromatics and HO_2 in the presence of oxygen, (b) formation ring cleavage products (such as aldehydes) from cyclohexadienyl peroxy intermediates and (c) formation of aromatic radical cations after protonation of the radical derivative and the elimination of water. The latter will in turn also react and form hydroxy substituted aromatics. All these pathways are included in Reaction 9 which is just a very simple expression for this complex reaction mechanism and in which non considered products (such as peroxy) are simply written as "derivative(ox)". All the data used in this "aromatic extension of "CAPRAM 2.4, MODAC mechanism" are from Ervens (2001).

Finally, all the hydroxy substituted aromatics will undergo acid/base dissociation, which is highly influenced by the pH (and limited in acidic droplets), leading to anions which are very reactive toward NO_2. Such reactions will proceed through electron transfer reactions from the aromatic ring to form nitrite ions (or its associated acid, i.e. HONO), corresponding kinetic data are listed in Table 2.

Simulations were carried out for a total duration of 10 simulated days, the first five days being considered as an initializing period. Our box-model calculations were performed mostly without any aerosol being present in our air mass. In fact, "fresh" aerosols 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 h). During the rest of time, the air mass was purely homogeneous. The aerosol injection timing was chosen in such a manner that it can "simulate" somehow the secondary particle formation resulting from the combined effect of early morning photochemistry and simultaneous high emissions from car traffic in urban environments.

Also to allow meaningful simulation over long periods of time (e.g. 10 days), it is obvious that the code must consider emissions (from the ground as far the boundary layer is concerned the height of which is considered to be 1 km) and deposition in order to provide some stability to the simulated system. We therefore used data from the Edgar database, which was developed for global modelling purposes and has a resolution of $1^\circ \times 1^\circ$. This database considers both anthropogenic and biogenic emission. The more detailed NMVOC database underlying EDGAR was used to obtain the specification of non-methane-hydrocarbons needed to include in the RACM mechanism. Natural hydrocarbon emissions were specified using the database of Guenther et al. (1995). The maximum, 80% median and minimum emission values of all 1 × 1 gridboxes over Europe were determined and the two first data sets used in the present simulation as being representative of an urban polluted site. All details concerning deposition and emissions are given by Ervens et al. (2002).

Initial conditions were chosen to be representative of an urban case. The parameters such as temperature and pressure were constant during the simulation ($T = 291$ K, $p = 1$ atm, rh = 76%). Droplets were considered as being liquid, monodispersed with a mean radius of 0.1 μm and a liquid content (LC) of 50 μg m^{-3}. Ionic strength effects were ignored in order to maintain a straightforward simulation of the multiphase processes. The large range of data of concentrations of aromatics in particles (including hydrometeors or solid aerosols) reflect on one side the difficulty of getting reliable data from field experiments (because of the extreme difficulty in analysing so complex matrices) and on the other side, the large panel of potential sources (which may have large local influences). Particle aromatic mass concentrations were reported up to about 103 nmol/molC in an urban area (Finlayson-Pitts and Pitts, 1986). Fuzzi and co-workers (Fuzzi et al., 2001) in their simplified proxy for the water soluble fraction of organic aerosols estimated a content of about 0.05 μgC m^{-3} for aromatic compounds. Liousse and co-workers (Liousse et al., 1996) calculated average organic submicrometer particle concentrations of 1–2 μg m^{-3} for the eastern

United states, 0.5–1.0 μg m^{-3} for the southwestern United States, and as high as over 10–12 μg m^{-3} in central Europe, the Amazon basin, west central Africa, eastern China, and northern Australia. Water soluble organic compounds (WSOC) mass concentration up to 1–25 μgC m^{-3} were measured in highly polluted urban areas (Sempere and Kawamura, 1996). Aumont and co-workers (2000) calculated WSOC mass concentration up to 10 μgC m^{-3} in polluted areas. All together, these observations underline that depending on the kind of aerosol considered the condensed phase concentration of aromatics is highly variable. Since our main topic was to investigate the influence of the chemistry of NO_2 with aromatics in the particle phase on the HONO budget, we used many different initial condensed phase concentrations, ranging from 0 M (i.e. the aerosol concentration is driven by the gas phase uptake process) to 10^{-2} M (where our droplet may be regarded as a proxy for an organic aerosol with a high WSOC content). We believe this allowed us to simulate the chemistry for pure water droplets up to organic aerosols (but by still keeping in mind, the limitations introduced by these simple proxies).

