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FT-IR product study of the reactions of NO₃ radicals with
ortho-, *meta*- and *para*-cresol

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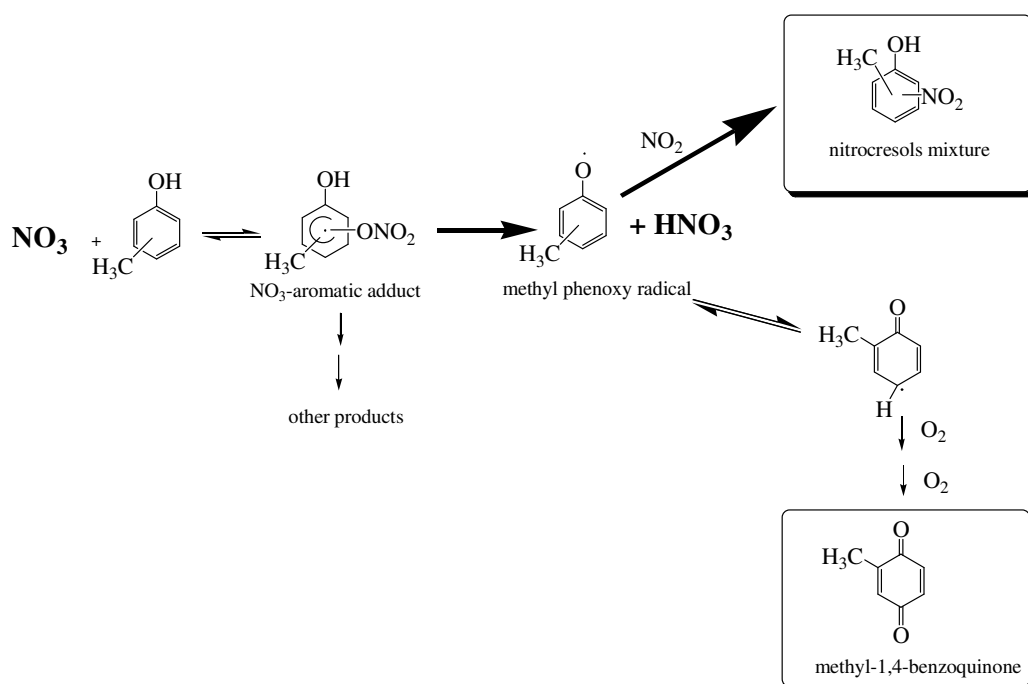
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Abstract

Product analyses of the NO₃ radical-initiated oxidation of *ortho*-, *meta*- and *para*-cresol have been performed in large-volume chamber systems at the University of Wuppertal (1080 L quartz glass reactor: QUAREC) and the European Photoreactor, Valencia, Spain (EUPHORE). The reaction of O₃ with NO₂ was used for the *in situ* generation of NO₃ radicals in both QUAREC and EUPHORE. The gas-phase reaction of all three cresol isomers with NO₃ yielded nitrocresols and HNO₃. Moreover, methyl-1,4-benzoquinone was detected and quantified from the reaction of NO₃ with *ortho*- and *meta*-cresol. The product formation yields determined in both chambers are compared with literature data. Based on all the identified products and yields, a gas-phase mechanism is proposed for the reactions of NO₃ with cresols.

INTRODUCTION

Aromatic hydrocarbons such as benzene, toluene and the xylene isomers (BTX) constitute ~20% of non-methane volatile organic compounds in urban areas. They are released into the atmosphere from solvent use, vaporization of gasoline and diesel fuel, and vehicle exhaust.¹⁻³ In the troposphere, gas-phase BTX photo-oxidation is dominated by OH radicals. These reactions are responsible for a substantial proportion of the photooxidant and secondary organic aerosol (SOA) formation in urban areas,^{1,4-6} with detrimental consequences for both human health and ecosystems.⁷

The reaction of OH with BTX proceeds by direct H-atom abstraction from alkyl substituents on the ring, and upon ring addition to form intermediate hydroxycyclohexadienyl radicals, often termed OH-aromatic adducts. The latter is the dominant pathway.^{1,8} Further reactions of OH-aromatic adducts produce ring-hydroxylated and ring-opening compounds, such as 1,2-dicarbonyls and unsaturated 1,4-dicarbonyls.^{1,8} In the cases of benzene and toluene, the ring addition of OH produces phenol⁹⁻¹⁴ and the cresol isomers, with respective yields of up to approximately 60% and 20%.^{1,15-17} The yield of phenol from OH + benzene is sensitive to the amount of NO_x and is between 50-60% under atmospheric NO_x concentrations.¹¹⁻¹⁴ There has been debate in the literature concerning the possible formation of phenol and cresols from xylenes *via* a dealkylation pathway, but this process probably occurs to a minor extent in the atmosphere.¹⁸⁻²¹

In addition to the *in situ* atmospheric production of phenolic compounds from BTX

photooxidation, other significant inputs include automobile exhaust,²²⁻²⁴ wood burning^{25,26} and industrial sources.^{27,28} Phenol and cresols react slowly with O₃,^{1,29} but they undergo rapid reactions with OH^{1,30-32} and NO₃.^{1,30,31,33-35} Therefore, rapid atmospheric removal is expected upon reactions with OH during the day and NO₃ during the night.

The gas-phase chemistry of the nitrate radical and its important atmospheric role have been extensively discussed.^{1,33,36-39} The night-time atmospheric concentrations of NO₃ can be highly variable depending on NO_x levels, ranging from nearly zero to 2.0×10⁹ molecule cm⁻³ or higher.^{40,41} Evidence has recently emerged that NO₃ could be a significant daytime oxidant for certain unsaturated biogenic and anthropogenic VOCs, in shaded forest and urban areas where the processing of NO_x and O₃ is large enough to produce significant NO₃.^{40,42} Small daytime NO₃ mixing ratios comparable to peak OH concentrations have been observed, suggesting that VOCs reacting with NO₃ at comparable rates as with OH (*e.g.* isoprene, monoterpenes and hydroxylated aromatics) can be oxidized by NO₃ during the day. The radical NO₃ could for instance contribute to the daytime oxidation of phenol and cresols in urban air,^{42,43} and to as much as 40% of daytime catechols oxidation.⁴⁴

The main reaction products of OH with phenol and cresols are now fairly well established,^{30,32,45-47} differently from the case of NO₃. Nitrophenol formation has been observed from the NO₃-initiated oxidation of phenol,^{30,35} and methylated nitrophenols from the oxidation of cresols.^{30,45} There are significant differences in the reported nitrophenol yields, and *meta*- and *para*-cresol have only been investigated by one group.³⁰ With the exception of phenol and *para*-cresol, the observed products account for only a very modest fraction of parent compound degradation. Note that nitration reactions have a potentially considerable impact on health and the environment, as they can enhance the mutagenic potency of phenols and other aromatic compounds.⁴⁸

The reactions of NO₃ with phenols should proceed *via* an overall H-atom abstraction mechanism, which occurs after ring addition of NO₃.³⁰ From this simple mechanistic picture one would expect to observe nitrophenols in a combined yield of 100%. This is not the case, however, with the partial exception of product studies on phenol and *para*-cresol where respective nitroderivative yields of up to 25 and 74% have been reported.³⁰

Recent computational studies on the reactions of NO₃ with cresols^{49,50} predict that NO₃ is added to the hydroxylated carbon, followed by addition of NO₂ to a directly adjacent carbon. This pathway has the lowest energy barrier for the elimination of HNO₃ and it has the most stable transition state. Therefore, it could be energetically favorable to add both NO₃ and NO₂ before elimination of HNO₃. Such a mechanism contrasts sharply with that proposed by

Atkinson et al.,³⁰ where HNO₃ is eliminated prior to addition of NO₂. If the computational studies are correct, the nitration of cresols should occur mostly at the *ortho* position. This would be supported by the reaction of NO₃ with *para*-cresol, showing formation of 4-methyl-2-nitrophenol with a yield of (74±16)%.³⁰ However, it would disagree with the results concerning the reactions of NO₃ with the other cresol isomers where, as indicated above, a considerable fraction of the products is still unidentified.

The present work reports on product studies of the reactions between NO₃ and *ortho*-, *meta*- and *para*-cresol, performed in a medium-sized laboratory chamber (QUAREC) in Wuppertal, Germany and a in large-volume chamber (EUPHORE) in Valencia, Spain. The main target was to improve the product balance for the reactions of NO₃ with cresols, thereby elucidating the reaction mechanisms and enabling a better representation of the chemistry of these important aromatic compounds in atmospheric models.

EXPERIMENTAL

The experiments were carried out in the QUAREC reactor at the University of Wuppertal and in the European photoreactor EUPHORE, Valencia, Spain. The latter is a large-volume outdoor smog chamber, operated under conditions approximating as closely as reasonably possible those in the real atmosphere. The origin and purity of the chemicals and gases used in the investigations are given in Supplementary Information (SI), Table SI-1.

