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Secondary organic aerosol formation from the gas-phase reaction of guaiacol (2-methoxyphenol) with NO₃ radicals

Lingshuo MENG^(1,2), Cécile COEUR^{(1)*}, Layal FAYAD⁽¹⁾, Nicolas HOUZEL⁽¹⁾, Paul GENEVRAY⁽³⁾, Hichem BOUZIDI⁽¹⁾, Alexandre TOMAS⁽²³⁾, Weidong CHEN⁽¹⁾

⁽¹⁾Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque 59140, France

⁽²⁾IMT Lille Douai, Univ. Lille, SAGE – Sciences de l'Atmosphère et Génie de l'Environnement, 59000 Lille, France

⁽³⁾Centre Commun de Mesures, Université du Littoral Côte d'Opale, Dunkerque 59140, France

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*Corresponding author. Tel.: +33 328 23 76 42.

Address: Université du Littoral Côte d'Opale, Bâtiment IREnE, 189A, Avenue Maurice Schumann, 59140 DUNKERQUE - FRANCE

Email address: coeur@univ-littoral.fr (C. Coeur).

Abstract

Methoxyphenols are oxygenated aromatic compounds emitted by wood combustion (consequently to the pyrolysis of lignin). The atmospheric reaction of nitrate radical (NO_3) with guaiacol (2-methoxyphenol), one of the principal representatives of this class of compounds has been investigated in the dark at (294 ± 2) K, atmospheric pressure and low relative humidity ($\text{RH} < 2\%$). The formation of secondary organic aerosols (SOAs) has been studied in two simulation chambers. The concentrations time profiles of guaiacol were followed with a PTR-ToF-MS (Proton Transfer Mass Reaction – Time of Flight – Mass Spectrometer) and those of SOAs by an SMPS (Scanning Mobility Particle Sizer). Aerosol yields (Y) were calculated from the ratio of the suspended aerosol mass concentration corrected for wall losses (M_0), to the total reacted guaiacol concentration assuming a particle density of 1.4 g cm^{-3} . The aerosol yield increases as the initial guaiacol concentration rises, leading to yield values ranging from 0.01 to 0.21. A very good agreement was observed between the experiments performed in both chambers which gives confidence in the data obtained in this study. The organic aerosol formation can be represented by a one-product gas/particle partitioning absorption model with a stoichiometric coefficient $\alpha = 0.32 \pm 0.04$ and an equilibrium constant $K = (4.2 \pm 1.0) \times 10^{-3} \text{ m}^3 \mu\text{g}^{-1}$. The chemical composition of the aerosols formed was studied after sampling on quartz fiber filter, ultrasonic extraction and analysis by ESI-LC-QToF-MS-MS (ElectroSpray Ionization - Liquid Chromatography - Quadrupole - Time of Flight – Tandem Mass Spectrometry). The oxidation products observed in the condensed phase are mostly nitro-aromatics; they display chemical structures with one, two and three aromatic rings. A reaction mechanism leading to these products has been proposed. To our knowledge, this work represents the first study on the SOAs formation from the reaction of guaiacol with NO_3 radicals.

1. Introduction

During the last decades, air pollution has been a major issue and environmental policies have been developed to reduce its impacts on climate and air quality (Gurjar et al. 2010). Some field campaigns have shown that aromatic compounds represent about 20% of non-methane hydrocarbons in urban areas. These volatile organic compounds (VOCs) contribute to the formation of photo-oxidants (Derwent et al., 1996; Derwent et al., 1998) and Secondary Organic Aerosols (SOAs) (Calvert et al., 2002; Hallquist et al., 2009) and may involve risks for human health (Hanson et al., 1996).

The use of renewable energy is encouraged by environmental policies to help to decrease the dependence to fossil fuels. Biomass burning is one of the major alternative energy sources; nevertheless, it is well recognized that it also contributes to important emissions of atmospheric aerosols (Fourtziou et al., 2017), VOCs (Bruns et al., 2017) and have significant impacts on human health (Lighty et al., 2000; Sarigiannis 2015), regional and global air quality (Lelieveld et al., 2001) and climate (Chen et al., 2010; Langmann et al., 2009). Natural fires, human-initiated burning of vegetation and residential wood combustion are included in the term of “biomass burning” (Hays et al., 2002; Mazzoleni et al., 2007; McDonald et al., 2000; Schauer et al., 2001; Simpson et al., 2005).

The pyrolysis of lignin, one of the major components of wood, produces methoxyphenols. The principal atmospheric representatives of this class of compounds are guaiacol (2-methoxyphenol), syringol (2,6-dimethoxyphenol) and their derivatives (Hays et al., 2002; Mazzoleni et al., 2007; McDonald et al., 2000; Schauer et al., 2001; Simpson et al., 2005). They are semi-volatile compounds with high molecular weight and are distributed between gas- and particle- phases.

The reactivity of methoxyphenols toward hydroxyl radicals (Coeur-Tourneur et al., 2010a; Lauraguais et al., 2012, 2014a, 2015), chlorine atoms (Lauraguais et al., 2014b), ozone (El

Zein et al., 2015) and nitrate radicals (Lauraguais et al., 2016; Yang et al., 2016; Zang et al., 2016) has been investigated. The determination of the rate coefficients for these reactions has demonstrated their high reactivity toward OH, Cl and NO₃ and their low reactivity with O₃. The corresponding atmospheric lifetimes are about 2 h (OH), 20 h (Cl), 1 min (NO₃) and 12 days (O₃), respectively. Therefore, under atmospheric conditions, the main degradation pathways for the methoxyphenols are their reactions with hydroxyl radicals in the daytime and with NO₃ radicals, during the night.

The formation of secondary organic aerosols from guaiacol and syringol with respect to their reaction with OH has also been investigated (Lauraguais et al., 2012; Lauraguais et al., 2014a). In most environments, atmospheric aerosol concentrations of around 5 µg m⁻³ can be found and in these atmospheric conditions the OH reactions of guaiacol and syringol contribute for a minor part to SOAs production.

The objective of this work was to study the reaction of guaiacol, a wood burning emitted compound, with NO₃ radicals in order to investigate its potential to form SOAs. The experiments were performed in the dark, in two simulation chambers at (294 ± 2) K, atmospheric pressure and low relative humidity (RH < 2 %). The SOA yields were measured and the data analyzed according to the absorptive gas-particle partitioning model developed by Pankow (1994a,b) and Odum et al. (1996). The oxidation products formed in the aerosols were analyzed by ESI-LC-QToF-MS-MS (ElectroSpray Ionization - Liquid Chromatography - Quadrupole - Time of Flight - Tandem Mass Spectrometry). The atmospheric implications of the reaction of guaiacol with NO₃ radicals were also discussed. To our knowledge, this work represents the first study on the formation of SOAs from the reaction of guaiacol with nitrate radicals.

2. Materials and methods

The experiments were performed in the dark in two simulation chambers, LPCA-ONE and CHARME at room temperature (294 ± 2 K), atmospheric pressure and low relative humidity ($RH < 2\%$).

LPCA-ONE is an 8.0 m^3 ($2 \text{ m} \times 2 \text{ m} \times 2 \text{ m}$) PMMA (PolyMethyl Methacrylate) cubic reactor stirred by a Teflon fan (diameter 30 cm) located in the center of the lower face. A detailed description of the chamber is available in Lauraguais et al. (2012). CHARME (Chamber for the Atmospheric Reactivity and the Metrology of the Environment) is a 9.2 m^3 evacuable cylinder (diameter $\approx 1.7 \text{ m}$ and length $\approx 4.0 \text{ m}$) made in stainless steel (304 L) and electropolished. Four fans (in stainless steel; diameter 50 cm) located in the bottom assure a fast homogenization of the reactive mixture.

Purified and dried air was introduced into both chambers using a generator (Parker Zander KA-MT 1-8) connected to a compressor (SLM-S 7.5 - Renner SCROLLLine). LPCA-ONE was flushed for a minimum of 12 h before each experiment and CHARME is coupled to a vacuum pump (Cobra NC0100-0300B), which allows to reduce the pressure down to 0.4 mbar. The time required to evacuate and fill this latter reactor was around 1 h. After cleaning the chambers, satisfactory background particle number concentrations below $10 \text{ particles cm}^{-3}$ could be detected by a Scanning Mobility Particle Sizer (SMPS TSI, CPC 3775 / DMA 3081). Guaiacol was introduced into the simulation chambers using an inlet system in which measured amounts of the substances were gently heated in a small flow of purified air.

