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The impact of multiphase reactions of NO$_2$ with aromatics: a modelling approach

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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 $0.1\,\mu$m and a liquid content (LC) 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 increase gas phase HONO levels under some conditions and that the extent of this effect is strongly pH dependent. Especially under moderate acidic conditions (i.e. pH above 4) this source may represent more than 75% of the total HONO/NO$_2^-$ production rate, but this contribution drops down close to zero in acidic droplets (as those often encountered in urban environments).

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

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is observed to increase gradually during night, while after sunrise it is rapidly photolysed leading to OH and NO, 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.

Recently, the heterogeneous conversion of NO$_2$ on soot particles emitted from combustion sources has been suggested as a more efficient HONO source than aqueous phase NO$_2$ disproportionation (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, b). Nevertheless, the fact that condensed phase organic species seemed to be involved shed a light on other possible 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 condensed 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).

While the identity of these species remained mostly unknown in the study by Gutzwiller et al. (2002), 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 photooxidation of aromatic compounds
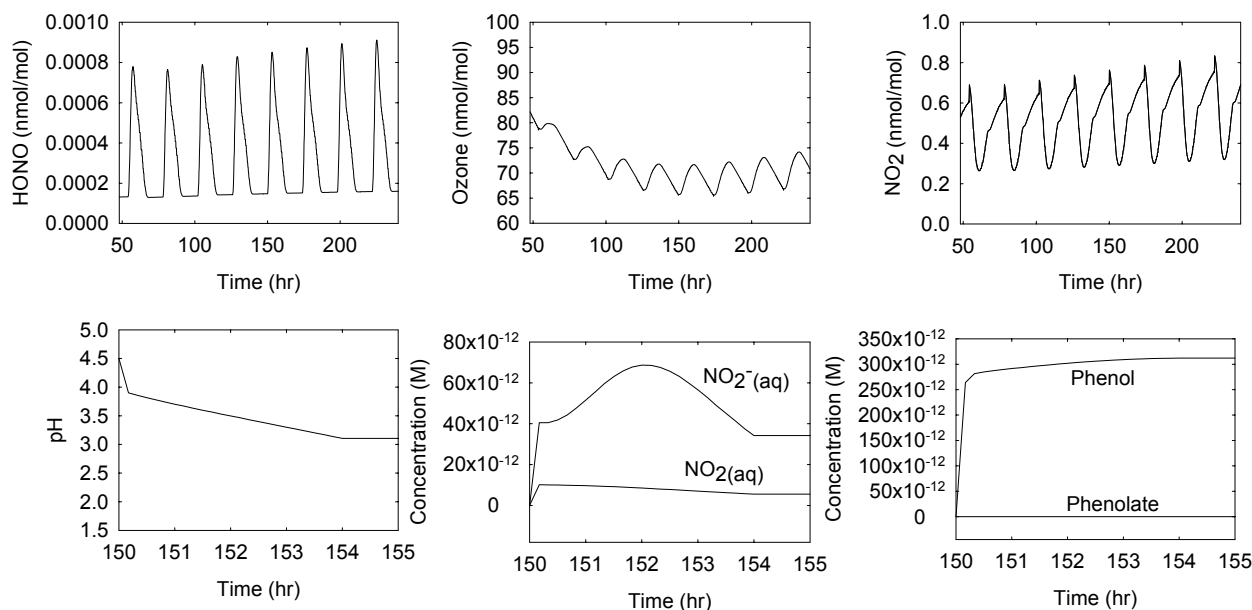
Fig. 1. Diurnal behaviour of gas phase HONO, O_3 and NO_2 and liquid phase pH, NO_2, NO_2^-, phenol and phenolate during the exposure of monodispersed droplets (with a radius of 0.1 μm and $LC = 50\,\mu g\,m^{-3}$), initially free of aromatics. The multiphase chemistry was activated between 06:00 and 10:00 LT.

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, hydroxy substituted aromatics may also react 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 aromatic species identified in aerosols is not really known. They may originate from primary emissions, and both gas and particle phase oxidation processes. A number of studies have shown that combustion processes (e.g. wood combustion and many other) releases very high concentrations of gas phase and condensed-phase phenols (Nolte et al., 2001). It is also known that such phenolic compounds are ubiquitous in particulate matter (Fraser et al., 1998, 2000; Hawthorne et al., 1992). Although not fully characterised, this group of compounds includes a number of large phenols, wich have very low volatility, that will primarily exist in the condensed phase. The impact of such particles will be explored below.