Quartz glass reactor (1080 L), Wuppertal (QUAREC)

A detailed description of the QUAREC reactor can be found in the literature,⁵¹ thus only a brief description is given here. The reactor consists of two tubes connected by a central flange, with a combined total length of 6.2 m and 0.47 m inner diameter. The reactor is closed at both ends by aluminum flanges bearing various inlet ports, and can be evacuated to <10⁻³ mbar by a turbo-molecular pump system. To ensure homogeneous mixing of the reactants, three fans with Teflon blades are mounted inside the reactor.

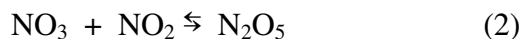
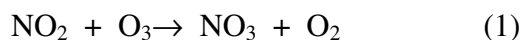
The chamber is equipped with a White type multiple-reflection mirror system, with a base length of (5.91±0.01) m, for sensitive *in situ* long path absorption monitoring of reactants and products in the infrared spectral range of 4000-600 cm⁻¹. The White system was operated at 82 traverses, giving a total optical path length of (484.7±0.8) m. IR spectra were recorded with a resolution of 1 cm⁻¹ using a Bruker IFS 88 FT-IR spectrometer, equipped with a mercury-cadmium-telluride (MCT) detector cooled by liquid nitrogen.

EUPHORE Photoreactor, CEAM, Valencia, Spain

The European photoreactor (EUPHORE), a large-scale outdoor smog-chamber facility, is located at the Centro de Estudios Ambientales del Mediterraneo (CEAM) in Valencia. A detailed description of EUPHORE can be found elsewhere.^{52,53} It consists of two half-spherical FEP (fluorine ethene propene) foil chambers mounted on aluminum floor panels, each with a volume of about 200 m³. The foil is highly transparent even to short-wavelength sunlight, with transmission ranging from 85% between 500 - 320 nm to > 75% at 290 nm. To maintain realistic atmospheric temperature conditions during experiments, the aluminum floor panels are fitted with an active cooling system that keeps temperature constant even during long irradiation periods in summertime. When not in use, or for dark chemistry experiments such as those presented in this study, the chambers are protected by hydraulically operated steel housings. A White mirror system, located inside the chamber and operated at an optical path length of 326.8 m was used for the *in situ* monitoring of reactants and products by FT-IR spectroscopy, with a Nicolet Magna 550 spectrometer equipped with liquid-nitrogen cooled MCT detector having spectral resolution of 1 cm⁻¹.

Experimental procedure

The reaction of O₃ with NO₂ was used for the *in situ* generation of NO₃ in both chambers.



QUAREC reactor. Liquid and gaseous reactants were added with calibrated gas-tight syringes. They were injected into a flow of bath gas entering the chamber *via* inlet ports, located on one of the reactor end flanges. Solid compounds were transferred to the partially evacuated reaction chamber using a specially constructed inlet system, in which weighed amounts of the compounds contained in a glass tube were gently heated in a flow of nitrogen. To avoid condensation of the semi-volatile compounds on the inlet lines, these were also heated.

Between the experiments, the chamber was evacuated and flushed several times using synthetic air. Blank experiments after pumping showed that there was no off-gassing of residual reactants or products from the chamber walls. Reaction mixtures consisting of a cresol isomer and NO₂ in 1000 mbar of synthetic air were introduced into the chamber. FT-IR spectra were collected using 64 co-added interferograms, giving a time resolution of around 1 min. After recording 5-6 spectra to measure the wall loss of cresols, O₃ produced by a commercial generator (corona discharge in O₂) was added for 1 min directly into the chamber, through a Teflon line. Spectra were then recorded continuously for 30-40 min. Wall loss rates of cresols were fairly low, in the range of (4.4-5.9)×10⁻⁵ s⁻¹.

The concentrations of reactants and products were determined by computer-aided subtraction using calibrated reference spectra, generated using a method previously described.⁵⁴ The infrared wavenumbers used for monitoring and the values of the FT-IR absolute and/or integral cross sections for quantification are given in SI.

EUPHORE chamber. Five experiments were performed in the EUPHORE chamber with the protective housing closed, *i.e.* in the absence of sunlight: *ortho*-cresol (2 experiments), *meta*-cresol (1 experiment) and *para*-cresol (2 experiments). They were carried out in chamber A, at atmospheric pressure and at (296±2) K in purified air.

Before each experiment, the chamber was cleaned by flushing with purified air overnight for approximately 12-15 h. In a typical experiment the cresol isomer was added to the chamber using a spray inlet system. Prior to injection, a weighed cresol amount was dissolved in 5 mL CH₃CN. NO₂ was then introduced by injection from a syringe into a glass tube (impinger), flushed with 4 L min⁻¹ of purified air and connected to the chamber by a Teflon line. Ozone, produced by photolysis of O₂ at 184.9 nm using a Pen-ray low-pressure mercury lamp, was added directly to the chamber through a Teflon line to initiate the reaction. Each experiment on a cresol-NO₂-O₃ mixture was carried out over a period of approximately 5-7 h, using *in situ* FT-IR spectroscopy to monitor the time evolution of reactants and products. Infrared spectra were derived from 210 co-added interferograms, giving a time resolution of 3.5 min. Measurements of temperature, pressure, NO_x (ECO-Physics analyzer, CLD 770 AL ppt/ PLC 760) and ozone (Monitor Labs. UV-analyzer) were also made. All information was collected by a data acquisition system linked with the chamber instrumentation.

To compensate for losses due to leaks and air drawn by external analytical instrumentation, the chamber was pressurized continuously during the experiments. This dilution was monitored by FT-IR using SF₆ as inert tracer gas: the dilution loss was typically 3% h⁻¹. Apart from reaction with NO₃ radicals and dilution, wall deposition is an additional potentially important loss process for cresols and their oxidation products in EUPHORE. The combined dilution and surface deposition rates of cresols were determined by observing the decay of their IR absorption features prior to addition of O₃ and NO₂. The combined surface deposition and dilution rates of products were determined by observing the decay of IR absorption features after the experiments, by adding a large concentration of NO to the system to completely remove O₃ and NO₃ and thus terminate any ongoing oxidation.

The initial and final concentrations of cresols, O₃ and NO₂ in the experiments performed in both chambers are summarized in Tables SI-2 and SI-3.

RESULTS

QUAREC results

Figure 1, trace A, shows a typical FT-IR product spectrum in the fingerprint wavenumber range 1800-700 cm^{-1} , obtained from the NO_3 -initiated oxidation of *ortho*-cresol, after subtraction of the spectral features belonging to water, reactants (*ortho*-cresol, O_3 , NO_2) and HNO_3 . Traces B and C show reference spectra of methyl-1,4-benzoquinone and 6-methyl-2-nitrophenol, respectively. The latter was not commercially available and was synthesized using the method of Winzor.⁵⁵ Similar product spectra are given in SI for the reactions of NO_3 with *meta*- and *para*-cresol (Figures SI-1 and SI-2, respectively). Analysis of the FT-IR spectra showed formation of methyl-nitrophenols and HNO_3 for all of the cresol isomers. Formation of methyl-1,4-benzoquinone was only observed in the experiments with *ortho*- and *meta*-cresol. Searches were made for the formation of other potential nitro-cresol isomers, *i.e.* 2-methyl-3-nitrophenol and 2-methyl-5-nitrophenol using available reference spectra, but no evidence for their formation could be found. Therefore, if formed, their yields were relatively minor.

2-Methyl-4-nitrophenol could also possibly be formed in the reaction of NO_3 with *ortho*-cresol but, unfortunately, no reference spectrum is available. However, the residual product spectrum obtained after subtraction of methyl-1,4-benzoquinone and 6-methyl-2-nitrophenol from spectrum (A) in Figure 1 shows several intense absorptions around 1601, 1548, 1358, 1266, 1219, 1166, 1095, 817 and 749 cm^{-1} . They are characteristic of nitrophenol compounds and, since all of the other possible nitro-cresols have either been positively identified or eliminated through comparison with reference spectra, it is quite probable that 2-methyl-4-nitrophenol is being formed in the *ortho*-cresol/ NO_3 reaction system. Formation of dinitrocresols is also a possibility but, due to their very low volatility, they are not expected to remain in the gas phase. Concentration-time profiles of the reactants and identified products in a typical NO_3 + *ortho*-cresol experiment in the QUAREC reactor are shown in Figure 2.

In the case of NO_3 + *meta*-cresol, analysis of the FT-IR product spectra obtained in QUAREC showed the formation of 5-methyl-2-nitrophenol, 3-methyl-2-nitrophenol, 3-methyl-4-nitrophenol, methyl-1,4-benzoquinone and HNO_3 (see SI, Figure SI-1). The residual product spectrum obtained after subtraction of the spectral features belonging to reactants and identified products indicates that some minor products have probably not been identified.