Nitrate radicals were generated using two methods:

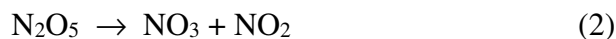
- (i) in situ formation of NO_3 from reactions (1):



NO_2 was injected first with a gas syringe and O_3 was then introduced using an ozone generator (by Corona discharge in O_2 , Model C-Lasky, C-010-DTI). The injection of both gases were performed in a few seconds. The nitrogen dioxide and ozone concentrations were

measured with a chemiluminescence NO_x analyzer (Thermo Scientific, 42i) and a photometric ozone analyzer (Thermo Scientific, 49i), respectively.

- (ii) thermal decomposition of dinitrogen pentoxide (N₂O₅) (Atkinson et al., 1984):



N₂O₅ was first synthesized in a vacuum line through the reaction of NO₂ with an excess of O₃ according to reaction (1) followed by reaction (-2):



The first phase of the synthesis consisted in trapping NO₂ (in the form of N₂O₄ crystals) at 193 K in a cold tube. In a second phase, the tube was flushed with ozone (C-Lasky C-010-DTI) to form N₂O₅. Dinitrogen pentoxide crystals were gathered in a second cold trap and kept for several weeks at 188 K.

The experiments were performed with guaiacol initial concentrations in the range (84 - 537 ppb). After allowing a few minutes for guaiacol mixing, NO₂ (500 - 1500 ppb) and O₃ (500 - 1000 ppb) or N₂O₅ were then introduced (in a few seconds) into the chambers. The concentration of guaiacol was monitored every 10 s with a Proton Transfer Reaction - Time of Flight - Mass Spectrometer (PTR-ToF-MS 1000, Ionicon Analytik GmbH). The air samples were collected through a heated (333 K) peek inlet tube with a flow of 50 mL min⁻¹ into the PTR-ToF-MS drift tube and guaiacol was monitored from the peak at m/z 125.

The aerosol formation was followed with a SMPS using a 2 min scan time and a 16 s delay between samples, providing a size distribution from 15 to 661 nm. The aerosol mass concentration M₀ was calculated assuming a density of 1.4 for the organic aerosol (recommended value, Hallquist et al., 2009).

Preliminary experiments were performed to verify that the guaiacol ozonolysis was negligible in the experiments where NO₃ was formed in-situ from NO₂ + O₃ (this was expected as the

rate constant for the ozone reaction with guaiacol is low ($k_{(\text{guaiacol}+\text{O}_3)} = 4 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, El Zein et al., 2015)).

Background aerosol formation could occur from the reaction of nitrate radicals with impurities in the purified air and/or with offgasing of compounds from the reactor walls. To characterize this particle formation, purified air was left in the dark in the presence of NO_3 for ≈ 1 h. These test experiments yielded aerosol mass concentrations of $0.2 \mu\text{g m}^{-3}$, which is negligible compared to the SOAs mass concentrations observed from the reaction of NO_3 with guaiacol (between 7 and $547 \mu\text{g m}^{-3}$).

The SOAs wall loss rates were determined by monitoring the aerosol mass concentrations over a period of ≈ 1 h at the end of each experiment. SOA wall losses are described by a first order law, with a dependence on the aerosol size. They were obtained from the plot of $\ln[M]_0/\ln[M]_t$ versus the time, where M is the aerosol mass concentration (in $\mu\text{g m}^{-3}$) and the subscripts 0 and t indicate concentrations after aerosol chemical production has stopped and at a time t , respectively.

The decay rates estimated in this study were in the range 5 - 44 % h^{-1} . These values are within the range reported for other chamber experiments (Coeur-Tourneur et al., 2009, 2010b; Henry et al., 2008; Hurley et al., 2001; Lauraguais et al., 2012, 2014a; Takekawa et al., 2003).

To determine the chemical composition of SOAs, quartz fiber filters were sampled at 7.5 L min^{-1} during 3 h (47 mm diameter Whatman 1851-047 QMA). Before the sample collection, filters were fired at 500°C for 12 h, and were then stored in an aluminum foil below 4°C until analysis. For these experiments performed with higher initial concentrations of guaiacol (2 ppm), SOA masses and yields were not determined because a high fraction of the particles was outside the measurement range of the SMPS.

The collected aerosols were analyzed by ESI-LC-QToF-MS/MS (Agilent LC 1100 - MS 6540) using the negative ionization mode (proton abstraction). The chromatographic column

used was a ZORBAX Extend-C18 (50 mm long \times 2.1 mm i.d., 1.8 μ m pore size) thermostated at 40 °C. The MS analyses allow to access the molar mass of the identified products and the MS/MS analyses, performed at three different energies (10 eV, 20 eV and 40 eV) permit to identify the functional groups of the compounds and to propose chemical structures.

The filters were ultrasonically extracted twice during 30 min in 5 mL of methanol. The solution was then filtered (pore sizes 0.45 μ m; PTFE Membrane, Whatman) and the volume was gently reduced to 100 μ L under a flow of gaseous nitrogen. Finally, the volume was diluted to 1 mL with ultrapure water in order to improve the separation of the compounds during the chromatographic analysis. The mobile phase used is a mixture of water (+0.1 % formic acid) and acetonitrile (+5 mM ammonium formate); the gradient varied from 90 % water / 10 % acetonitrile at the beginning of the analysis to 100 % acetonitrile at the end.

4-nitroguaiacol and 5-nitroguaiacol were both commercially available, so their identification was confirmed by the correlation of the LC retention times and the mass spectra recorded under the same chromatographic conditions.

The compounds used in this study, their manufacturer and stated purity were: guaiacol (Alpha Aesar, 98 %), 4-nitroguaiacol (Acros Organics, 97 %), 5-nitroguaiacol (TCI, 97 %), methanol (Aldrich, 99.9%), acetonitrile (VWR, > 99.9 %), water (VWR, > 99.9 %), sodium formate (VWR, > 99 %), formic acid (Acros Organics, 99 %), dioxygen (Praxair, 99.5 %) and nitrogen dioxide (Praxair, 99 %).

3. Results and Discussion

3.1. SOA yields

A series of guaiacol/NO₃ experiments were carried out in the dark, at atmospheric pressure, room temperature (294 \pm 2) K and low relative humidity (< 2 %). The initial concentrations of NO₂ ([NO₂]₀), O₃ ([O₃]₀) and guaiacol ([guaiacol]₀), the guaiacol reacted concentrations

corrected for wall losses ($\Delta[\text{guaiacol}]$), the organic aerosol mass concentrations corrected for wall losses (M_0) and the overall SOA yields (Y defined below) are summarized in Table 1. Guaiacol was totally consumed (within 15-60 min) in all experiments, so the reacted concentrations $\Delta[\text{guaiacol}]$ correspond to $[\text{guaiacol}]_0$.

All experiments investigating SOA yields were achieved without inorganic seed aerosol and were conducted until the suspended aerosol mass (corrected for wall losses) M_0 was stable.

Typical time profiles of guaiacol and SOA mass concentrations are presented in Fig. 1 together with time-dependent aerosol size distributions (experiment guaiacol #10; initial conditions: guaiacol (276 ppb; $1429 \mu\text{g m}^{-3}$); NO_2 (750 ppb) and O_3 (500 ppb). The formation of particles started after about 45 min when almost all guaiacol has reacted. The first aerosol size distributions were centered on a few tens of nm. Then, particle number concentrations as well as SOA mass rapidly increased to reach a plateau after $\sim 2\text{h}$ reaction time, consistent with a slower reaction rate due to the total consumption of the organic precursor. These observations suggest that the aerosol formation is due to the NO_3 reaction with guaiacol as well as with its first and second (or even further) generation products. The organic aerosol yield Y was experimentally determined as the ratio of the SOA formed (M_0 in $\mu\text{g m}^{-3}$) to the reacted guaiacol concentration ($\Delta[\text{guaiacol}]$ in $\mu\text{g m}^{-3}$) at the end of each experiment:

$$Y = \frac{M_0}{\Delta[\text{guaiacol}]} \quad (\text{I})$$

The uncertainty on the SOA yield values can be estimated at about 30%, due to statistical and possible systematic errors on M_0 and $\Delta[\text{guaiacol}]$. The results reported in Table 1 indicate that the initial concentration of guaiacol influenced the aerosol mass concentration formed: a higher guaiacol initial concentration led to higher SOA yields. Furthermore, as the organic aerosol mass directly affects the gas/particle partitioning by acting as the medium into which oxidation products can be absorbed, higher SOA mass leads to higher SOA yields.