3. Results and discussion

The gas phase part of our reaction scheme (i.e. RACM) contains a few reactions producing nitrous acid. The first reaction involves NO and OH and proceeds according to:

$$NO + OH \rightarrow HONO \qquad (10)$$

The other set of gas phase reactions is also driven by OH but involves the lumped aromatic compounds i.e. CSL, TOL and XYL (as defined previously). The latter react, in RACM, with OH forming an adduct which then reacts with NO_2 to form HONO and liberate the initial aromatic. In RACM, all these HONO sources are driven by OH and can therefore be mainly active during the day (which in our simulations lasts from

6:00 am to 8:00 pm). However, HONO is readily photolysed leading to daytime maximum concentrations of less than 1 pptv while NO and NO_2 reach about 0.06 nmol/mol and 0.7 nmol/mol. Under these urban polluted conditions, ozone is about 70 nmol/mol.

Aerosol particles might be a source of nitrous acid and especially soot particles. As already discussed the latter have been subject of many laboratory and modelling studies. For instance, Aumont et al. (1999) showed that the impact of the NO_2 + soot reaction may be overestimated if the deactivation of the soot surface is not taken into account (Kotamarthi et al., 2001). In fact, the surface ageing of aerosol is a key issue when considering their atmospheric impact because reactant renewal will be very limited. Nevertheless, Aumont et al. (1999) noticed a potential contribution of this reaction as a source of night-time HONO. However, in our approach we inject the aerosol in the air mass only during day time and we consider only liquid particles (no soot) meaning that we avoid any night time source of HONO leading potentially to underestimated concentrations. However, this seems to be appropriate as Arens et al. (2001) shows that the HONO yield per soot mass is even less than Aumont et al. (1999) assumed. As already mentioned, we consider only multiphase chemistry in our air mass between typically 6:00 and 8:00 am (or 10:00 am) meaning that night-time built HONO will be photolysed rapidly, still enabling us an assessment of the potential contribution of the chemistry on liquid particles. It must already be underlined that reactions on liquid droplets may be sustained for much longer times (compared to solid substrates) simply because diffusion processes are much faster than in solids allowing a replenishment of reactants from the droplets' bulk or from the gas phase. When we switch on the multiphase chemistry (i.e. the “CAPRAM 2.4, MODAC mechanism”), several other pathways are forming HONO. In fact, this code contains following reactions:

$$2NO_2 \rightarrow HONO + HNO_3 \qquad (11)$$

$$NO_2 + O_2^- \rightarrow NO_2^- + O_2 \qquad (12)$$

$$HNO_4 \rightarrow NO_4^- + H^+ \rightarrow\rightarrow NO_2^- + O_2 \qquad (13)$$

$$XNO_2 + Y^- \rightarrow NO_2^- + XY \text{(where X and Y are halogens)} \qquad (14)$$

The latter is a potential source only under special conditions as those encountered in the marine boundary layer. However, the other reactions are potentially occurring everywhere. It was shown that (R13) can act as an effective HONO source in aqueous solution (Ervens et al., 2002). Additionally, we start also following reaction scheme in the liquid droplet:

$$C_6H_5O^- + NO_2 \rightarrow C_6H_5O + NO_2^- \tag{15}$$

$$p\text{-}C_6H_4OHO^- + NO_2 \rightarrow p\text{-}C_6H_4OHO + NO_2^- \tag{16}$$

$$o\text{-}C_6H_4OHO^- + NO_2 \rightarrow o\text{-}C_6H_4OHO + NO_2^- \tag{17}$$

$$p\text{-}C_6H_4OCH_3O^- + NO_2 \rightarrow p\text{-}C_6H_4OCH_3O + NO_2^- \tag{18}$$

$$m\text{-}C_6H_4OCH_3O^- + NO_2 \rightarrow m\text{-}C_6H_4OCH_3O + NO_2^- \tag{19}$$

$$C_6H_4CH_3O^- + NO_2 \rightarrow C_6H_4CH_3O + NO_2^- \tag{20}$$

All these reactions are proceeding through electron exchange from the aromatic ring to NO_2 producing nitrite ions and therefore gas phase HONO depending on the pH of the droplet. The latter is changing, from its initial value of 4.5 to about 2, according to chemistry due to gases being taken up during the lifetime of the droplets. Of course the above reaction scheme is also depending on the condensed phase concentration of both NO_2 and aromatics. While the droplets were always initially free of any NO_2, the aromatic content was drastically changed from 0 to 10^{-2} M. Figures 1 and 2 show the diurnal behaviour of gas phase HONO over several days for these two extreme cases.