For NO_3 + *para*-cresol, analysis of the FT-IR product spectra clearly showed the formation of 4-methyl-2-nitrophenol and HNO_3 (Figure SI-2). The residual product spectrum exhibited several intense absorptions around 1573, 1395, 1336 and 874 cm^{-1} , which are characteristic of nitrophenol compounds (see for instance Figure SI-1, traces B, C and D and Figure SI-3, traces B and C). 4-Methyl-3-nitrophenol is a possible product of the reaction of NO_3 with *para*-cresol, but this nitrocresol isomer is unfortunately not commercially available.

Concentration-time profiles for reactants and products obtained from reactions of NO_3 with *meta*- and *para*-cresol are given in SI (Figures SI-4 and SI-5, respectively).

EUPHORE results

The main products observed with NO_3 + *meta*- and *para*-cresol in EUPHORE match closely those identified in QUAREC experiments. For NO_3 + *ortho*-cresol in EUPHORE, neither 2-methyl-4-nitrophenol nor 6-methyl-2-nitrophenol could be found. There was evidence of formation of methyl-1,4-benzoquinone, but quantification was not possible. Product spectra gave no indication of the formation of other compounds: after subtraction of residual *ortho*-cresol, NO_2 , O_3 , HNO_3 etc. from FT-IR product spectra, only very weak absorptions remained.

The QUAREC experiments showed that the yields of methyl-nitrophenol isomers and methyl-1,4-benzoquinone from NO_3 + *ortho*-cresol are relatively low. Therefore, failure to detect such compounds in EUPHORE is not surprising and actually helps to confirm QUAREC findings. With the optical path length of 326.8 m used in EUPHORE chamber A, the minimum reliably detectable concentrations of 6-methyl-2-nitrophenol and methyl-1,4-benzoquinone are about 40 and 20 ppb, respectively. Based on these detection limits, on the yields measured in QUAREC and on the amount of *ortho*-cresol consumed in EUPHORE experiments (~200 ppb), one would *not* expect detectable amounts of methyl-nitrophenols and methyl-1,4-benzoquinone to be formed in EUPHORE. This fact was unfortunately not known at the time of EUPHORE experiments.

The *meta*-cresol- NO_2 - O_3 reaction system showed the formation of 3-methyl-2-nitrophenol, 5-methyl-2-nitrophenol, 3-methyl-4-nitrophenol and HNO_3 (also see Figure SI-6), in good agreement with QUAREC results. The residual product spectrum is practically absorption free, which excludes significant occurrence of methyl-1,4-benzoquinone in EUPHORE. Formation of this compound was observed in low yield in QUAREC but, under EUPHORE conditions, the amount that could be formed is below detection limit. Concentration-time profiles of reactants and products identified in a typical *meta*-cresol- NO_2 - O_3 experiment in EUPHORE are shown in Figure 3.

The *para*-cresol-NO₂-O₃ experiments at EUPHORE (see SI, Figure SI-7) showed the formation 4-methyl-2-nitrophenol and HNO₃, in good agreement with QUAREC results. The residual product spectrum showed a relatively intense absorption centered around 874 cm⁻¹, which was also observed in QUAREC. Concentration-time profiles of reactants and products identified in the NO₃-initiated oxidation of *para*-cresol for a typical EUPHORE experiment are shown in SI, Figure SI-8.

DISCUSSION

Product yields in QUAREC

The loss processes for nitrocresol and benzoquinone compounds in QUAREC (wall deposition and further reaction with NO₃) need to be considered to determine reaction yields. Rate coefficients between NO₃ and nitrocresols or methyl-1,4-benzoquinone are not available in the literature. Using a structure-reactivity relationship based on ionization potential, it has been estimated that NO₃ reacts slowly with nitrocresols with rate constants around 1×10⁻¹⁴ cm³ molecule⁻¹ s⁻¹.⁵⁶ With average NO₃ concentration around (6-10)×10⁶ molecule cm⁻³, one would obtain a nitrocresol loss of ~2% under QUAREC conditions. Based on rate coefficients between NO₃ and other unsaturated compounds,^{33,38} it is reasonable to assume that reaction of NO₃ with methyl-1,4-benzoquinone will be even slower than with the nitrocresols. Available evidence suggests that secondary reactions of nitrocresols and methyl-1,4-benzoquinone with NO₃ are negligible, and they were neglected in the determination of formation yields. Corrections were only made for loss *via* deposition to the reactor surface.

The wall-loss corrected concentrations of nitrocresols, methyl-1,4-benzoquinone and HNO₃ formed from the reaction of NO₃ with cresols are reported in Figure SI-9 (*ortho*-cresol), Figure SI-10 (*meta*-cresol) and Figure SI-11 (*para*-cresol). They show reasonable linearity with time and near-zero intercepts. The yields, determined from the four individual experiments on each of the three cresol isomers are given in Table SI-4. The final formation yields given in Table 1 are averages obtained from the individual measurements listed in Table SI-4.

Product yields in EUPHORE

The product formation yields in EUPHORE experiments were obtained in a similar way as above. Also here corrections were only made for the combined wall deposition and dilution losses. The loss-corrected concentrations of nitro-cresols and HNO₃ in EUPHORE are shown

in Figure SI-12 (*meta*-cresol) and Figure SI-13 (*para*-cresol). The yields determined in individual experiments are given in Table SI-5. The final average yields are reported in Table 1.

Comparison of results

Table 1 shows that where the nitrocresols could be observed in both reactors, the agreement between measured yields is very good. The only exception is for *ortho*-cresol, because nitrocresol and methyl-1,4-benzoquinone were not observed in EUPHORE but the expected amounts formed were below detection limits. Measured HNO₃ yields were about 20% higher in EUPHORE for *ortho*-cresol and *meta*-cresol, while there was good agreement for *para*-cresol. The HNO₃ yields from cresols + NO₃ have not been reported in previous studies.^{30,35,45}

Table 1 also includes product yields from the literature.^{30,45} In reference 30, gas samples were analyzed by gas chromatography with flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC-MS). The reported yield of 6-methyl-2-nitrophenol from *ortho*-cresol³⁰ is in good agreement with that determined in this study. In reference 45, samples were collected in impingers containing aqueous KOH and analyzed by ion chromatography with ultraviolet detection (IC-UV). It is reported a range of 2.4-23% for the combined yields of 6-methyl-2-nitrophenol and 2-methyl-4-nitrophenol,⁴⁵ which encompasses the yields obtained by GC³⁰ and those of this work (both around 11-13%). However, 2-methyl-4-nitrophenol has not been observed by GC.³⁰ The combined product yield of the two isomers in the study by IC-UV decreased with increasing reaction time, indicating a significant loss process for methyl-nitrophenols in the reaction chamber. Detection of 6-methyl-2-nitrophenol, 2-methyl-4-nitrophenol and 2-methyl-4,6-dinitrophenol in the aerosol phase was also reported.⁴⁵ The product spectrum in our QUAREC experiment shows a residual absorption that could be tentatively assigned to 2-methyl-4-nitrophenol, for which a yield of approximately 10% can be estimated based on our calibrated IR spectrum of 6-methyl-2-nitrophenol.

In the *meta*-cresol/NO₂/O₃ reaction system, formation of 3-methyl-2-nitrophenol, 5-methyl-2-nitrophenol and 3-methyl-4-nitrophenol was observed. The yields for 3-methyl-2-nitrophenol and 5-methyl-2-nitrophenol agree reasonably well with previous ones.³⁰ However, we also observed formation of 3-methyl-4-nitrophenol that was apparently not observed before.

In the case of *para*-cresol, 4-methyl-2-nitrophenol was observed as the main product in both QUAREC and EUPHORE, with a yield just over 40%. Formation of 4-methyl-2-nitrophenol from NO₃ + *para*-cresol has been observed previously, but the reported yield is

nearly double than ours.³⁰ Potential reasons for the discrepancy may include errors in calibration procedures somewhere, or perhaps some dependence of the yield of 4-methyl-2-nitrophenol on experimental conditions. In a liquid-phase study of the NO₃-mediated nitration of *para*-cresol, 4-methyl-2-nitrophenol was a major reaction product with 38-83% yield.⁵⁷

We observed formation of methyl-1,4-benzoquinone (yield ~4%) from both *ortho*- and *meta*-cresol, while this compound cannot be formed from *para*-cresol. This is the first report about this compound in cresol/NO₂/O₃/air reaction systems in the gas phase. In this study, the observed products account for approximately 16% (~26% if the yield estimate for 6-methyl-4-nitrophenol is included), 72% and 44% of reacted carbon in the NO₃-initiated oxidation of *ortho*-, *meta*- and *para*-cresol, respectively. As noted before not all oxidation products have been identified, and a large fraction of the missing carbon may consist of unidentified nitrogen-containing compounds and ring-fragmentation products. Interestingly, the loss of NO₂ in the experiments was much larger than that of the cresol (see Tables SI-2 and SI-3).