The aerosol growth curve, represented by a plot of M_0 versus $\Delta[\text{guaiacol}]$ at the end of the experiments is shown in Fig. 2. Each experiment is represented by a single data point. The figure displays a linear correlation ($R^2 = 0.92$), with a slope of 0.25. This latter value can be compared with the highest SOA yields determined for the reaction of guaiacol with NO_3 ($Y = 0.21$; see Table 1) and seems to represent the high-limit aerosol yield for this reaction. Extrapolation of the data shown in Fig. 2 suggests that the SOA production would be negligible for guaiacol reacted concentrations lower than $\approx 550 \mu\text{g m}^{-3}$ ($\approx 110 \text{ ppb}$). This observation is corroborated by the results obtained for the less concentrated experiments (guaiacol #1 and guaiacol #7 with initial guaiacol concentrations of $436 \mu\text{g m}^{-3}$ and $604 \mu\text{g m}^{-3}$, respectively) in which the aerosol mass concentrations M_0 was low (around $10 \mu\text{g m}^{-3}$). A widely-used semi-empirical model based on absorptive gas-particle partitioning of semi-volatile products (Odum et al., 1996; Pankow, 1994a,b) allows to describe the SOA yields. In this model, the SOA yield (Y) of a particular hydrocarbon (i) is given by:

$$Y = \sum_i M_0 \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_0} \quad (\text{II})$$

where α_i is the mass-based stoichiometric coefficient of the semi-volatile product i and $K_{om,i}$ is the gas-particle partitioning equilibrium constant. In this study, since no organic aerosol seed was used, the total aerosol mass is equal to the mass of the SOAs formed. Eq. II can be fitted to the guaiacol experimental data to determine the values for α_i and $K_{om,i}$ (see Fig. 3). The simulation of Y versus M_0 with the one-product model is able to satisfactorily reproduce the experimental data ($R^2 = 0.94$). The two-products model was not retained as it leads to high uncertainties on the values of α_i and $K_{om,i}$ (sometimes more than 100% error). The fitting parameters α and K_{om} corresponding to the one-product semi-empirical model are 0.32 ± 0.04 and $(4.2 \pm 1.0) \times 10^{-3} \text{ m}^3 \mu\text{g}^{-1}$, respectively. Many studies on SOAs yields from aromatic compounds have reported that the aerosol yields data should be fitted assuming two

hypothetical products (Odum et al., 1997; Song et al., 2005). However, a number of recent works have shown that the organic aerosol yields formed in aromatic photo-oxidation systems could be well described by assuming only one hypothetical product (Coeur-Tourneur et al., 2009, 2010a; Henry et al., 2008; Lauraguais et al., 2012, 2014a; Olariu et al., 2003; Takekawa et al., 2003). Although the organic aerosol-phase is often composed of many oxidation products, the present simulation with the one-product model indicates either that one semi-volatile organic compound is the major component of the condensed phase or that the few organics present in SOAs have similar α_i and $K_{om,i}$ values. In this latter case, the obtained constants α_i and $K_{om,i}$ would not have any intrinsic physical meaning but would rather represent mean values.

In their study on the reaction of guaiacol with OH performed under high NO_x conditions, Lauraguais et al. (2014a) reported a gas-particle partitioning equilibrium constant K_{om} of $(4.7 \pm 1.2) \times 10^{-3} \text{ m}^3 \mu\text{g}^{-1}$, which is very close to the value determined in the present study for the reaction of guaiacol with NO_3 . So, it can be assumed that the products formed in the particle phase from the gas-phase oxidation of guaiacol with both oxidants have probably similar chemical compositions, including nitrate compounds. In contrast, the mass-based stoichiometric coefficient determined for the semi-volatile products formed from the reaction of guaiacol with OH ($\alpha = 0.83$) is more than twice the value of α obtained for the reaction with NO_3 . This suggests that the reaction products from guaiacol + OH are less volatile in general compared to those from guaiacol + NO_3 . This lower volatility makes them prone to go readily into the condensed phase.

It is interesting to compare α (0.32) to the slope in Fig. 2 (0.25). α represents the total amount of the semi-volatile products formed both in the gas- and aerosol- phases, whereas Y corresponds to the semi-volatile products that have been formed in the particle phase only. So,

this suggests that about 80% of the low-volatile compounds formed in the guaiacol reaction with NO₃ radicals are transferred into the particle-phase.

3.2. SOA chemical composition

ESI-LC-QTOF-MS/MS analyses were performed to characterize the composition of the SOAs formed from the gas-phase reaction of NO₃ with guaiacol. A typical chromatogram is presented in Fig. 4. Once the molar mass of one product is determined (by LC-QTOF-MS), the corresponding peak is fragmented using three energy values (10 eV, 20 eV and 30 eV; MS/MS analysis). A higher energy value leads to a greater fragmentation of the molecules which allows to identify the functional groups and thus to assess the chemical structures of the compounds.

The compounds detected in the SOAs are listed in Table 2 (major compounds, relative abundance > 4 %) and Table S1 (minor compounds, relative abundance ≤ 2 %); the indicated masses correspond to the [M-H] product ions. The relative abundances (expressed in %) were calculated from the ratio of the sum of the chromatographic peak areas of the different isomers to the total chromatographic peak area of all the peaks. This approach assumes that the mass spectrometer has the same response for every detected chemical compound. The main compounds observed in the SOAs are nitrated aromatic compounds (see Table 2): nitromethoxybenzenes (m/z = 152, 2 isomers, 9.3%); nitrocatechol(s) (m/z = 154, 1 or 2 isomers (the peak width suggests the presence of two isomers, but this hypothesis could not be confirmed), 18.0%); nitroguaiacols (m/z = 168, 4 isomers, 11.7%); dinitromethoxybenzene (m/z = 197, 2 isomers, 7.6%); dinitrocatechols (m/z = 199, 3 isomers, 4.7%); dinitroguaiacols (m/z = 213, 6 isomers, 9.0%); dimeric compounds formed via the association of 1 nitroguaiacol and 1 nitrocatechol (m/z = 321, 12 isomers, 5.4%) or via the association of 2 nitroguaiacols (m/z = 335, 5 isomers, 18.1 %), and 2 unidentified compounds (m/z = 531,

8.2% and $m/z = 584$, 4.3%). So, this confirms that the oxidation products formed in the aerosols from the reaction of NO_3 radicals with guaiacol are both first and second generation products, as suggested by the data shown in Fig. 1. However, as more than $\approx 75\%$ of the SOA mass is generated after complete depletion of guaiacol, it is highly probable that the aerosol products are formed through reactions in the gas-phase and/or in the condensed phase (in the chamber or on the filter during the sampling). Additional experiments using lower initial guaiacol concentrations would probably reduce potential reactions occurring in the condensed phase. Figures S1-S8 (see supporting information) display $[\text{M-H}]^+$ product ions MS/MS spectra obtained at 20 eV for the major compounds identified in the SOAs ($m/z = 152$, Fig. S1; $m/z = 154$, Fig. S2; $m/z = 168$, Fig. S3; $m/z = 197$, Fig. S4; $m/z = 199$, Fig. S5; $m/z = 213$, Fig. S6; $m/z = 321$, Fig. S7 and $m/z = 335$, Fig. S8). The different fragments allowed to propose consistent chemical structures for the oxidation products of $\text{NO}_3 + \text{guaiacol}$ found in the particle phase.

The minor compounds detected in the aerosols are shown in Table S1.

Among the major reaction products, 4-nitroguaiacol and 5-nitroguaiacol were clearly identified by comparing their chromatographic retention times and their MS-MS spectra to those of standards commercially available. The most abundant nitroguaiacol formed in the particle phase was 4-nitroguaiacol (91.5%), in large excess compared to 5-nitroguaiacol (5.4%) and 3-nitroguaiacol and/or 6-nitroguaiacol (3.1% for both; the standards of these two isomers do not exist, so it was not possible to distinguish them).