For the present study, we extended the CAPRAM mechanism (Ervens et al., 2002) 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 and m-methoxyphenol. Different scenarii will be used, ranging from aromatic free droplets to concentrated droplets (see above). 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, b; Schall and Heumann, 1993). In order to test

whether these reactions are indeed sources of HONO, the fate of aromatics in the condensed phase needed to be described explicitly. This was performed by taking into account each oxidation step, potentially initiated by radicals or radical anions. Our model is described in the next section, along with the scenario used, whereas model outputs are discussed in the results section.

2 Model description

2.1 Gas phase and uptake processes

As our intentions were only to study the influence of given chemical reactions, we performed our simulations using a box model, without any horizontal or vertical transport considerations (i.e. our air mass is considered instantaneously well-mixed). The chemical scheme used is derived from "CAPRAM 2.4, MODAC mechanism" (Ervens et al., 2002). This scheme considers about 440 reactions in the condensed phase. The code was extended, by 62 reactions, in order to simulate the chemistry of aromatic compounds such as benzene, toluene, ortho-, meta- and para-xylene, ortho- and para-cresol and 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 values of the basic scheme can be found on

Table 1. Uptake parameters, solubilities 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$_6$H$_6$	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$_6$H$_5$CH$_3$	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$_3$C$_6$H$_4$CH$_3$	1.9×10^{-1}	-3400	1×10^{-2} estimated	0.8	(Heal et al., 1995; Robbins et al., 1993)
m-xylene CH$_3$C$_6$H$_4$CH$_3$	1.6×10^{-1}	-4000	1×10^{-2} estimated	0.8	(Dewulf et al., 1995; Heal et al., 1995)
p-xylene CH$_3$C$_6$H$_4$CH$_3$	1.7×10^{-1}	-4500	1×10^{-2} estimated	0.8	(Dewulf et al., 1995; Heal et al., 1995)
o-cresol CH$_3$C$_6$H$_4$OH	820	-7400	2.7×10^{-2}	0.8	(Betterton, 1992; Ervens, 2001; Heal et al., 1995; Hine and Mookerjee, 1975)
p-cresol CH$_3$C$_6$H$_4$OH	1300	-7400	2.7×10^{-2}	0.8	(Betterton, 1992; Ervens, 2001; Heal et al., 1995; Hine and Mookerjee, 1975)
phenol C$_6$H$_6$O	2900	-6800	2.7×10^{-2}	0.8	(Ervens, 2001; Heal et al., 1995; Hine and Mookerjee, 1975)

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 ("Regional Atmospheric Chemistry Mechanism"; Stockwell et al., 1997). RACM includes rate constants and product yields from most recent laboratory measurements, and it was tested against environmental chamber data. 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 comparisons with other modelling studies using RACM straightforward.

RACM contains reactions producing nitrous acid. The first involves NO and OH and proceeds directly according to:
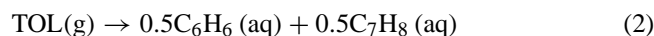
$$NO + OH \rightarrow HONO \tag{1}$$

A second set of gas phase reactions is also driven by OH but involves the lumped aromatic compounds, i.e. CSL, TOL and XYL (as defined below). The latter react, in RACM, with OH forming an adduct which then reacts with NO$_2$ to form HONO, liberating the CSL compound family.
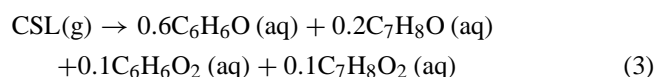
In RACM, all these HONO sources are driven by OH and can therefore be mainly active during the day (which in our simulations last from 06:00 to 20:00 LT). HONO is readily photolysed leading to daytime maximum concentrations of less than 1 pmol/mol, while NO and NO$_2$ reach about 0.06 nmol/mol and 0.7 nmol/mol, respectively. Under these

urban polluted conditions, ozone is about 70 nmol/mol (see Fig. 1).