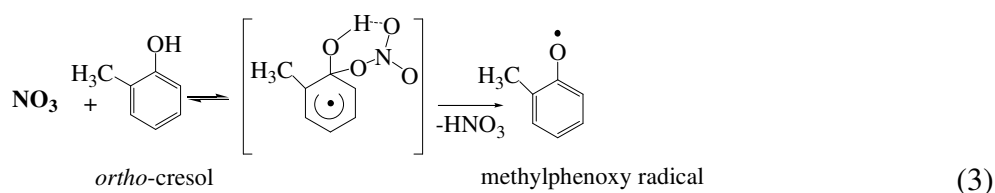
Formation of HNO₃

We found HNO₃ as an important product of the reaction of NO₃ with cresols. The formation yield of HNO₃ was calculated using literature cross sections.⁵⁸ Nitric acid can be formed in the gas phase through several reactions: (i) NO₃ + cresols; (ii) N₂O₅ + water vapor, and (iii) heterogeneous reactions of NO₂ and N₂O₅ on the reactor surface. The fast reaction of NO₃ with cresols and the experimental procedure used to generate NO₃ ensure that formation of N₂O₅ is minimized. Moreover, no spectral features characteristic of N₂O₅ were observed in the FTIR spectra in either reactor, suggesting that its concentration was very low. Water vapor concentration in QUAREC was extremely low because synthetic air was employed as bath gas, ensuring negligible HNO₃ formation from N₂O₅ + H₂O. In blank experiments performed in EUPHORE with N₂O₅/air mixtures, dark formation of HNO₃ was found to be negligible. Finally, HNO₃ is formed at a rate similar to that of cresol decay, which is much faster than a possible diffusion-controlled transport of NO_x to the reactor surface followed by reaction to form HNO₃. Hence, in the present work the formation of HNO₃ can be largely attributed to reaction between cresols and NO₃. In EUPHORE the HNO₃ yield was ~90% with all the three cresol isomers. In QUAREC the HNO₃ yield with *para*-cresol agrees well with the EUPHORE one, but the yields with both *ortho*- and *meta*-cresol were ~20% lower than in EUPHORE. The reason for this discrepancy is not clear, but the wall loss of HNO₃ is probably being underestimated in the smaller QUAREC reactor, since it may not be constant as it was assumed in the applied corrections.

The high yields of HNO₃ observed in this study suggest that the NO₃ + cresol reaction is largely proceeding via an overall mechanism involving H-atom abstraction.

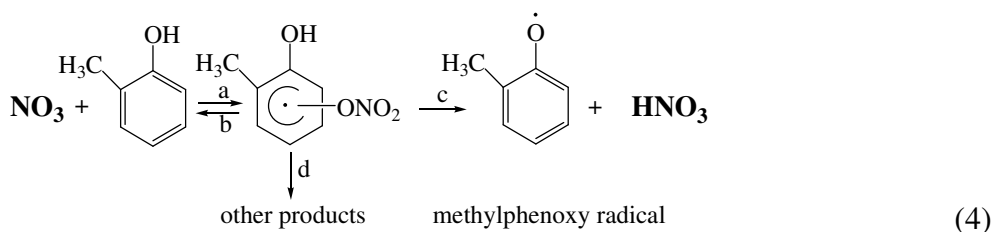
Proposed formation mechanism of nitrocresols

It has been postulated that the gas-phase reactions of NO₃ with phenolic compounds proceed via an overall H-atom abstraction mechanism through the intermediacy of a six-membered transition state, as shown below for *o*-cresol (reaction 3).³⁰ This is in agreement with the concentration-time behavior of HNO₃ formation and the high HNO₃ yields observed in this study.



The methylphenoxy radicals thus formed have been postulated to react further with NO₂ to form nitrocresols.³⁰ Actually, generation of nitrocresol isomers as observed in the present study can be reasonably explained only by further reaction of methylphenoxy radicals with NO₂. The reaction mechanism is supported by a consideration of the electronic structure of phenoxy radicals. This structure has been calculated using the Amsterdam Density Functional (ADF) code, showing that the Mulliken spin densities are higher at the phenoxy oxygen and at *ortho*- and *para*-carbon positions.⁵⁹ This would favor the formation of *ortho*- and *para*-nitrocresols *via* addition of NO₂ and would explain the experimental results of this study. As an example, the possible electron resonance structures for the methylphenoxy radical formed from NO₃ + *meta*-cresol and the subsequent reactions with NO₂ to form 5-methyl-2-nitrophenol, 3-methyl-2-nitrophenol and 3-methyl-4-nitrophenol are reported in SI, Figure SI-14.

However, such a simple reaction mechanism would be expected to lead to a unit, or near-unit, yield of nitrophenols.³⁰ As can be seen from Table 1, the combined yields of the identified nitrocresol compounds are well below unity. This would suggest that the mechanisms of the NO₃ radical reactions with cresols are more complex than previously thought and that other reaction pathways may occur. A general mechanism has been proposed to explain the oxidation reactions of phenols by NO₃, which takes into account the occurrence of other possible reaction pathways (see reaction (4) of NO₃ with *ortho*-cresol).³⁰



The proposed mechanism envisages additional loss pathways for the NO_3 -phenol intermediate adducts. However, the product data from the present work and in particular the high yield of HNO_3 suggest that $k_c \gg k_d$. Therefore, alternative reaction pathways for the phenoxy radicals are a more likely reason for the less-than-unity yields of nitrocresols. The formation of methyl-1,4-benzoquinone from *ortho*- and *meta*-cresol makes additional evidence that reaction pathways different from nitrocresol formation are operational for the methylphenoxy radicals.

Possible formation mechanism for methyl-1,4-benzoquinone

The reaction between phenoxy radical and O_2 is unimportant: an upper-limit rate coefficient of $5.0 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was estimated at 296 K.⁵⁹ Unpublished results from our group about the reaction of NO_3 with phenol did not show formation of 1,4-benzoquinone,⁴⁶ which was not unexpected based on previous findings.⁵⁹ The formation of methyl-1,4-benzoquinone from *ortho*- and *meta*-cresol + NO_3 suggests that the methyl group, with its positive inductive effect may be influencing the reaction pathways of methylphenoxy radicals compared to the phenoxy one. In particular, it may affect reactivity with O_2 .

A few test experiments on the reaction of Cl atoms with *ortho*-cresol in the presence and absence of NO_x have been performed in QUAREC. With *ortho*-cresol/ Cl_2 /air mixtures, formation of methyl-1,4-benzoquinone was observed with a yield similar to that obtained from *ortho*-cresol/ NO_2 / O_3 /air. Moreover, the formation of methyl-1,4-benzoquinone in the chlorine experiments was strongly dependent on the presence of NO_2 : at high NO_2 concentration, the formation of methyl-1,4-benzoquinone was completely suppressed. This suggests a possible competition between O_2 and NO_2 for reaction with intermediate methylphenoxy radicals.

A simplified, tentative mechanism for the formation of methyl-1,4-benzoquinone is shown in Scheme 1 for NO_3 + *ortho*-cresol (a similar scheme would apply to *meta*-cresol). The mechanism involves addition of O_2 to the resonance form of methylphenoxy radical containing a carbonyl group, to produce a ring-retaining peroxy radical. Depending on the reaction system the peroxy radicals can undergo self-reaction, reaction with other peroxy

radicals or reaction with NO to produce mainly cyclic alkoxy radicals. The latter could further react with O₂ to give methyl-1,4-benzoquinone and HO₂. The presence of high concentrations of NO₂ could result in the intermediate formation of a labile cyclic peroxyxynitrate. Apart from the radical producing channel in peroxy-peroxy radical reactions, a molecular reaction channel could yield a cyclic alcohol and a corresponding carbonyl compound. Thus, apart from methyl-1,4-benzoquinone that was detected in this study, other products would include a cyclic alcohol and a nitrate. Of course, the methylphenoxy radical could also react with NO₂ to give nitrocresols.