The mechanism leading to the main oxidation products identified in the SOAs is proposed in Fig. 5. It has been postulated by Atkinson et al., (1992), that the NO_3 radical initiated reaction of aromatic compounds may first proceed by an ipso-addition to the OH substituent which forms a six-membered transition state intermediacy. A second mechanism starts with the electrophilic addition of the nitrate radical on the aromatic ring. These two ways lead to the

formation of nitric acid and a phenoxy radical, which then react with NO_2 to produce nitroguaiacol isomers. Similarly, the formation of dinitroguaiacols and trinitroguaiacol can be explained by the reaction of nitroguaiacols with NO_3 and NO_2 .

The initial oxidation steps starting from guaiacol and going to nitromethoxybenzenes and nitrocatechols are not known, as indicated in Figure 5. Since the present gas-phase chemistry knowledge of aromatic compounds is not able to address these issues, we suggest that an oxidation chemistry could take place in the condensed phase and produce the observed nitromethoxybenzenes and nitrocatechols. Investigations of the liquid-phase guaiacol oxidation would be very useful to support this assumption. In their study on gas-phase reaction products of NO_3 + guaiacol, Yang et al. (2016) also reported the presence of nitroguaiacols (4-nitroguaiacol and 6-nitroguaiacol; 4-nitroguaiacol being the most abundant), dinitroguaiacol (4,6-dinitroguaiacol), catechol (1,2-dihydroxybenzene) and nitromethoxybenzene in the products formed from the gas-phase of NO_3 reaction guaiacol. They also identified catechols from the oxidation of creosol (4-methyl-guaiacol) and syringol (6-methoxy-guaiacol). The formation of catechols was reported by Zhang et al. (2016) as well, who studied the reaction of eugenol (4-allyl-guaiacol) and ethyl-guaiacol with NO_3 radicals. The mechanism leading to catechols from guaiacol and its derivatives was not explained in both previous articles.

The formation of nitrocatechols and dinitrocatechols can then result from the reaction of NO_3 and NO_2 with catechol and nitrocatechols, respectively. The compounds with high molecular masses ($m/z > 300$) display 2 to 3 aromatic cycles; they can be produced from the combination of phenoxy radicals formed from nitroguaiacol(s) and/or nitrocatechol(s).

For the main identified products, one isomer was always more abundant than the others (the corresponding relative abundances vary from 85 % to 99 %; see table S2).

The oxidation products formed in the aerosols from the gas-phase reaction of guaiacol with nitrate radicals can also be compared to those identified for the reaction of guaiacol with hydroxyl radicals under high NO_x conditions (Ahmad et al., 2017). The ATR-FTIR analyses performed by Ahmad et al., (2017) also reveal the presence of 4-nitroguaiacol in the SOAs. So, this observation suggests that the oxidation products generated in the particulate phase, via the oxidation of guaiacol by NO₃ or OH/NO_x reaction, are probably similar as it has been previously postulated from the comparison of the gas-particle partitioning equilibrium constants ($K_{om,i}$) obtained with both oxidants.

4. Conclusions

The formation of secondary organic aerosols from the reaction of guaiacol (2-methoxyphenol) with nitrate radicals has been studied in two simulation chambers. The SOAs yields have been shown to be influenced by the initial guaiacol concentration, which leads to aerosol yields ranging from 0.01 to 0.21. A very good agreement was observed between the experiments performed in both chambers which gives confidence in the data obtained in this study. The aerosols data have been fitted with the absorptive gas-particle partitioning model developed by Pankow (1994a,b) and Odum et al. (1996) using the one-product model.

Aerosol organic carbon concentration is typically 5 $\mu\text{g m}^{-3}$ in many environments, though it can occasionally rise to 50 $\mu\text{g m}^{-3}$ or more in highly polluted areas. Extrapolating to a particle loading of 5 $\mu\text{g m}^{-3}$ from the yield data (Fig. 3) gives a 2% SOA yield. Based on this result, one can infer that the contribution of the reaction between guaiacol and NO₃ radicals to SOAs production under atmospheric conditions is probably relatively minor. However, in polluted areas this reaction can be an important source of secondary aerosols.

ESI-LC-QToF-MS/MS analyses were performed to characterize the chemical composition of the aerosols. Nitro-aromatics compounds were identified as the main oxidation products,

confirming previous studies (Yang et al., 2016; Zhang et al., 2016) on the products formed from the gas-phase reaction of NO₃ radicals with guaiacol derivatives.

A well-established tracer for primary biomass burning aerosols (BBA) is levoglucosan (1,6-anhydro- β -anhydroglucose), which originates from the pyrolysis of cellulose or hemicelluloses (Simoneit et al., 2002). Several nitro-aromatic compounds were detected in urban aerosols, and nitrocatechols as well as nitroguaiacols are recognized to be suitable tracers for secondary BBA (Iinuma et al., 2010; Kitanovsky et al., 2012). Further research efforts on the reactivity of these compounds would allow to measure their rate constants with the main oxidants and to determine the corresponding lifetimes. To our knowledge, only a few data are available in the literature concerning the atmospheric reactivity of nitro-aromatics (Bejan et al., 2007; 2015).

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References

- Atkinson, R., Carter, W.P.L., Plum, C.N., Winer, A.M., Pitts, J.N., 1984. Kinetics of the gas-phase reactions of NO₃ radicals with a series of aromatics at 296 \pm 2 K. *Int. J. Chem.* 16, 887-898.
- Atkinson R., Aschmann S. M., Arey J, 1992. Reactions of hydroxyl and nitrogen trioxide radicals with phenol, cresols, and 2-nitrophenol at 296 \pm 2 K. *Environ. Sci. Technol.* 26, 1397-1403.

397 Ahmad, W., Coeur C., Tomas A., Fagniez T., Brubach J-B., Cuisset A., 2017. Infrared
 398 spectroscopy of secondary organic aerosol precursors and investigation of the
 399 hygroscopicity of SOA formed from the OH reaction with guaiacol and syringol.
 400 Appl. Opt., 56, 116-122.

401 Bejan, J., Barnes, I., Olariu, O., Zhou, S., Wiesen, P., Bentera, T., 2007. Investigations on the
 402 gas-phase photolysis and OH radical kinetics of methyl-2-nitrophenols. Phys. Chem.
 403 Chem. Phys., 9, 5686-5692.

404 Bejan, J., Duncianu, M., Olariu, O., Barnes, I., Seakins, P., Wiesen, P., 2015. Kinetic study of
 405 the gas-phase reactions of chlorine atoms with 2-chlorophenol, 2-nitrophenol, and four
 406 methyl-2-nitrophenol isomers. J. Phys. Chem. A, 2015, 20, 4735-4745.

407 Bruns E.A. , Slowik J.G., El Haddad I., Kilic D., Klein F., Dommen J., Temime-Roussel B.,
 408 Marchand N., Baltensperger U., Prévôt A.S.H. 2017. Characterization of gas-phase
 409 organics using proton transfer reaction time-of-flight mass spectrometry: fresh and
 410 aged residential wood combustion emissions. Atmos. Chem. Phys., 17, 705-720.

411 Calvert, J.G., Atkinson, R., Becker, K.H., Kamens, R.M., Seinfeld, J.H., Wallington, T.J.,
 412 Yarwood, G., 2002. The mechanisms of atmospheric oxidation of aromatic
 413 hydrocarbons, Oxford University Press, New York, N.Y.

414 Chen Y., Bond T.C., 2010. Light absorption by organic carbon from wood combustion.
 415 Atmos. Chem. Phys. 10, 1773–1787.

416 Coeur-Tourneur, C., Tomas, A., Guilloteau, A., Henry, F., Ledoux, F., Visez, N., Riffault, V.,
 417 Wenger, J.C., Bedjanian, Y., 2009. Aerosol formation yields from the reaction of
 418 catechol with ozone. Atmos. Environ. 43, 2360-2365.

419 Coeur-Tourneur C., Cassez A., Wenger J.C., 2010a. Rate constants for the gas-phase reaction
 420 of hydroxyl radicals with 2-methoxyphenol (guaiacol) and related compounds, J. Phys.
 421 Chem. A 114, 11645-11650.