First for very diluted droplets (i.e. aromatics initial concentrations below μM levels), the contents of the reactants of reactions 15 to 20 is controlled by the material being captured from the gas phase but still leads to an additional formation of daytime HONO of about 1 pptv. During the 2 h period, in which the reaction sequence 15 to 20 is possible, the pH of the droplets is decreasing from 4.5 to about 2 (or less if the droplets are exposed over longer times) leading to an efficient out-gassing of nitrous acid. For droplets with a high load of aromatics (i.e. being taken as proxies for liquid organic aerosols with a high fraction of WSOC), the model simulate an additional content of day time HONO of about 300 pptv, i.e. the HONO source is enhanced over several orders of magnitude. This HONO peak is of course subsequent to the aerosol injection into the air mass and is not sustained when the latter is removed. However, such a peak may well arise under real conditions in a polluted urban environment. Figure 3 shows the variation of the HONO excess due to multiphase chemistry of NO_2 with aromatics. This figure shows the logarithm of the difference of the HONO concentrations (expressed in nmol/mol) between a given simulation run and a base case (where all reactions are considered except the reaction sequence from 15 to 20). It clearly shows that beyond μM levels, the NO_2 reactions with aromatics may be a significant source of day time HONO. This simple model does of course not reproduce diurnal HONO behaviour as observed, because other HONO sources were not included.

The impact of this HONO source on the gas phase chemistry is, however, still minor since none of the HO_x–NO_x–O_x cycles were disturbed within our simulations due to reactions 15 to 20. All gas phase modifications are at the percentage level and therefore not really substantial. However, the aerosol load used here of about 50 $\mu g\,m^{-3}$ may easily be reached in heavily polluted places and certainly even be exceeded, especially under heavy road traffic influences (as those encountered in large cities, but of course this aerosol loading will be limited by soot or dust and not water). Under those circumstances, this additional HONO source may be very important leading to early morning HONO concentrations of more than 1 nmol/mol (under solar irradiation!). Of course, most of the influence of these reactions is seen in the liquid phase where the nitrite content is largely modified and mostly trapped in the particles depending on the pH. This is a critical factor for these simulations as too acidic conditions would result in a very low fraction of hydroxyl substituted aromatics being dissociated, and in too alkaline solutions all HONO would be trapped in the liquid phase as nitrite ions.

4. Conclusions

In this explorative study, we applied a multiphase model, i.e. “CAPRAM 2.4, MODAC mechanism” in order to simulate the chemistry occurring on liquid aerosols, in the early morning, under polluted conditions. The code was extended to take into account the multiphase reactions of NO_2 with dissociated hydroxyl substituted aromatics. As these reactions proceed through electron transfer, they produce nitrite ions in the liquid phase which, depending on the pH, would lead to HONO out-gassing. The strength of this source was explored. It was shown that it leads to HONO even when considering very dilute liquid droplets but increased in importance when the aromatic content of the droplets was increased. However, the influence of these reactions on daytime photochemistry is still minor with a notable impact only at heavily polluted locations.

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Table 1. Solubilities, mass accommodation and diffusion coefficients for aromatic compounds

Species	K_H M atm^{-1}	$\Delta H / R$ *K*	α	D [10^5 m^2 s^{-1}]	References
benzene C_6H_6	2.1×10^{-1}	-3800	1×10^{-2} estimated	0.8	(Dewulf et al., 1995; Heal et al., 1995; Robbins et al., 1993)
toluene $C_6H_5CH_3$	1.8×10^{-1}	-3400	1×10^{-2} estimated	0.8	(Dewulf et al., 1995; Heal et al., 1995; Robbins et al., 1993)
o-xylene $CH_3C_6H_4CH_3$	1.9×10^{-1}	-3400	1×10^{-2} estimated	0.8	(Heal et al., 1995; Robbins et al., 1993)
m-xylene $CH_3C_6H_4CH_3$	1.6×10^{-1}	-4000	1×10^{-2} estimated	0.8	(Dewulf et al., 1995; Heal et al., 1995)
p-xylene $CH_3C_6H_4CH_3$	1.7×10^{-1}	-4500	1×10^{-2} estimated	0.8	(Dewulf et al., 1995; Heal et al., 1995)
o-cresol $CH_3C_6H_4OH$	820	-7400	2.7×10^{-2}	0.8	(Betterton, 1992; Ervens, 2001; Heal et al., 1995; Hine and Mookerjee, 1975)
p-cresol $CH_3C_6H_4OH$	1300	-7400	2.7×10^{-2}	0.8	(Betterton, 1992; Ervens, 2001; Heal et al., 1995; Hine and Mookerjee, 1975)
Phenol C_6H_6O	2900	-6800	2.7×10^{-2}	0.8	(Ervens, 2001; Heal et al., 1995; Hine and Mookerjee, 1975)