However, in 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). For gas phase reactions, we used the lumped families, while the aqueous phase scheme of "CAPRAM 2.4, MODAC mechanism" and its extension for aromatics treat all species explicitly. We therefore had to detail the aromatic compounds once transferred to the aerosol. This was done using following assumptions (taken from Ferrari et al., 1998):

$$TOL(g) \rightarrow 0.5C_6H_6\,(aq) + 0.5C_7H_8\,(aq) \tag{2}$$

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

$$CSL(g) \rightarrow 0.6C_6H_6O\,(aq) + 0.2C_7H_8O\,(aq)$$
$$+0.1C_6H_6O_2\,(aq) + 0.1C_7H_8O_2\,(aq) \tag{3}$$

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

$$XYL(g) \rightarrow (CH_3)_2C_6H_4(aq) \tag{4}$$
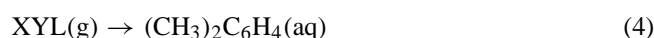
(i.e. 100% xylene, no differences in reactivity of o-,m-,p-xylene assumed) where the subscripts (g) and (aq) refer to the gas and aqueous phases, respectively. It is obvious that this splitting into explicit compounds is somewhat arbitrary

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 such 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. Furthermore the ratios given above change with the age of the air parcels due to the different reactivity of the species included. Nevertheless, we believe that our approach is still justified within the case studies reported in the results section.
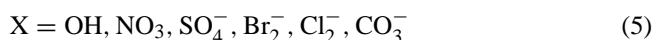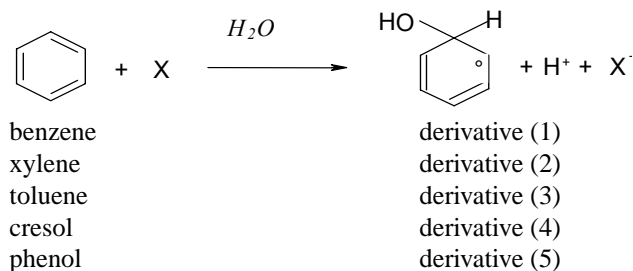
Our reaction scheme does not have any heterogeneous reactions (i.e. gas-solid interactions such as soot reactions) as it is a purely multiphase model meaning that trace gases are transferred into the aerosol, assumed to be liquid, and react only in the bulk of the droplet. Therefore, we deal only with two kinds of reactions, which are in the gas phase (treated according to the RACM scheme) and in the liquid phase (treated according to the extended CAPRAM-MODAC scheme). Details regarding the aqueous phase chemistry are given in the section below. Both atmospheric compartments are connected by uptake processes (treated according to the methodology derived by Schwartz, 1986). Accordingly, the chemistry in the aerosol is treated similarly to cloud chemistry and makes use of the model derived for use in dilute solutions (without treatment of ionic strength effects).

2.2　Aqueous phase processes

All of the above detailed aromatics undergo condensed phase oxidation via primary attack of radicals or radical anions such as Cl_2^-, Br_2^-, CO_3^-, NO_3, OH or SO_4^-, via pathways including H-atom abstraction (at side-chains or at the aromatic ring), addition at the aromatic ring or electron transfer. Several investigators (Herrmann et al., 1995; Merga et al., 1994; O'Neill et al., 1975; Steenken et al., 1990) reported possible pathways 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 "sum 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 react in the same way (considering different rate constants) and that all reactions occur directly at the aromatic ring (i.e. side-chain reactions are omitted). It is obvious that these assumptions do highly simplify the oxidation mechanism for aromatics but we believe that this approach retains the main fate of these oxidation processes. It must also be emphasized that our knowledge of the aqueous chemistry of aromatics is scarce, and does not permit, at the present time, a realistic detailed mechanism

to be expressed and used. All reaction pathways end with ring maintaining products because the knowledge about ring cleavage processes in the aqueous phase is very restricted.

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. 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)

$$X = OH, NO_3, SO_4^-, Br_2^-, Cl_2^-, CO_3^- \qquad (5)$$

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 observed experimentally 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 of 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 further decay of these 'derivatives' is due to the addition of oxygen. Several pathways for this reaction are described by Pan et al. (1993). Based on these data a kinetic simulation was performed by Ervens (2001), obtaining a rate constant and product yields for the sum reaction as given in reaction (6):

$$\text{Derivative(i)} + O_2 \longrightarrow 0.4\,\text{ArOH} + 0.4\,\text{HO}_2$$
$$+ 0.6\,\text{derivative(ox)(i)} \qquad (6)$$

Here 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). The derivatives will in turn also react and form hydroxy substituted aromatics. All these pathways are included in reaction (6) which is a simplified expression of this complex reaction mechanism and in which some oxygenated 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 to the anions, which are very reactive toward NO$_2$. Such reactions will proceed through electron