422 Coeur-Tourneur C., Foulon V., Laréal M., 2010b. Determination of aerosol yields from 3-
 423 methylcatechol and 4-methylcatechol ozonolysis in a simulation chamber, *Atmos.*
 424 *Environ.* 44, 852-857.

425 Derwent, R.G., Jenkin, M.E., Saunders, S., 1996. Photochemical ozone creation potentials for
 426 a large number of reactive hydrocarbons under European conditions. *Atmos. Environ.*
 427 30, 181–199.

428 Derwent, R.G., Jenkin, M.E., Saunders, S.M., Pillings, M. J., 1998. Photochemical ozone
 429 creation potentials for organic compounds in northwest Europe calculated with a
 430 master chemical mechanism. *Atmos. Environ.* 32, 2429–2441.

431 El Zein, A., Coeur, C., Obeid, E., Lauraguais, A., Fagniez, T., 2015. Reaction kinetics of
 432 catechol (1,2-Benzenediol) and guaiacol (2-Methoxyphenol) with ozone. *J. Phys.*
 433 *Chem. A* 119, 6759-6765.

434 Fourtziou L., Liakakou E., Stavroulas I., Theodosi C., Zarnpas P., Psiloglou B., Sciare J.,
 435 Maggos T., Bairachtari K., Bougiatioti A., Gerasopoulos E., Sarda-Estève R.,
 436 Bonnaire N., Mihalopoulos N. 2017. Multi-tracer approach to characterize domestic
 437 wood burning in Athens (Greece) during wintertime. *Atmos. Environ.*, 148, 89-101.

438 Gurjar B.R., Molina L.T., Ojha C.S.P. 2010. *Air Pollution: Health and Environmental*
 439 *Impacts*. CRC Press Taylor & Francis Group.

440 Hallquist M., Wenger J. C., Baltensperger U., Rudich Y., Simpson D., Claeys M., Dommen
 441 J., Donahue N. M., George C., Goldstein A. H., Hamilton J. F., Herrmann H.,
 442 Hoffmann T., Iinuma Y., Jang M., Jenkin M. E., Jimenez J. L., Kiendler-Scharr A.,
 443 Maenhaut W., McFiggans G., Mentel Th. F., Monod A., Prévôt A. S. H., Seinfeld J.
 444 H., Surratt J. D., R. Szmigielski R., Wildt J., 2009. The formation, properties and
 445 impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem.*
 446 *Phys.* 9, 5155–5236.

447 Hanson D.J., 1996. Toxics release inventory report shows chemical emissions continuing to
 448 fall. Chem. Eng. News, July 15, 29-30.

449 Hays, M.D., Geron, C.D., Linna, K.J., Smith, N.D., Schauer, J. J., 2002. Speciation of gas-
 450 phase and fine particle emissions from burning of foliar fuels. Environ. Sci. Technol.
 451 36, 2281-2295.

452 Henry, F., Coeur-Tourneur, C., Ledoux, F., Tomas, A., Menu, D., 2008. Secondary organic
 453 aerosol formation from the gas phase reaction of hydroxyl radicals with m-, o- and p-
 454 cresol. Atmos. Environ. 42, 3035–3045.

455 Hurley, M.D., Sokolov, O., Wallington, T.J., Takekawa, H., Karasawa, M., Klotz, B., Barnes,
 456 I., Becker, K.H., 2001. Organic aerosol formation during the atmospheric degradation
 457 of toluene. Environ. Sci. Technol. 35, 1358–1366.

458 Iinuma, Y, Böge, O., Agräfe R., Herrmann H., 2010. Methyl-Nitrocatechols: Atmospheric
 459 tracer compounds for biomass burning secondary organic aerosols. Environ. Sci.
 460 Technol., 44, 8453-8459.

461 Kitanovsky, Z., Grgi, I., Yasmeen, F., Claeys, M., A., 2012. Development of a liquid
 462 chromatographic method based on ultraviolet-visible and electrospray ionization mass
 463 spectrometric detection for the identification of nitrocatechols and related tracers in
 464 biomass burning atmospheric organic aerosol, Rapid Commun. Mass Sp., 26, 793-804.

465 Langmann, B., Duncan, V., Textor, C., Trentmann, J., van der Werfe, G.R., 2009. Vegetation
 466 fire emissions and their impact on air pollution and climate. Atmos. Environ. 43, 107-
 467 116

468 Lauraguais, A., Coeur-Tourneur, C., Cassez, A., Seydi, A., 2012. Rate constant and secondary
 469 organic aerosol yields for the gas-phase reaction of hydroxyl radicals with syringol
 470 (2,6-dimethoxyphenol). Atmos. Environ. 55, 43-48.

471 Lauraguais, A., Bejan, I., Coeur-Tourneur, C., Cassez, A., Deboudt, K., Fourmentin, M.,
 472 Choël, M., 2014a. Atmospheric reactivity of hydroxyl radicals with guaiacol (2-
 473 methoxyphenol), a biomass burning emitted compound : secondary organic aerosol
 474 formation and gas-phase oxidation products. *J. Phys. Chem. A* 86, 155-163.

475 Lauraguais, A., Bejan, I., Barnes, I., Wiesen, P., Coeur-Tourneur, C., Cassez, A., 2014b. Rate
 476 coefficient for the gas-phase reaction of chlorine atoms with a series of methoxylated
 477 aromatic compounds. *J. Phys. Chem. A* 118, 1777-1784.

478 Lauraguais, A., Bejan, I., Barnes, I., Wiesen, P., Coeur, C., 2015. Rate coefficients for the
 479 gas-phase reaction of hydroxyl radicals with a series of methoxylated aromatic
 480 compounds. *J. Phys. Chem. A* 119, 6179-6187.

481 Lauraguais, A., El Zein, A., Coeur, C., Obeid, E., Rayez, M-T., Rayez, J-C., 2016. Rate
 482 coefficient for the gas-phase reaction of nitrate radicals with a series of
 483 methoxyphenol compounds: experimental and theoretical approaches. *J. Phys. Chem.*
 484 *A*, 120, 2691-2699 (2016).

485 Lelieveld, J., Crutzen, P.J., Ramanathan, V., Andreae, M.O., Brenninkmeijer, C.A.M.,
 486 Campos, T., Cass, G.R., Dickerson, R.R., Fischer, H., de Gouw, J.A., Hansel, A.,
 487 Jefferson, A., Kley, D., de Laat, A.T.J., Lal, S., Lawrence, M.G., Lobert, J.M., Mayol-
 488 Bracero, O.L., Mitra, A.P., Novakov, T., Oltmans, S.J., Prather, K.A., Reiner, T.,
 489 Rodhe, H., Scheeren, H.A., Sikka, D., Williams, J., 2001. The Indian ocean
 490 experiment: widespread air pollution from South and Southeast Asia. *Science* 291,
 491 1031-1036.

492 Lighty, J.S., Veranth, J.M., Sarofim, A.F., 2000. Combustion aerosols: factors governing their
 493 size and composition and implications to human health. *J. Air Waste Manag.* 50,
 494 1565-1618.

495 Mazzoleni, L.R., Zielinska, B., Moosmüller, H., 2007. Emissions of levoglucosan,
 496 methoxyphenols, and organic acids from prescribed burns, laboratory combustion of
 497 wildland fuels, and residential wood combustion. *Environ. Sci. Technol.* 41, 2115-
 498 2122.

499 McDonald, J.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., Watson, J.G., 2000.
 500 Fine particle and gaseous emission rates from residential wood combustion. *Environ.*
 501 *Sci. Technol.* 34, 2080-2091.

502 Odum, J.R., Hoffmann, T., Bowman, F.M., Collins, D., Flagan, R.C., Seinfeld, J.H., 1996.
 503 Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.*
 504 3, 2580-2585.

505 Odum, J.R., Jungkamp, T.P.W., Griffin, R.J., Forstner, H.J.L., Flagan, R.C., Seinfeld, J.H.,
 506 1997. Aromatics, reformulated gasoline, and atmospheric organic aerosol formation.
 507 *Environ. Sci. Technol.* 31, 1890–1897.