Atmospheric implications

This work shows for the first time that the reaction of NO₃ with cresols results in near-unity yield of HNO₃, and it has confirmed that nitrocresols are the most important gas-phase co-products. The atmospheric concentration values of the latter compounds would depend on the formation-transformation budget. Processes that can potentially play a role in determining the atmospheric lifetime of nitrocresols include reaction with OH, NO₃ and O₃, wet and dry deposition and photolysis. Reactions with O₃ are unlikely to be important, as inferred from the behavior of similar compounds: nitrophenols react very slowly with O₃, cresols have O₃ rate coefficients in the range of $2\text{-}5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and in the case of nitrobenzene one has $< 7 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹

2-Nitrophenol reacts slowly with OH ($9.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).³⁴ However, reactions of OH with methylated *ortho*-nitrophenols are at least one order of magnitude faster compared to 2-nitrophenol. This is probably due to electronic resonance effects generated by the position of the CH₃- group on the aromatic ring relative to the OH- group.⁶⁰

The rate coefficients for the reactions of NO₃ with nitrocresols are much lower than those of the corresponding cresols,¹ at least of a factor of 5,³⁰ and they would have minor atmospheric importance.⁴⁵ Estimated rate coefficients for NO₃ + nitrocresols are $\sim 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁵⁶

Reported Henry's Law coefficients for methylated nitrophenols range from 70 to 10^4 M atm^{-1} .⁶¹ The method of Brimblecombe and Dawson⁶² has been used successfully to estimate the wet deposition rate of oxidation products of hydroxyl-nitrate isoprene⁶³ and of first-generation products formed from NO₃ + isoprene.⁶⁴ By using the same assumptions for mid-latitude meteorology as previously reported^{62,63} and with the above-given range of Henry's law coefficients, one obtains nitrocresol lifetimes of 2 days or more with respect to

wet deposition. However, at higher precipitation rates than assumed the wet removal rate could be much higher.

Nitrophenols and nitrocresols absorb in the tropospheric actinic region and can undergo photolysis. It has even been calculated that nitrocresols can potentially lower the actinic flux and slow down primary photochemical processes. However, these effects have been estimated for a 1 ppbv total concentration of nitrophenols and nitrocresols.⁶⁵ This is considerably higher than the levels reported by gas-phase measurements, which suggest an aggregated level of ~0.03 ppbv.^{66,67} By measuring the photolysis frequencies of some nitrocresols in the gas phase, it has been concluded that photolysis is probably the dominant gas-phase loss process for these compounds.⁶⁰ Interestingly, while nitroaromatic compounds could (perhaps unimportantly) decrease the oxidizing capacity of the atmosphere by reducing the actinic flux, nitrophenols and nitrocresols with OH- and NO₂- groups in *ortho* to one another are important photochemical sources of nitrous acid (HONO) upon photolysis.⁶⁸ The photolysis of HONO is in turn an important source of OH, which plays a pivotal role in determining the oxidizing capacity of the atmosphere.⁶⁹⁻⁷¹

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References

- (1) Calvert, J. G.; Atkinson, R.; Becker, K. H.; Kamens, R. M.; Seinfeld, J. H.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*. Oxford University Press: Oxford, U.K., 2002.
- (2) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Traverse, M. Impact of California reformulated gasoline on motor vehicle emissions. 1. Mass emission rates. *Environ. Sci. Technol.* **1999**, *33*, 318-328.
- (3) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Hesson, J. M. Impact of California reformulated gasoline on motor vehicle emissions. 2. Volatile organic compound speciation and reactivity. *Environ. Sci. Technol.* **1999**, *33*, 329-336.
- (4) Derwent, R. G.; Jenkin, M. E.; Saunders, S. M.; Pilling, M. J. Photochemical ozone creation potentials for organic compounds in northwest Europe calculated with a Master Chemical Mechanism. *Atmos. Environ.* **1998**, *32*, 2429-2441.
- (5) Derwent, R.G.; Jenkin, M.E.; Saunders, S.M.; Pilling, M.J.; Simmonds, P.G.; Passant, N.R.; Dollard, G.J.; Dumitrean, P.; Kent, A. Photochemical ozone formation in North West Europe and its control. *Atmos. Environ.* **2003**, *37*, 1983–1991.
- (6) Derwent, R.G.; Jenkin, M. E.; Passant, N. R.; Pilling, M. J. Photochemical ozone creation potentials (POCPs) for different emission sources of organic compounds under European conditions estimated with a Master Chemical Mechanism. *Atmos. Environ.* **2007**, *41*, 2570–2579.
- (7) Kroll, J. H.; Seinfeld, J. H. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos. Environ.* **2008**, *42*, 3593–3624.
- (8) Atkinson, R.; Arey, J. Atmospheric degradation of volatile organic compounds. *Chem. Rev.* **2003**, *103*, 4605-4638.
- (9) Bjergbakke, E.; Sillesen, A.; Pagsberg, P. UV Spectrum and kinetics of hydroxycyclohexadienyl radicals. *J. Phys. Chem.* **1996**, *100*, 5729-5736.
- (10) Berndt, T.; Böge, O.; Herrmann, H. On the formation of benzene oxide/oxepin in the gas-phase reaction of OH radicals with benzene. *Chem. Phys. Lett.* **1999**, *314*, 435-442.
- (11) Berndt, T.; Böge, O. Gas-phase reaction of OH radicals with benzene: products and mechanism. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4946-4956.
- (12) Berndt T.; Böge, O. Formation of phenol and carbonyls from the atmospheric reaction of OH radicals and benzene. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1205-1214.

- (13) Klotz, B.; Volkamer, R.; Hurley, M. D.; Sulbaek Andersen, M. P.; Nielsen, O. J.; Barnes, I.; Imamura, T.; Wirtz, K.; Becker, K. H.; Platt, U.; Wallington, T. J.; Washida, N. OH-initiated oxidation of benzene. Part II. Influence of elevated NO_x concentrations. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4399-4411.
- (14) Volkamer, R.; Klotz, B.; Barnes, I.; Imamura, T.; Wirtz, K.; Washida, N.; Becker, K. H.; Platt, U. OH-initiated oxidation of benzene. Part I. Phenol formation under atmospheric conditions. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1598-1610.
- (15) Atkinson, R.; Aschmann, S. M.; Arey, J.; Carter, W. P. L. Formation of ring-retaining products from the OH radical-initiated reactions of benzene and toluene. *Int. J. Chem. Kin.* **1989**, *21*, 801-827.
- (16) Klotz, B.; Sørensen, S.; Barnes, I.; Becker, K. H.; Etkorn, T.; Volkamer, R.; Platt, U.; Wirtz, K.; Montserrat Martín-Reviejo, M. Atmospheric oxidation of toluene in a large-volume outdoor photoreactor: In situ determination of ring-retaining product yields. *J. Phys. Chem. A* **1998**, *102*(50), 10289–10299.
- (17) Smith, D. F.; McIver, C. D.; Kleindienst, T. E. Primary product distribution from the reaction of hydroxyl radicals with toluene at ppb NO_x mixing ratios. *J. Atmos. Chem.* **1998**, *30*, 209-228.
- (18) Noda, J.; Volkamer, R.; Molina, M. J. Dealkylation of alkylbenzenes: A significant pathway in the toluene, o-, m-, p-xylene + OH reaction. *J. Phys. Chem. A* **2009**, *113*, 9658-9666.
- (19) Aschmann, S. M.; Arey, J.; Atkinson, R. Extent of H-atom abstraction from OH + p-cymene and upper limits to the formation of cresols from OH + m-xylene and OH + p-cymene. *Atmos. Environ.* **2010**, *44*, 3970-3975.
- (20) Bohn, B.; Zetzsch, C. Kinetics and mechanism of the reaction of OH with the trimethylbenzenes – experimental evidence for the formation of adduct isomers. *Phys. Chem. Chem. Phys.* **2012**, *14*, 13933-13948.
- (21) Loison, J-C.; Rayez, M-T.; Rayez, J-C.; Gratien, A.; Morajkar, P.; Fittschen, C.; Villenave, E. Gas-phase reaction of hydroxyl radical with hexamethylbenzene. *J. Phys. Chem. A* **2012**, *116*, 12189-12197.
- (22) Mulawa, P.A. Measurement of phenols in automobile exhaust. *Anal. Lett. Pt A – Chem. Analys.* **1981**, *14*, 671-687.
- (23) Tremp, J.; Mattrel, P.; Fingler, S.; Giger, W. Phenols and nitrophenols as tropospheric pollutants - emissions from automobile exhausts and phase-transfer in the atmosphere. *Water Air Soil Poll.* **1993**, *68*, 113-123.