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 $C_6H_5O^- + NO_2 \rightarrow C_6H_5O + NO_2^-$	1.5×10^7	4125	(Alfassi et al., 1986; Alfassi et al., 1990)
hydroquinone (p-hydroxyphenol) $C_6H_4OHO^- + NO_2 \rightarrow C_6H_4OHO + NO_2^-$	1.1×10^9		(Alfassi et al., 1986)
resorcinol (o-hydroxyphenol) $C_6H_4OHO^- + NO_2 \rightarrow C_6H_4OHO + NO_2^-$	3.8×10^8		(Alfassi et al., 1986)
p-methoxyphenol $C_6H_4OCH_3O^- + NO_2 \rightarrow C_6H_4OCH_3O + NO_2^-$	1.4×10^8		(Huie and Neta, 1986)
m-methoxyphenol $C_6H_4OCH_3O^- + NO_2 \rightarrow C_6H_4OCH_3O + NO_2^-$	1.8×10^7		(Alfassi et al., 1986)
p-cresol $CH_3C_6H_4O^- + NO_2 \rightarrow CH_3C_6H_4O + NO_2^-$	3.4×10^7		(Alfassi et al., 1986)
m-cresol $CH_3C_6H_4O^- + NO_2 \rightarrow CH_3C_6H_4O + NO_2^-$	1.3×10^7		(Alfassi et al., 1986)

Table 3. Acid-base dissociation reactions of the hydroxy substituted aromatics, i.e. equilibrium constants and estimated rate constant. (data from Weast, 1988)

	K M	k^*_{298} (forward) [s^{-1}]	k^*_{298} (back) [$M^{-1}\,s^{-1}$]
$C_6H_5OH \leftrightarrow C_6H_5O^- + H^+$	1.0×10^{-10}	5.00	5.0×10^{10}
$p{-}C_6H_4(OH)_2 \leftrightarrow p{-}C_6H_5O_2^- + H^+$	4.5×10^{-11}	2.24	5.0×10^{10}
$o{-}C_6H_4(OH)_2 \leftrightarrow o{-}C_6H_5O_2^- + H^+$	1.6×10^{-11}	7.75	5.0×10^{10}
$CH_3C_6H_4OH \leftrightarrow CH_3C_6H_4O^- + H^+$	7.4×10^{-11}	3.71	5.0×10^{10}
$p{-}C_6H_4OCH_3OH \leftrightarrow p{-}C_6H_4OCH_3O^- + H^+$	4.5×10^{-11}	2.24	5.0×10^{10}
$m{-}C_6H_4OCH_3OH \leftrightarrow m{-}C_6H_4OCH_3O^- + H^+$	1.6×10^{-10}	7.75	5.0×10^{10}

* The rate of the "back" reactions were set to this upper limit and the "forward" rate constants calculated accordingly in order to match the equilibrium constant.

transfer from the aromatic ring to form nitrite ion (or its associated acid, HONO depending of pH); corresponding kinetic data are listed in Table 2. The acidity constants of these compounds are listed in Table 3; all pKa values are about 10 meaning that only a minor fraction of these aromatics is dissociated under acidic conditions encountered in the atmosphere. In our simulation, we only considered the charge exchange reaction between NO_2 and dissociated hydroxy-substituted aromatics despite that recently Vione et al. (2001) showed that NO_2 (or N_2O_4) may react, by H-abstraction, with undissociated phenol and produce HONO (or NO_2^-) in the first oxidation step. However the corresponding mechanistic and kinetic information is not yet available inhibiting

any attempt to simulate the impact of these reactions. Accordingly, they were not considered in the present study.

2.3 Model parameters

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 21 June at latitude of $51°$ N (i.e. the longest day

Table 4. Initial concentrations in both phases (i.e. gas and liquid). The terminology for gas phase species is strictly taken from Stockwell et al. (1997)

Species	Gaseous concentration (nmol/mol)
NO_2	4.5
HNO_3	1
CH_4	1700
H_2O_2	1
O_3	90
HCl	0.2
NH_3	5
CO_2	3.75×10^5
SO_2	5.0
HCHO	1.0
Ethane (ETH)	2.0
Alkanes with OH rate constant between $2.7\ 10^{-13}$ and $3.4\ 10^{-12}$ cm^3 s^{-1} (298 K, 1 atm), (HC3)	2.0
Alkanes with OH rate constant between $3.4\ 10^{-12}$ and $6.8\ 10^{-12}$ cm^3 s^{-1} (298 K, 1 atm), (HC5)	1.0
Alkanes with OH rate constant greater than $6.8\ 10^{-12}$ cm^3 s^{-1} (298 K, 1 atm), (HC8)	0.1
C_2H_4	1.0
Terminal alkene (OLT)	0.1
Toluene and less reactive aromatics (TOL)	0.1
Cresol and other hydroxy substituted aromatics (CSL)	0.001
Xylene and more reactive aromatics (XYL)	0.1
Aldehyde (ALD)	0.1
Ketone (KET)	1.0
Glyoxal (GLY)	0.1
Methylglyoxal (MGLY)	0.1
Peroxyacetylnitrate (PAN)	0.5
CH_3OOH (OP1)	1.0
Higher organic peroxide (OP2)	0.1
$CH_3C(O)OOH$ (PAA)	0.001
CH_3OH	5.0
EtOH	1.0