508 Olariu, R.I., Tomas, A., Barnes, I., Wirtz, K., 2003. Atmospheric ozone degradation reaction
 509 of 1,2-dihydroxybenzene: aerosol formation study. In: *The European Photoreactor*
 510 *EUPHORE, fourth report 2001.* Ed. Institute of Physical Chemistry, Bergische
 511 Universität Wuppertal, Germany, 54–71.

512 Pankow, J.F., 1994a. An absorption model of gas/particles partitioning of organic compounds
 513 in the atmosphere. *Atmos. Environ.* 28, 185–188.

514 Pankow, J.F., 1994b. An absorption model of the gas/aerosol partitioning involved in the
 515 formation of secondary organic aerosol. *Atmos. Environ.* 28, 189–193.

516 Sarigiannis D.A., Karakitsios S.P. , Kermenidou, M.V. 2015. Health impact and monetary
 517 cost of exposure to particulate matter emitted from biomass burning in large cities.
 518 *Sci. Total Environ.*, 15, 319-330.

519 Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2001. Measurement of emissions
 520 from air pollution sources. 3. C₁-C₂₉ organic compounds from fireplace combustion of
 521 wood. *Environ. Sci. Technol.* 35, 1716-1728.

522 Simoneit, B. R. T., 2002. Biomass burning - a review of organic tracers for smoke from
 523 incomplete combustion. *Appl. Geochem.* 17, 129-162.

524 Simpson, C.D., Paulsen, M., Dills, R.L., Liu, L.J.S., Kalman, D.A., 2005. Determination of
 525 methoxyphenols in ambient atmospheric particulate matter: tracers for wood
 526 combustion. *Environ. Sci. Technol.* 39, 631-637.

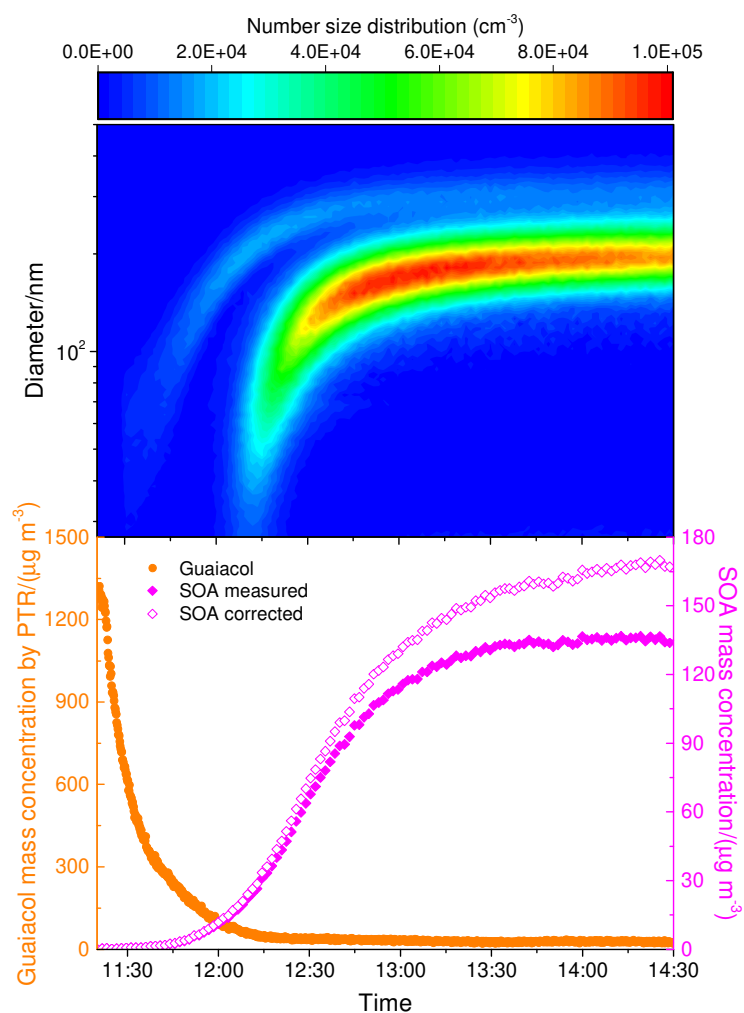
527 Song, C., Na, K., Cocker, D.R., 2005. Impact of the hydrocarbon to NO_x ratio on secondary
 528 organic aerosol formation. *Environ. Sci. Technol.* 39, 3143-3149.

529 Takekawa, H., Minoura, H., Yamazaki, S., 2003. Temperature dependence of secondary
 530 organic aerosol formation by photo-oxidation of hydrocarbons. *Atmos. Environ.* 37,
 531 3413-3424.

532 Yang, B., Zhang, H., Wang, Y., Zhang P., Shu, J., Sun, W., Ma, P., 2016. Experimental and
 533 theoretical studies on gas-phase reactions of NO₃ radicals with three methoxyphenols:
 534 guaiacol, creosol, and syringol. *Atmos. Environ.*, 125, 243-251.

535 Zhang H., Yang, B., Wang, Y., Shu, J., Zhang, P., Ma, P., Li, Z. 2016. Gas-phase reactions of
 536 methoxyphenols with NO₃ radicals: kinetics, products, and mechanisms. *J. Phys.*
 537 *Chem. A*, 120, 1213-1221.

1 Fig. 1. Typical concentration-time profiles obtained for guaiacol (PTR-ToF-MS) and SOAs
 2 (SMPS; measured and corrected for wall losses). Experiment guaiacol #10 (initial mixing
 3 ratios: guaiacol (276 ppb; $1429 \mu\text{g m}^{-3}$); NO_2 (750 ppb) and O_3 (500 ppb).



7 Fig. 2. Aerosol growth curve: SOA mass concentration (M_0) against the reacted guaiacol
8 concentration ($\Delta[\text{guaiacol}]$) measured at the end of the experiments. Each data point
9 represents a separate experiment.

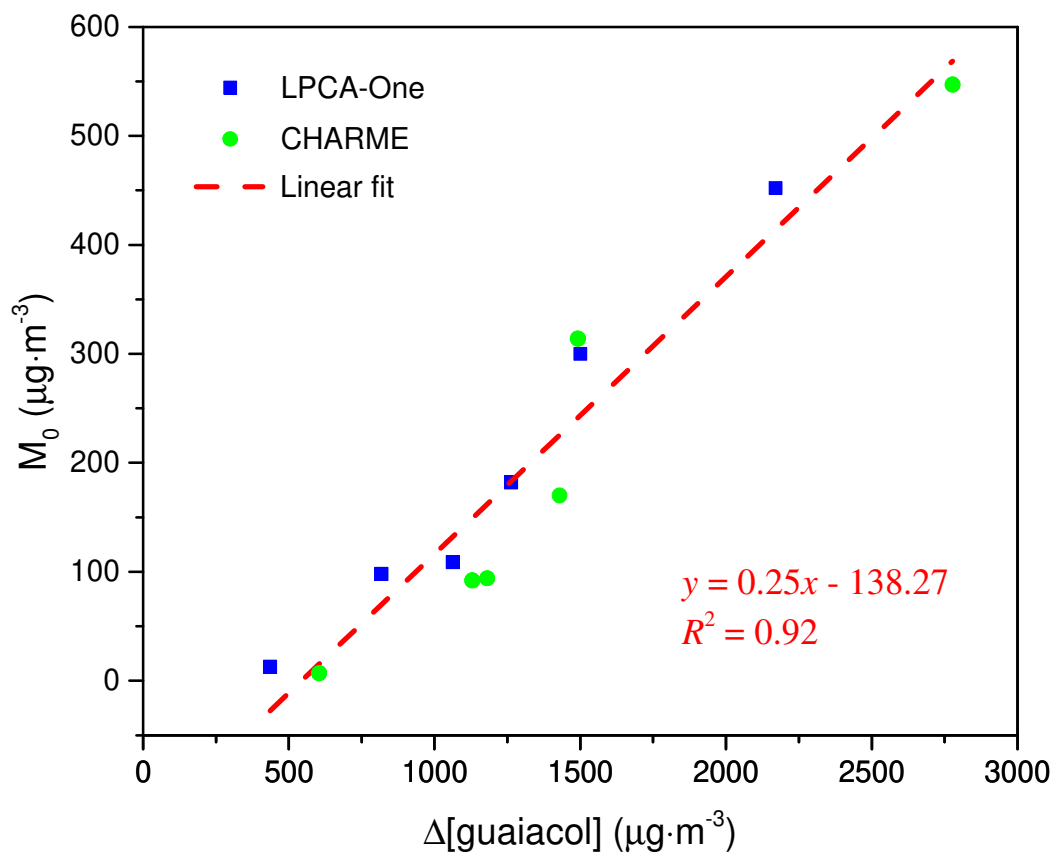


Fig. 3. Yield curve (SOA yield Y versus the organic aerosol mass formed M_0) for guaiacol/ NO_3 experiments in LPCA-One (blue squares) and in CHARME (green circles). The line represents the best fit to the data considering one semi-volatile major product. The fitting parameters used are $\alpha = 0.32 \pm 0.04$ and $K_{\text{om}} = (4.2 \pm 1.0) \times 10^{-3} \text{ m}^3 \mu\text{g}^{-1}$.