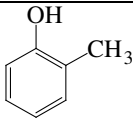
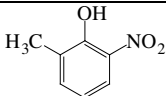
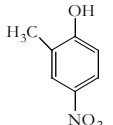
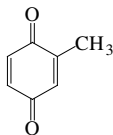
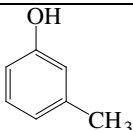
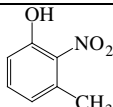
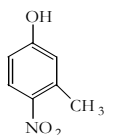
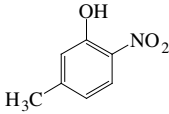
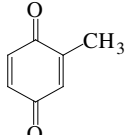
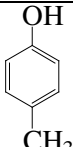
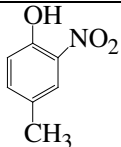
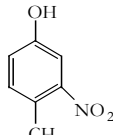
- (24) Misawa, K.; Tanaka, K.; Yamada, H.; Goto, Y.; Matsumoto, J.; Yamato, Y.; Ishiuchi, S.; Fujii, M.; Endo, K.; Hayashi, S. Time-resolved measurements of low concentration aromatic hydrocarbons in diesel exhaust using a resonance enhanced multi-photon ionization method. *Int. J. Engine Res.* **2009**, *10*, 409-417.
- (25) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 3. C1-C29 organic compounds from fireplace combustion of wood. *Environ. Sci. Technol.* **2001**, *35*, 1716-1728.
- (26) Mazzoleni, L. R.; Zielinska, B.; Moosmüller, H. Emissions of levoglucosan, methoxy phenols, and organic acids from prescribed burns, laboratory combustion of wildland fuels, and residential wood combustion. *Environ. Sci. Technol.* **2007**, *41*, 2115-2122.
- (27) Rogozen, M. B.; Rich, H. E.; Gutman M. A.; Grosjean, D. Evaluation of potential toxic air contaminants, Phase 1. Final report Dec. 23, Contract A4-131-132, State of California Air Resources Board, Sacramento, CA. 1987.
- (28) Levshina, S. Petroleum products and phenols in snow cover in Khabarovsk, Southern Russian Far East. *Water Air Soil Poll.* **2012**, *223*, 3553-3563.
- (29) Atkinson, R.; Carter, W. P. L. Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. *Chem. Rev.* **1984**, *84*, 437-470.
- (30) Atkinson, R.; Aschmann, S. M.; Arey, J. Reactions of OH and NO₃ radicals with phenol, cresols, and 2-nitrophenol at 296±2 K. *Environ. Sci. Technol.* **1992**, *26*, 1397-1403.
- (31) Atkinson, R.; Baulch, D. L. ; Cox, R. A.; Hampson, Jr.; R. F., Kerr J. A.; Troe, J. Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement IV. *J. Phys. Chem. Ref. Data* **1992**, *21*, 1125-1568.
- (32) Coeur-Tourneur, C.; Henry, F.; Janquin, M-A.; Brutier, L. Gas-phase reaction of hydroxyl radicals with m-, o- and p-cresol. *Int. J. Chem. Kin.* **2006**, *38*, 553-562.
- (33) Atkinson, R. Kinetics and mechanisms of the gas-phase reactions of the NO₃ radical with organic compounds. *J. Phys. Chem. Ref. Data* **1991**, *20*, 459-507.
- (34) Atkinson, R., Gas-phase tropospheric chemistry of organic compounds. *J. Phys. Chem. Ref. Data* **1994**, *Monograph 2*, 1-216.
- (35) Bolzacchini, E.; Bruschi, M.; Hjorth, J.; Meinardi, S.; Orlandi, M.; Rindone, B.; Rosenbohm, E. *Environ. Sci. Technol.* **2001**, *35*, 1791-1797.
- (36) Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; Le Bras, G.; Moortgat, G. K.; Perner, D.; Poulet, G.; Restelli, G.; Sidebottom, H. The nitrate radical: Physics, chemistry, and the atmosphere. *Atmos. Environ.* **1991**, *25A*, 1-203.

- (37) Platt, U.; Heintz, F. Nitrate radicals in tropospheric chemistry. *Isr. J. Chem.* **1994**, *34*, 289-300.
- (38) Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of the Alkenes*; Oxford University Press: New York, 2000.
- (39) Atkinson, R. Atmospheric chemistry of VOCs and NO_x. *Atmos. Environ.* **2000**, *34*, 2063-2101.
- (40) Brown, S. S.; Osthoff, H. D.; Harald Stark, H.; Dubé, W. P.; Ryerson, T. B.; Warneke, C.; de Gouw, J. A.; Wollny, A. G.; Parrish, D. D.; Fehsenfeld, F. C.; Ravishankara, A. R. Aircraft observations of daytime NO₃ and N₂O₅ and their implications for tropospheric chemistry. *J. Photochem. Photobiol. A: Chem.* **2005**, *176*, 270–278.
- (41) Brown, S. S.; deGouw, J. A.; Warneke, C.; Ryerson, T. B.; Dubé, W. P.; Atlas, E.; Weber, R. J.; Peltier, R. E.; Neuman, J. A.; Roberts, J. M.; Swanson, A.; Flocke, F.; McKeen, S. A.; Brioude, J.; Sommariva, R.; Trainer, M.; Fehsenfeld, F. C.; Ravishankara, A. R. Nocturnal isoprene oxidation over the Northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol. *Atmos. Chem. Phys.* **2009**, *9*, 3027–3042.
- (42) Geyer, A.; Alicke, B.; Ackermann, R.; Martinez, M.; Harder, H.; Brune, W.; di Carlo, P.; Williams, E.; Jobson, T.; Hall, S.; Shetter, R.; Stutz, J. Direct observations of daytime NO₃: Implications for urban boundary layer chemistry. *J. Geophys. Res.* **2003**, *108*, 4368.
- (43) Kurtenbach, R.; Ackermann, R.; Becker, K. H.; Geyer, A.; Gomes, J. A. G.; Lörzer, J. C.; Platt, U.; Wiesen, P. Verification of the contribution of vehicular traffic to the total NMVOC emissions in Germany and the importance of the NO₃ chemistry in the city air. *J. Atmos. Chem.* **2002**, *42*, 395–411.
- (44) Olariu, R. I.; Bejan, I.; Barnes, I.; Klotz, B.; Becker, K. H.; Wirtz, K. Rate coefficients for the gas-phase reaction of NO₃ radicals with selected dihydroxybenzenes. *Int. J. Chem. Kin.* **2004**, *36*, 577-583.
- (45) Grosjean, D. Reactions of o-cresol and nitrocresol with NO_x in sunlight and with ozone-nitrogen dioxide mixtures in the dark. *Environ. Sci. Technol.* **1985**, *19*, 968-974.
- (46) Olariu, R. I., Atmospheric oxidation of selected aromatic hydrocarbons. PhD thesis, University of Wuppertal, Germany, 2001.
- (47) Olariu, R. I.; Klotz, B.; Barnes, I.; Becker, K. H.; Mocanu, R. FT-IR study of the ring-retaining products from the reaction of OH radicals with phenol, o-, m-, and p-cresol. *Atmos. Environ.* **2002**, *36*, 3685-3697.

- (48) Bonnefoy, A.; Chiron, S.; Botta, A. Environmental nitration processes enhance the mutagenic potency of aromatic compounds. *Environ. Toxicol.* **2012**, *27*, 321-331.
- (49) Jessen, C. E.; Gross, A.; Kongsted, J.; Jørgensen, S. A theoretical investigation of gas phase NO₃ initiated nitration of p-cresol. *Chem. Phys.* **2011**, *389*, 39-46.
- (50) Jørgensen, S., Gas-phase oxidation of cresol isomers initiated by OH or NO₃ radicals in the presence of NO₂. *Int. J. Chem. Kin.* **2012**, *44*, 165-178.
- (51) Barnes, I.; Becker, K. H.; Mihalopoulos, N. An FT-IR product study of the photo-oxidation of dimethyl disulfide. *J. Atmos. Chem.*, **1994**, *18*, 267-289.
- (52) Becker, K. H. Final Report of the EC-Project "The European Photoreactor EUPHORE". Contract EV5V-CT92-0059, 1995.
- (53) Wängberg, I.; Etzkorn, T.; Barnes, I.; Platt, U.; Becker, K. H. Absolute determination of the temperature behavior of the NO₂ + NO₃ + (M) ⇌ N₂O₅ + (M) equilibrium. *J. Phys. Chem. A* **1997**, *101*, 9694-9698.
- (54) Etzkorn, T.; Klotz, B.; Sørensen, S.; Patroescu, I.; Barnes, I.; Becker, K. H.; Platt, U. Gas-phase absorption cross sections of 24 monocyclic aromatic hydrocarbons in the UV and IR spectral ranges. *Atmos. Environ.* **1999**, *33*, 525-540.
- (55) Winzor, F.L. The colouring matters of drosera whittakeri. Part III. The synthesis of hydroxydroserone. *J. Chem. Soc. London* **1935**, 336-338.
- (56) Grosjean, D. Atmospheric chemistry of toxic contaminants, 1. Reaction rates and atmospheric persistence. *J. Air Waste Manag. Assoc.* **1990**, *40*, 1397-1402.
- (57) Barletta, B.; Bolzacchini, E.; Meinardi, S.; Orlandi, M.; Rindone, B. The NO₃ radical-mediated liquid phase nitration of phenols with nitrogen dioxide. *Environ. Sci. Technol.* **2000**, *34*, 2224-2230.
- (58) Mentel, Th. F.; Bleilebens, D.; Wahner, A. A. Study of night-time nitrogen oxide oxidation in a large reaction chamber - the fate of the NO₂, N₂O₅, HNO₃, and O₃ at different humidities. *Atmos. Environ.* **1996**, *30*, 4007-4020.
- (59) Platz, J.; Nielsen, O. J.; Wallington, T. J.; Ball, J. C.; Hurley, M. D.; Straccia, A. M.; Schneider, W. F.; Sehested, J. Atmospheric chemistry of the phenoxy radical, C₆H₅O·: UV spectrum and kinetics of reactions with NO, NO₂ and O₂. *J. Phys. Chem. A* **1998**, *102*, 7964-7974.
- (60) Bejan, I.; Barnes, I.; Olariu, R.; Zhou, S.; Wiesen, P.; Benter, T. Investigations on the gas-phase photolysis and OH radical kinetics of methyl-2-nitrophenols. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5686-5692.
- (61) <http://www.mpch-mainz.mpg.de/sander/res/henry.html>