Species	Aqueous concentration (M)
pH	4.5
Cl^-	1.0×10^{-4}
Br^-	3.0×10^{-7}
Fe^{3+}	5.0×10^{-7}
Mn^{3+}	2.0×10^{-8}
Cu^+	2.0×10^{-8}
HSO_4^-	3.0×10^{-7}
SO_4^{2-}	5.0×10^{-5}
$C_2O_4^{2-}$	5.0×10^{-7}
aromatics	Variable (see text)

of the year with high photolysis rates). 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 and 20:00 LT, respectively and the photolysis rates follow a semi-sinusoidal diurnal cycle with a maximum at noon.

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 06:00 and 08:00 or 06:00 and 10:00 LT (i.e.

with an aerosol lifetime of 2 or 4 h). 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.

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 (Olivier et al., 1996), which was developed for global modelling purposes and has a resolution of $1° \times 1°$. This database considers both anthropogenic and biogenic emissions. The more detailed NMVOC database underlying EDGAR was used to specify non-methane-hydrocarbons needed in the RACM mechanism. Natural hydrocarbon emissions were specified using the database of Guenther et al. (1995). The maximum, 80%, median and minimum emissions values of all $1° \times 1°$ 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 values for deposition and emission rates are given by Ervens et al. (2002).

Initial conditions were chosen to be representative of an urban case as listed in Table 4. 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.
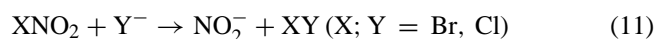
3 Results and discussion

In our explorative approach, we inject the aerosol in the air mass only during day-time and we consider only liquid particles (no soot). We are not including any night-time reactions on the aerosol or on the ground (note however that the latter could also be a reservoir for the aromatic species considered here). Therefore, we avoid any night-time source of HONO (potentially leading to underestimated concentrations). Since
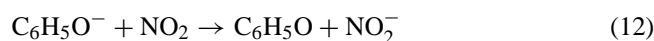
we consider only multiphase chemistry in our air mass between typically 06:00 and 08:00 LT (or 10:00 LT), HONO formed at night will be photolysed rapidly, enabling an assessment of the potential contribution of the chemistry in liquid particles. This "turning on" of aerosol particles for 2 or 4 h is 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 sources as the aerosol content is not replenished during time, leading to some numerical singularities which may be difficult to solve. 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.

Here it should be noted 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' interior or from the gas phase. This is a major change compared to the chemistry of soot particles where surface ageing is a key issue (Aumont et al., 1999; Kotamarthi et al., 2001)

When we switch on the multiphase chemistry (i.e. the "CAPRAM 2.4, MODAC mechanism"), several other pathways forming HONO are initiated. In fact, this code contains following reactions:

$$2NO_2(+H_2O) \rightarrow HONO + HNO_3 \tag{7}$$

$$NO_2 + O_2^- \rightarrow NO_2^- + O_2 \tag{8}$$

$$HNO_4 \leftrightarrow NO_4^- + H^+ \tag{9}$$

$$NO_4^- \rightarrow NO_2^- + O_2 \tag{10}$$

$$XNO_2 + Y^- \rightarrow NO_2^- + XY \,(X; Y = Br, Cl) \tag{11}$$

The last of these is a potential source only under special conditions such as those encountered in the marine boundary layer. The other reactions potentially occur everywhere. It was shown that reactions (9) and (10) can act as an effective HONO source in aqueous solution (Ervens et al., 2002). Additionally, we also include the following reaction scheme in the liquid droplet:

$$C_6H_5O^- + NO_2 \rightarrow C_6H_5O + NO_2^- \tag{12}$$

$$p-C_6H_4OHO^- + NO_2 \rightarrow p-C_6H_4OHO + NO_2^- \qquad (13)$$

$$o-C_6H_4OHO^- + NO_2 \rightarrow o-C_6H_4OHO + NO_2^- \qquad (14)$$

$$p-C_6H_4OCH_3O^- + NO_2 \rightarrow p-C_6H_4OCH_3O + NO_2^- \quad (15)$$

$$m-C_6H_4OCH_3O^- + NO_2 \rightarrow m-C_6H_4OCH_3O + NO_2^- \quad (16)$$

$$C_6H_4CH_3O^- + NO_2 \rightarrow C_6H_4CH_3O + NO_2^- \qquad (17)$$
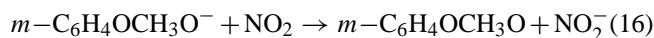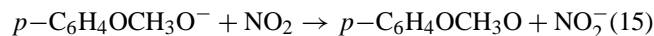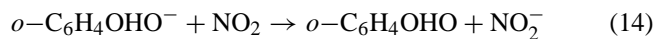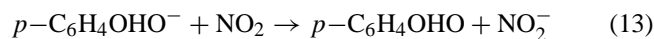
Each of these reactions proceed through electron exchange from the aromatic ring to NO_2, producing nitrite ion and therefore gas phase HONO depending on the pH of the droplet. The latter changes from its initial value of 4.5 to about 2, depending on the amount and chemistry of the gases being taken up during the lifetime of the droplets. Of course the above reaction scheme also depends on the condensed phase concentrations of both NO_2 and the aromatics.

Nitrogen dioxide has a very low physical solubility in water; its Henry's law constant is as low as $0.013 \, \text{Matm}^{-1}$ 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 NO_2 concentration is small and proportional to the gas phase density with a net flux of NO_2 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 NO_2 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 NO_2 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 NO_2 into NO_2^- 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 NO_2 into the droplet.

Figure 1 shows some temporal variation of some gas phase species (such as O_3, HONO and NO_2) over several days, and the liquid phase concentrations for one "aerosol period" for NO_2, nitrite, phenol, phenolate and pH, obtained with the assumption of a droplet initially free of any aromatic. First, for very diluted droplets (i.e. aromatics initial concentrations below μM levels), the contents of the reactants in reactions 12 to 17 is controlled by material captured from the gas phase. During the 2 h period in which the reaction sequence 12 to 17 is possible, the pH of the droplets decreases from 4.5 to about 3 (or less if the droplets are exposed over longer times), leading to an efficient out-gassing of nitrous acid. During the same time, the phenol concentration increases to about 10^{-10} M while the content of the phenolate anion is negligibly small under such acidic conditions. The NO_2 concentration initially increases (due to the uptake from the gas phase, see discussion above) and then decreases slightly because its gas phase counterpart density is affected by the increasing intensity of photolysis of gaseous nitrogen dioxide (among
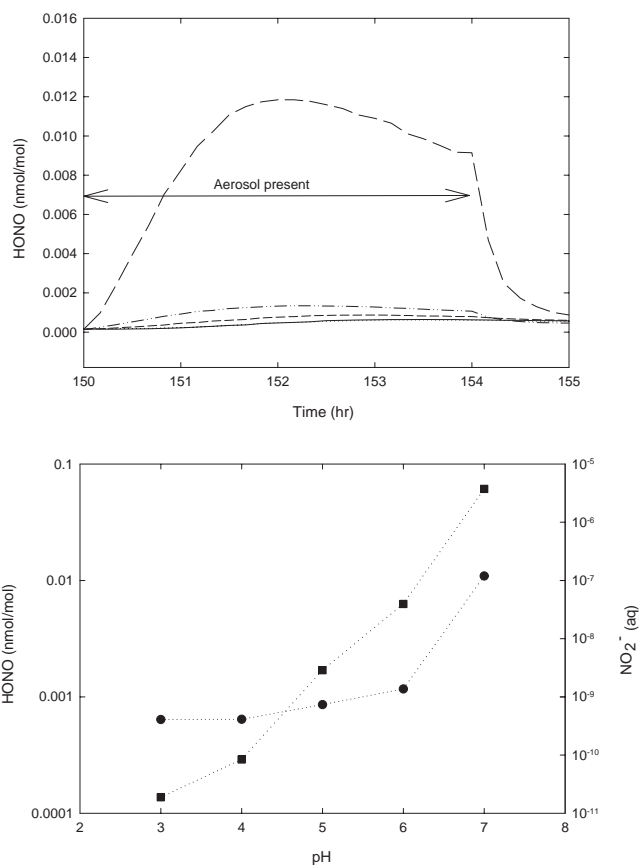
Fig. 2. Diurnal behaviour and pH dependence of gas phase HONO or condensed phase nitrite ions formed through reactions (12)–(17) during the exposure of monodispersed droplets (with a radius of $0.1 \, \mu$m and $L = 50 \, \mu\text{g m}^{-3}$) initially free aromatics with varying constant pH. The multiphase chemistry was activated between 06:00 and 10:00 LT, starting on the 5th day. The lower panel shows the behaviour of both HONO (circle) and NO_2^- (square) concentrations as a function of pH.