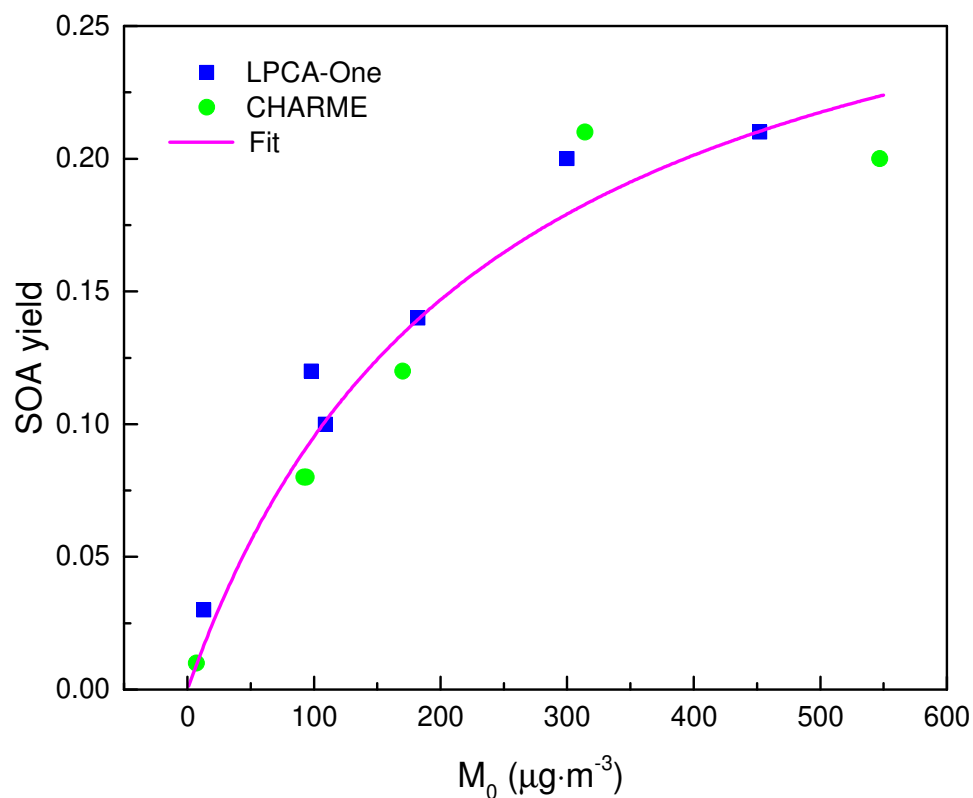
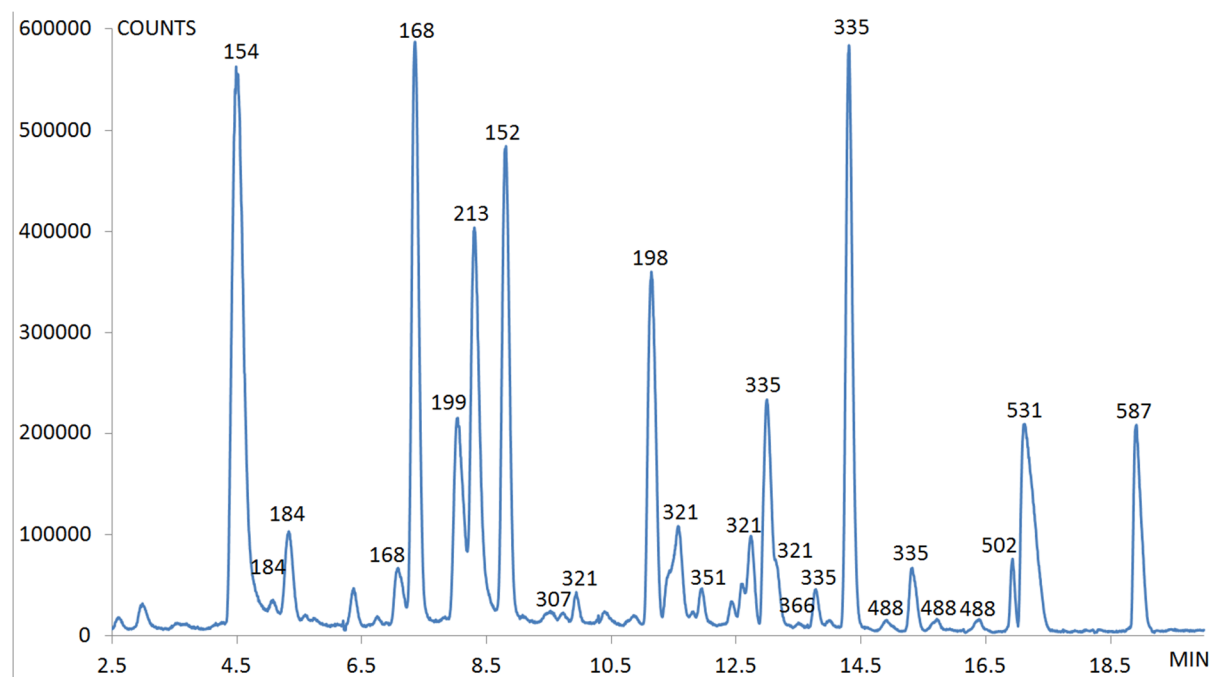
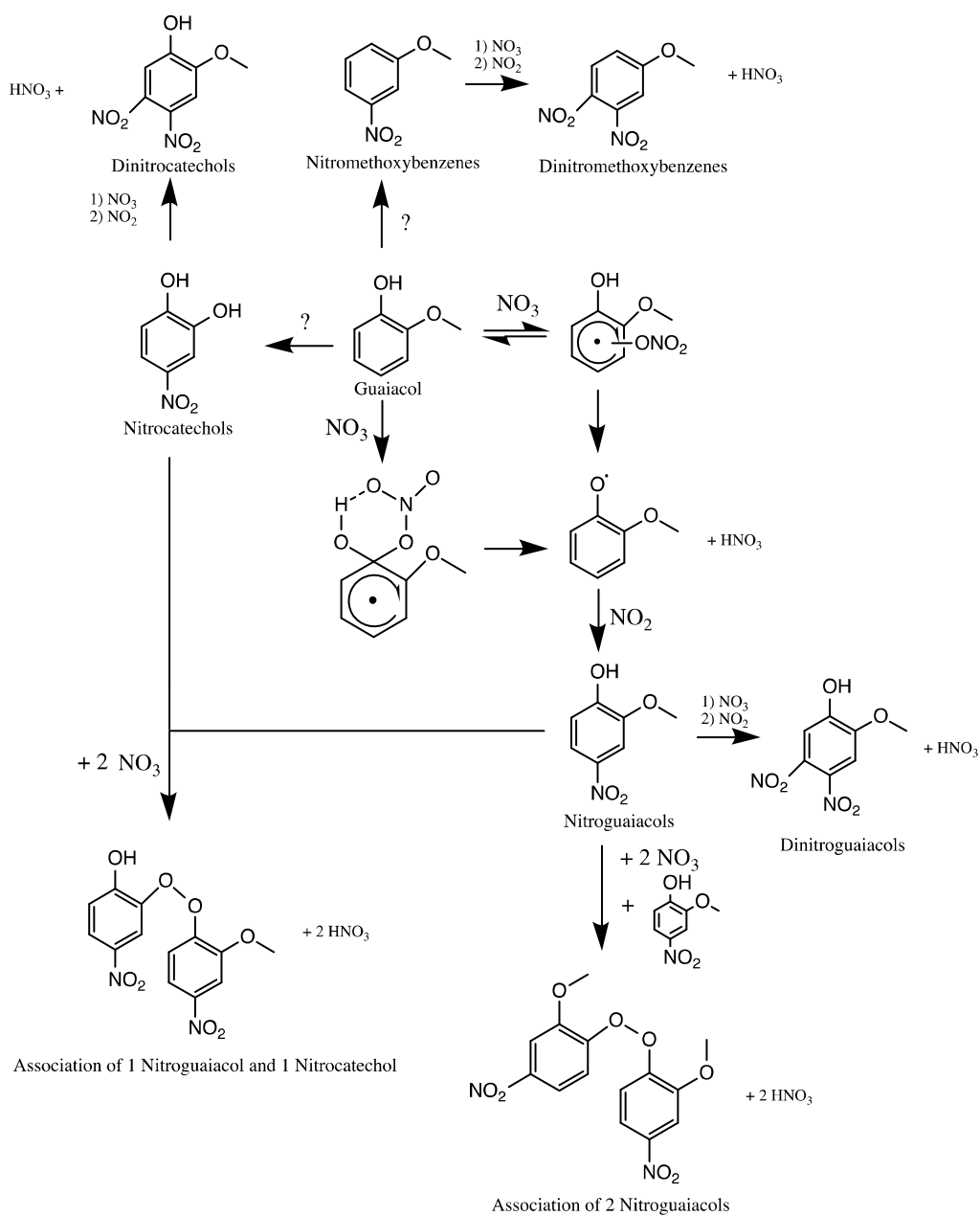