Table 2. Kinetic data for the reactions of NO_2 with dissociated hydroxyl substituted aromatic compounds

	K $M^{-1}\,s^{-1}$	$E_a\,/\,R$ K	Reference
phenol	1.5×10^7	4125	(Alfassi et al., 1986; 1990)
$C_6H_5O^- + NO_2 \rightarrow C_6H_5O + NO_2^-$			
hydroquinone (*p*-hydroxyphenol)	1.1×10^9		(Alfassi et al., 1986)
$C_6H_4OHO^- + NO_2 \rightarrow C_6H_5O + NO_2^-$			
resorcinol (*o*-hydroxyphenol)	3.8×10^8		(Alfassi et al., 1986)
$C_6H_4OHO^- + NO_2 \rightarrow C_6H_5O + NO_2^-$			
p-methoxyphenol	1.4×10^8		(Huie and Neta, 1986)
$C_6H_4OHO^- + NO_2 \rightarrow C_6H_5O + NO_2^-$			
m-methoxyphenol	1.8×10^7		(Alfassi et al., 1986)
$C_6H_4OHO^- + NO_2 \rightarrow C_6H_5O + NO_2^-$			
p-cresol	3.4×10^7		(Alfassi et al., 1986)
$C_6H_4CH_3O^- + NO_2 \rightarrow C_6H_5O + NO_2^-$			
m-cresol	1.3×10^7		(Alfassi et al., 1986)
$C_6H_4CH_3O^- + NO_2 \rightarrow C_6H_5O + NO_2^-$			

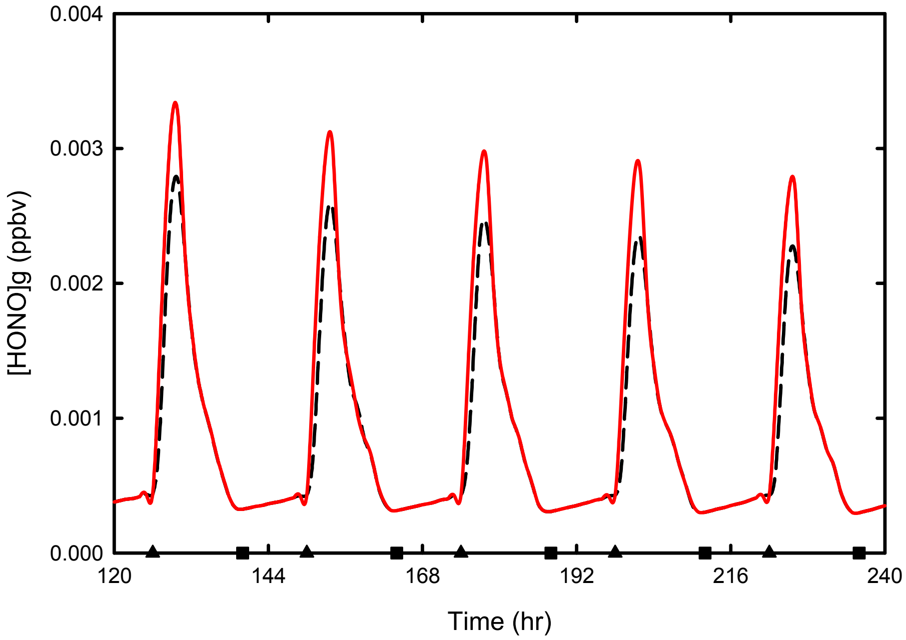

Fig. 1. Diurnal behaviour of gas phase HONO during the exposure of monodispersed droplets (with a radius of 0.1 μm and L = 50 μg m^{-3}) containing initially 10^{-8} M aromatics. The multiphase chemistry was activated between 6:00 and 10:00 am. Solid line is with the charge exchange reactions between NO_2 and dissociated hydroxyl substituted aromatics. The dashed line is the base case without these reactions (left scale). Triangles and squares on the *x*-scale are indicating sunrise and sunset respectively.