others). However, the behaviour of nitrite ions is different as it goes through a maximum. The latter is due to two opposite trends: as mentioned, the decreasing aqueous phase NO_2 concentration and the increasing acidity which favours several of the reactions (7)–(10) or the source reactions of these reactants, the product of both trends leading to the observed maximum. In this case (where the initial aromatic concentration is set to zero in the aqueous phase), the source of nitrite ions (or HONO) for the charge exchange process from an aromatic ring due to reactions (12)–(17) is negligibly small. Below, we will explore the conditions under which such processes will gain in importance.

The more obvious parameter is the acidity of the droplet as it controls the levels of dissociated aromatics - 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 corre-

sponding results are depicted in Fig. 2. Of course, fixing the pH has a very strong influence on many processes within the droplet that are far beyond just reactions (12)–(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,...) are more abundant. From Fig. 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)–(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)–(17) were initiated at higher pH.

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 aromatic 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 Fig. 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.

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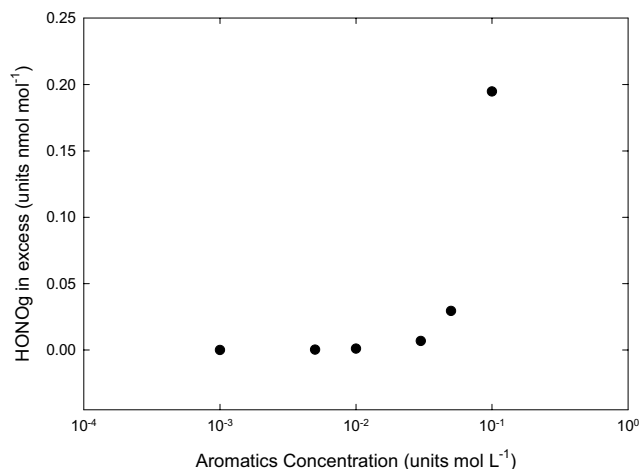
Fig. 3. Excess gas phase HONO concentrations (expressed in nmol/mol) compared to the base case as a function of aromatic initial concentrations (in molar) determined at maximum HONO concentration. The excess of gas phase HONO is defined as the difference in concentration between the base case and simulations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

centration of the aromatics and of their ions not only alters directly the rate of reactions (12)–(17) but also modifies the pH. In fact, as the initial concentration of all aqueous phase aromatics are increased from 0 to 0.1 M, the pH gets more and more alkaline (unrealistically, up to pH = 8 for the more concentrated solutions), which in turn shifts the equilibrium of the aromatic toward the anions and toward the formation of NO_2^-. It is clear that under such severe conditions, reactions (12)–(17) are important sources of $HONO/NO_2^-$. But such conditions are not those effectively encountered in the atmosphere; therefore this may not be extrapolated to real environmental conditions. Nevertheless, this shows again that the major controlling factor is the pH and that even moderate acidity will lead to some HONO formation through these charge exchange reactions involving NO_2 and an aromatic ring.