Fig. 4. Chromatogram (ESI-LC-QToF-MS/MS analysis) of the SOAs formed from the gas-phase reaction of guaiacol (2-methoxyphenol) with NO₃ radicals. The compounds corresponding to the labelled peaks are displayed in table 2. The indicated masses correspond to the [M-H]⁺ product ions.



26 Fig.5. Detailed mechanism leading to the main products observed in the SOAs formed from
 27 the gas-phase reaction of guaiacol (2-methoxyphenol) with NO₃ radicals.



1 **Table 1.** Experimental conditions and results.

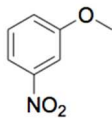
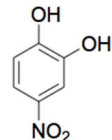
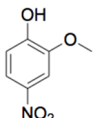
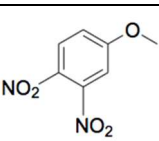
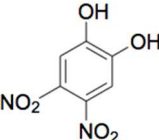
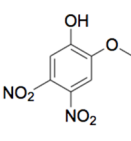
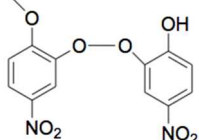
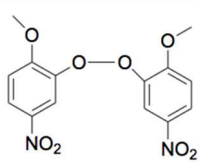
Expt.	[guaiacol] ₀ ^a	NO ₃ formation		Δ[guaiacol] ^b	M ₀ ^c	Y ^d
	(ppb)	[NO ₂] ₀	[O ₃] ₀	(μg m ⁻³)	(μg m ⁻³)	
		(ppb)	(ppb)			
In LPCA-ONE						
guaiacol #1	84	N ₂ O ₅ decomposition		436	13	0.03
guaiacol #2	158	N ₂ O ₅ decomposition		818	98	0.12
guaiacol #3	206	N ₂ O ₅ decomposition		1063	109	0.10
guaiacol #4	244	N ₂ O ₅ decomposition		1263	182	0.14
guaiacol #5	290	N ₂ O ₅ decomposition		1501	300	0.20
guaiacol #6	420	N ₂ O ₅ decomposition		2171	452	0.21
In CHARME						
guaiacol #7	117	N ₂ O ₅ decomposition		604	7	0.01
guaiacol #8	218	785 ^e	896 ^f	1130	92	0.08
guaiacol #9	228	535 ^e	620 ^f	1181	94	0.08
guaiacol #10	276	750 ^g	500 ^h	1429	170	0.12
guaiacol #11	288	1239 ^e	798 ^f	1492	314	0.21
guaiacol #12	537	1500 ^g	1000 ^h	2778	547	0.20

2

3 ^aInitial guaiacol volume ratio.

- 4 ^dReacted guaiacol concentration (guaiacol was totally consumed in all experiments, so the reacted
5 concentrations $\Delta[\text{guaiacol}]$ correspond to $[\text{guaiacol}]_0$).
- 6 ^eOrganic aerosol mass concentration (corrected for wall losses and assuming a particle density of 1.4).
- 7 ^dOverall SOA yield (Y) calculated as the ratio of M_0 to the total reacted guaiacol concentration.
- 8 ^eInitial NO_2 volume ratio measured in the chamber (chemiluminescence NO_x analyser).
- 9 ^fInitial O_3 volume ratio measured in the chamber (photometric O_3 analyser).
- 10 ^gInitial injected NO_2 volume ratio.
- 11 ^hInitial injected O_3 volume ratio.
- 12

Table 2. Major compounds observed in the SOAs (ESI-LC-QToF-MS/MS analyses) formed from the gas-phase reaction of guaiacol (2-methoxyphenol) with NO₃ radicals. The main fragments obtained by MS/MS analyses (see Fig. S1-S8 in supporting information) and the relative abundances (R, in %) are also indicated.

Molecular ion ^a	Main fragments	Brut Formula	Name ^e	Structure ^f	R (%) ^g
152	46 [NO ₂] ⁻ 93 [C ₆ H ₅ O] ⁻ 122 [C ₇ H ₆ O ₂] ⁻	C ₇ H ₆ NO ₃ ^d	Nitromethoxybenzene ²		9.3
154	69 [C ₃ HO ₂] ⁻ 95 [C ₅ H ₃ O ₂] ⁻ 123 [C ₆ H ₃ O ₃] ⁻	C ₆ H ₄ NO ₄ ^d	Nitrocatechol ¹⁻²		18.0
168	95 [C ₅ H ₃ O ₂] ⁻ 123 [C ₆ H ₃ O ₃] ⁻ 153 [C ₆ H ₃ NO ₄] ⁻	C ₇ H ₆ NO ₄ ^b	Nitroguaiacol ⁴		11.7
197	76 [C ₅ H ₂ N] ⁻ 109 [CH ₅ N ₂ O ₄] ⁻ 123 [C ₆ H ₅ NO ₂] ⁻	C ₇ H ₅ N ₂ O ₅ ^c	Dinitromethoxybenzene ²		7.6
199	67 [C ₄ H ₃ O] ⁻ 95 [C ₅ H ₃ O ₂] ⁻ 153 [C ₆ H ₃ NO ₄] ⁻	C ₆ H ₃ N ₂ O ₆ ^b	Dinitrocatechol ³		4.7
213	66 [C ₃ NO] ⁻ 78 [C ₅ H ₂ O] ⁻ 198 [C ₆ H ₂ N ₂ O ₆] ⁻	C ₇ H ₅ N ₂ O ₆ ^b	Dinitroguaiacol ⁶		9.0
321	153 [C ₆ H ₃ NO ₄] ⁻ 168 [C ₇ H ₆ NO ₄] ⁻ 306 [C ₁₂ H ₆ N ₂ O ₈] ⁻	C ₁₃ H ₉ N ₂ O ₈ ^b	Association of 1 nitroguaiacol and 1 nitrocatechol ¹²		5.4
335	153 [C ₆ H ₃ NO ₄] ⁻ 168 [C ₇ H ₆ NO ₄] ⁻ 320 [C ₁₆ H ₆ N ₃ O ₅] ⁻	C ₁₄ H ₁₁ N ₂ O ₈ ^b	Association of 2 nitroguaiacols ⁵		18.1

531	-	-	-	-	8.2
587	-	-	-	-	4.3

18 ^aThe indicated masses correspond to the [M–H] product ions.

19 ^bProbability given by the software between 98 and 100 %.

20 ^cProbability given by the software between 90 and 97 %.

21 ^dProbability given by the software between 70 and 89%.

22 ^eNumber of detected isomers.

23 ^fThe drawn structure correspond to one isomer only.

24 ^gThe relative abundances (in %) were calculated from the ratio of the sum of the chromatographic
25 areas of the different isomers to the total chromatographic area of all the peaks.