- (62) Brimblecombe, P.; Dawson, G. A. Wet removal of highly soluble gases. *J. Atmos. Chem.* **1984**, *2*, 95-107.
- (63) Shepson, P. B.; Mackay, E.; Muthuramu, K.; Henry's law constants and removal processes for several atmospheric beta-hydroxy alkyl nitrates. *Environ. Sci. Technol.* **1996**, *30*, 3618-3623.
- (64) Rollins, A. W.; Kiendler-Scharr, A.; Fry, J. L.; Brauers, T.; Bropwn, S. S.; Dorn, H.-P.; Dubé, W. P.; Fuchs, H.; Mensah, A.; Mentel, T. F.; Rohrer, F.; Tillmann, R.; Wegener, R.; Wouldridge, P. J.; Cohen, R. C. Isoprene oxidation by nitrate radical: alkyl nitrate and secondary organic aerosol yields. *Atmos. Chem. Phys.* **2009**, *9*, 6685-6703.
- (65) Chen, J.; Wenger, J.; Venables, D. Near-ultraviolet absorption cross-sections of nitrophenols and their potential influence on tropospheric oxidation capacity. *J. Phys. Chem. A* **2011**, *115*, 12235-12242.
- (66) Harrison, M. A. J.; Barra, S.; Borghesi, D.; Vione, D.; Arsene, C.; Olariu, R. I. Nitrated phenols in the atmosphere: a review. *Atmos. Environ.* **2005**, *39*, 231-248.
- (67) Cecinato, A.; Di Palo, V.; Pomata, D.; Sciano, M. C. T.; Possanzini, M. Measurement of phase-distributed nitrophenols in Rome ambient air. *Chemosphere* **2005**, *59*, 679-683.
- (68) Bejan, I.; Abd El Aal, Y.; Barnes, I.; Benter, T.; Bohn, B.; Wiesen, P.; Kleffmann, J. The photolysis of *ortho*-nitrophenols: a new gas phase source of HONO. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2028-2035.
- (69) Zhou, X.; Beine, H. J.; Honrath, R. E.; Fuentes, J. D.; Simpson, W.; Shepson, P. B.; Bottenheim, J. W. Snowpack photochemical production of HONO: A major source of OH in the Arctic boundary layer in springtime. *Geophys. Res. Lett.* **2001**, *28*, 4087-4090.
- (70) Ren, X.; Harder, H.; Martinez, M.; Leshner, R. L.; Oligier, A.; Simpas, J. B.; Brune, W. H.; Schwab, J. J.; Demerjian, K. L.; He, Y.; Zhou, X.; Gao, H. HOx concentrations and OH reactivity observations in New York City during PMTACS-NY2001. *Atmos. Environ.* **2003**, *37*, 3639-3651.
- (71) Kleffmann, J.; Gavriloaiei, T.; Hofzumahaus, A.; Holland, F.; Koppmann, R.; Rupp, L.; Schlosser, E.; Siese, M.; Wahner, A. Daytime formation of nitrous acid: A major source of OH radicals in a forest. *Geophys. Res. Lett.* **2005**, *32*, L05818, DOI: 10.1029/2005GL022524.

Table 1. Formation yields of the products observed in the gas-phase reactions of cresol isomers with NO₃ radicals.

Reagent	Products	Yield (%) (this work)		Yield (%) (literature)	
		QUAREC	EUPHORE		
 <i>ortho</i> -Cresol		6-Methyl-2-nitrophenol	11.5±0.8	n.d. ^a	} 2.4-23.0 ^c
		6-Methyl-4-nitrophenol	(~10) ^d	n.d.	
		Methyl-1,4-benzoquinone	4.4±0.3	trace	-
	HNO ₃	nitric acid	77.2±6.3	95.9±4.8	-
 <i>meta</i> -Cresol		3-Methyl-2-nitrophenol	21.2±1.4	22.3±1.6	16.8±2.9 ^b
		3-Methyl-4-nitrophenol	22.8±1.8	25.4±1.7	-
		5-Methyl-2-nitrophenol	23.5±1.8	22.4±1.5	19.6±3.6 ^b
		Methyl-1,4-benzoquinone	4.2±0.7	n.d.	-
	HNO ₃	nitric acid	72.3±6.4	91.1±6.3	-
 <i>para</i> -Cresol		4-Methyl-2-nitrophenol	41.3±3.7	44.3±3.3	74±16 ^b
		4-Methyl-3-nitrophenol	probably	n.d.	-
	HNO ₃	nitric acid	85.0±10.2	86.2±7.0	-

^a n.d. - not determined, below detection limit (see text); ^b Atkinson *et al.*, 1992; ^c Grosjean *et al.*, 1985 (sum of 6-methyl-2-nitrophenol and 6-methyl-4-nitrophenol); ^d estimated, see text (section 4.3).

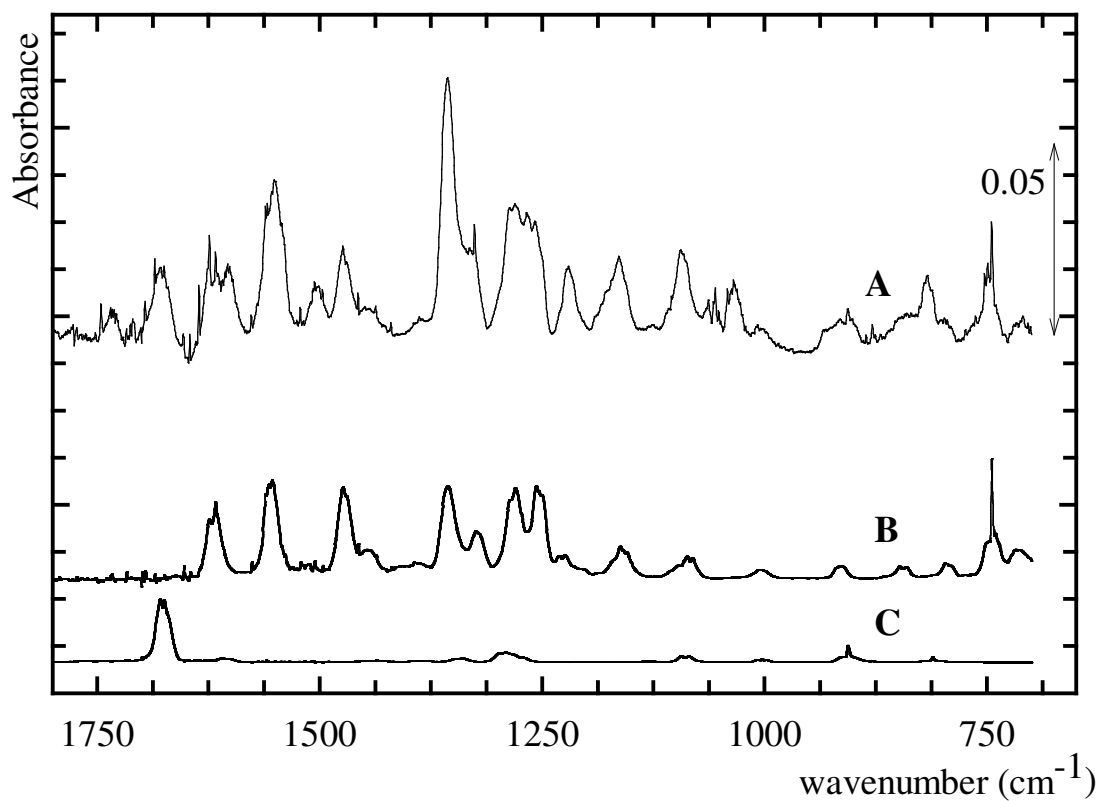


Figure 1. Infrared spectra from the NO₃ radical initiated oxidation of *ortho*-cresol in the QUAREC reactor: (A) product spectrum after subtraction of reactants; (B) reference spectrum of methyl-1,4-benzoquinone; (C) reference spectrum of 6-methyl-2-nitrophenol.