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 as a result of reactions (12)–(17). This is due to the fact that at such a low LC the fraction of the species in the particle phase is very small, so that the contributions of aqueous phase processes to the total budget of these species is very small. All gas phase modifications are at the percentage level and therefore not really substantial. However, the aerosol load of about $50 \, \mu g \, m^{-3}$ used here may easily be reached in heavily polluted places and even exceeded; especially under heavy road traffic influences (such as those encountered in large cities), even though this aerosol loading will be limited by soot or dust and not water. Under those circumstances, this addi-
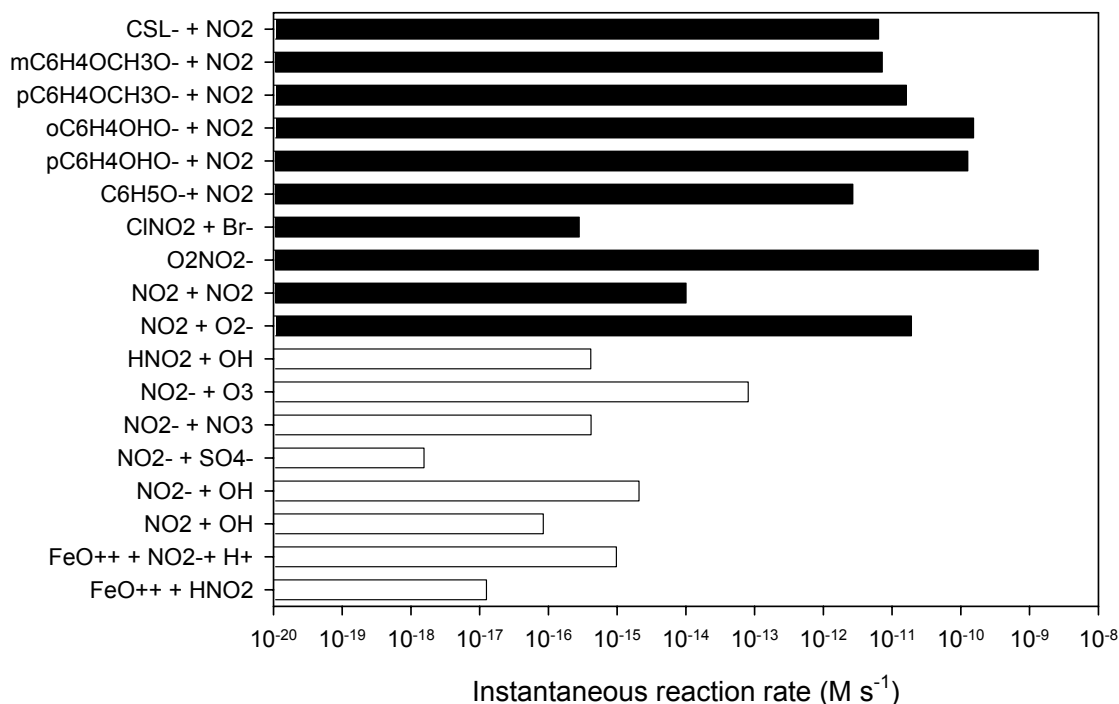
Fig. 4. Instantaneous reactions rates (in $M\,s^{-1}$) at 07:00 LT on the 7th day of simulation, which corresponds to one hour interaction time between the gas phase and the droplets, of chemical reactions affecting the nitrite ions (and therefore HONO) budget in the droplet. Filled bars are source processes whereas open bars are sink reactions.

tional HONO source from aged or secondary particles 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 greatly affected and mostly trapped in the particles depending on the pH. This is a critical factor in these simulations. More acidic conditions result in a very low fraction of hydroxyl substituted aromatics being dissociated. In more alkaline solutions, all HONO would be trapped in the liquid phase as nitrite ions.

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 NO_2 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 solu-

bility 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.

Figure 4 shows the instantaneous reaction rates of the system $NO_2/NO_2^-/HONO$ (in $M\,s^{-1}$) at 07:00 LT 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, 2000; Hawthorne et al.,1992) because it provides a better illustration of the competition between all pathways. In fact, under such conditions, the pH is about 5 where the reactions (12)–(17) start to be effective. It can be seen that the decomposition of HNO_4 is still the major source of nitrite ions (through reaction 10) but that the sum of the contributions of reactions (12) and (17) now slightly exceed the one by reactions (8) and (10), meaning that additional HONO is formed. The conditions chosen for the simulations depicted in Fig. 4 highlight the requirements for the reactions (12)–(17) to be an effective additional HONO source: a weak acidic media (i.e. pH above 4) and a substantial amount of aromatic com-

pound in the particle (that amount is highly variable as it is highly dependent on the pH: at very high pH, it can be very small; and inversely at low pH where it must be very high). It must be underlined from Fig. 4 that when comparing loss and source processes for HONO, that the latter is always produced from a liquid droplet and that reactions (12)–(17) are just an additional source that may become important under certain conditions. However such conditions, may readily be observed in urban environment under wood smoke influence but also and more generally under the influence of emissions which originate from combustion processes, which produce large concentrations of phenolic type compounds, i.e. reactants that may initiate reactions (12)–(17).

4   Conclusions

In this exploratory study, we applied a multiphase model, the "CAPRAM 2.4, MODAC mechanism", in order to simulate the chemistry occurring in liquid aerosol particles, 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. Since these reactions proceed through electron transfer, they produce nitrite ions in the liquid phase, which, depending on the pH, may lead to HONO out-gassing. The strength of this source was explored. It was shown that it leads to HONO even for very dilute liquid droplets under moderate acidic conditions, and increases in importance when the aromatic content of the droplets is 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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