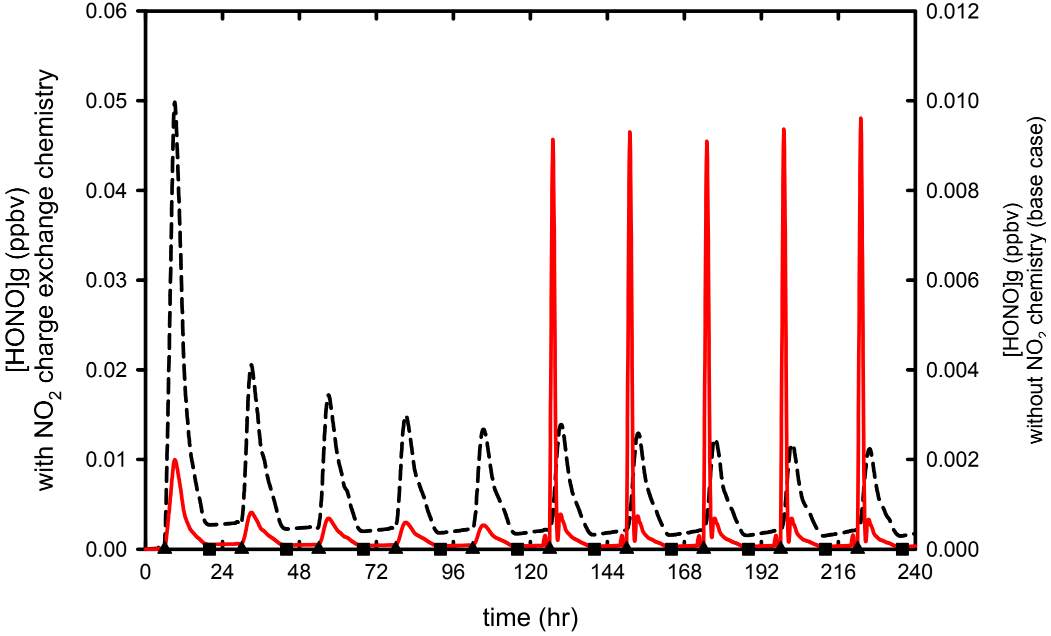

Fig. 2. Diurnal behaviour of gas phase HONO during the exposure of monodispersed droplets (with a radius of 0.1 μm and L = 50 μg m^{-3}) containing initially 10^{-3} M aromatics. The multiphase chemistry was activated between 6:00 and 10:00 am and started on the 5th day. Solid line is with the charge exchange reactions between NO_2 and dissociated hydroxyl substituted aromatics (left scale). The dashed line is the base case without these reactions (right scale). Triangles and squares on the *x*-scale are indicating sunrise and sunset respectively.

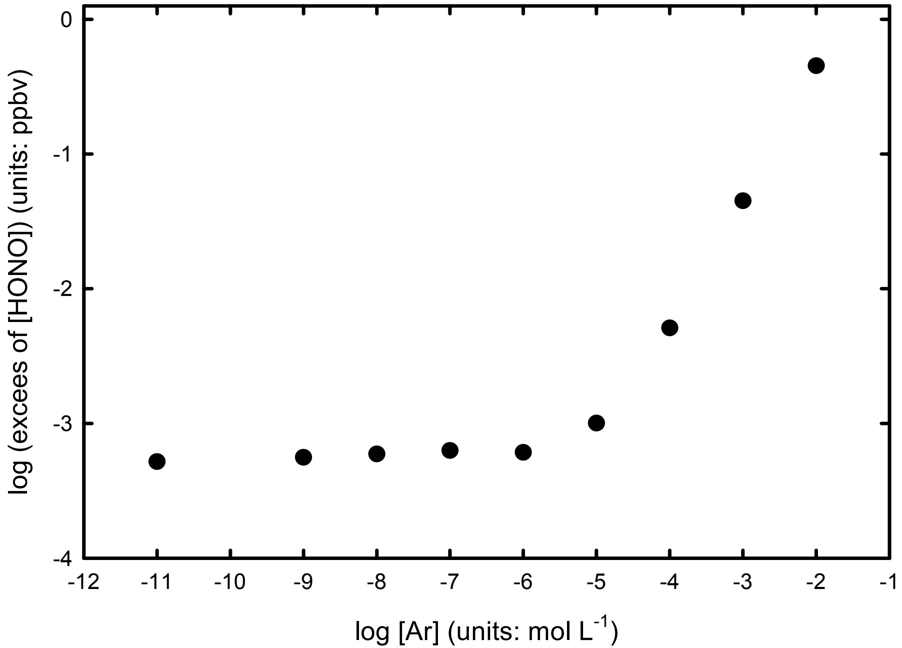

Fig. 3. Logarithm of the excess of gas phase HONO concentrations (expressed in nmol/mol) compared to the base case as a function of aromatic initial concentrations (in molar) determined at maximum HONO concentration. The excess of gas phase HONO is defined as the difference in concentration between the base case and simulations considering the charge exchange reactions between NO_2 and dissociated hydroxyl substituted aromatics.