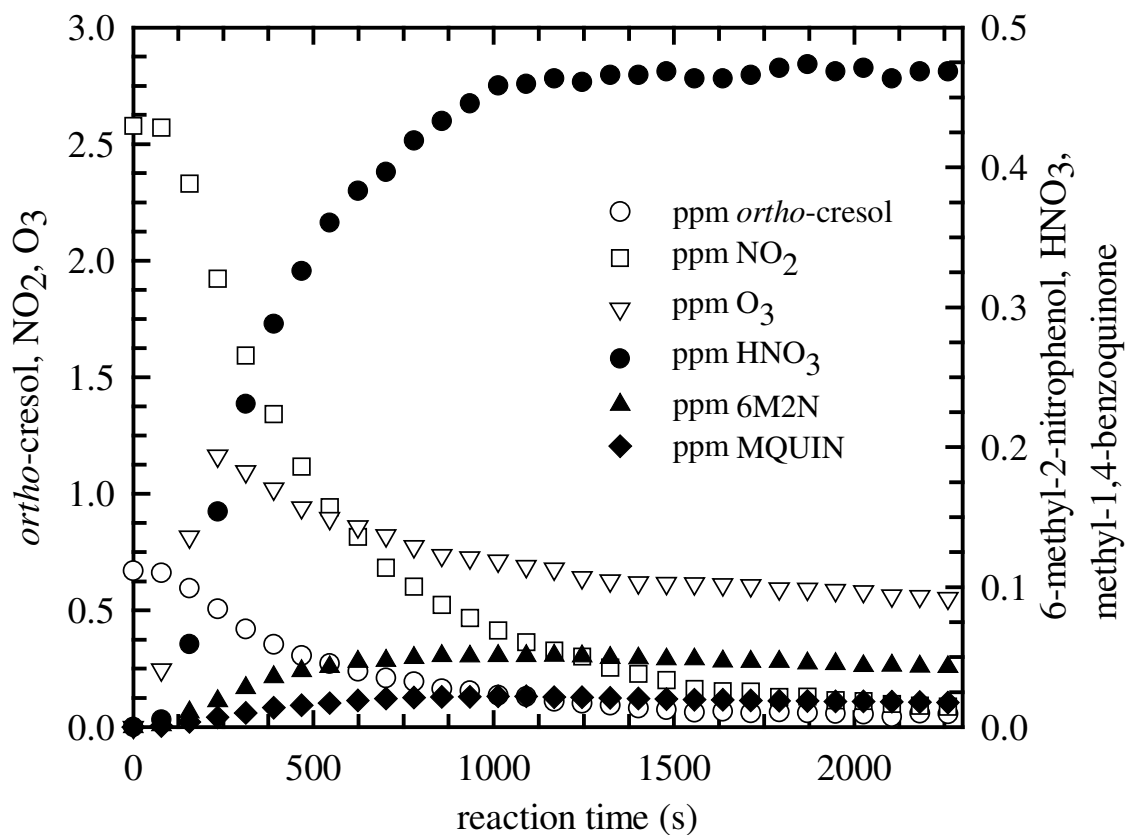


Figure 2. Concentration-time profile of the reactants and products identified in the NO_3 -initiated oxidation of *ortho*-cresol in the QUAREC reactor.

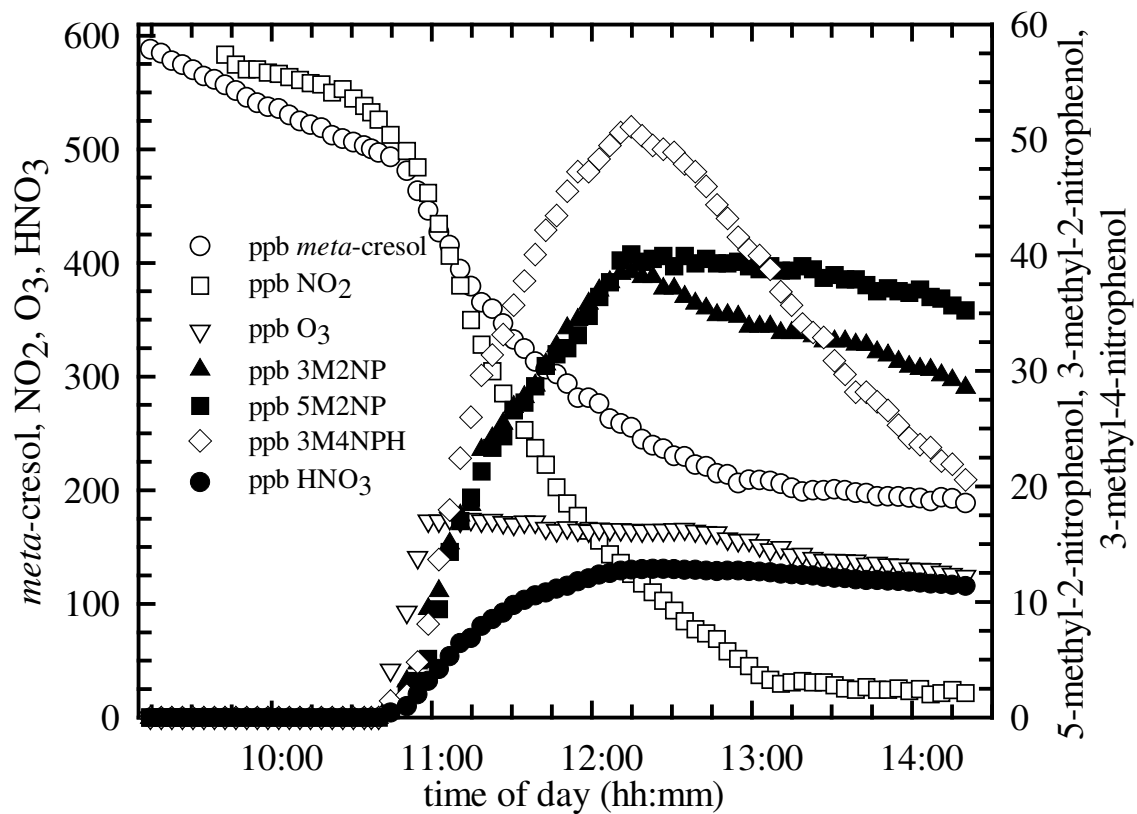
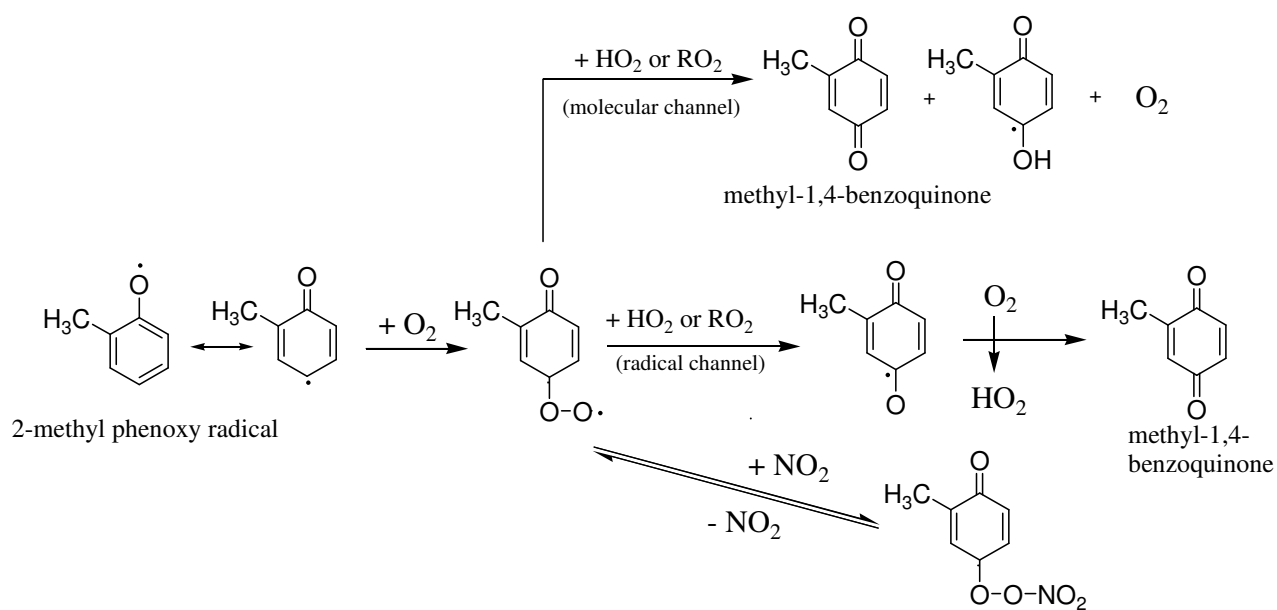


Figure 3. Concentration-time profiles of reactants and identified products in a *meta*-cresol/ NO_2 / O_3 oxidation EUPHORE experiment.



Scheme 1. Possible mechanism for the formation of methyl-1,4-benzoquinone from the reactions of the 2-methyl phenoxy radicals formed from the reaction of NO₃ with *ortho*-cresol in *ortho*-cresol/NO₂/O₃/air reaction mixtures.