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FT-IR product study of the reactions of NO_3 radicals with *ortho*-, *meta*- and *para*-cresol

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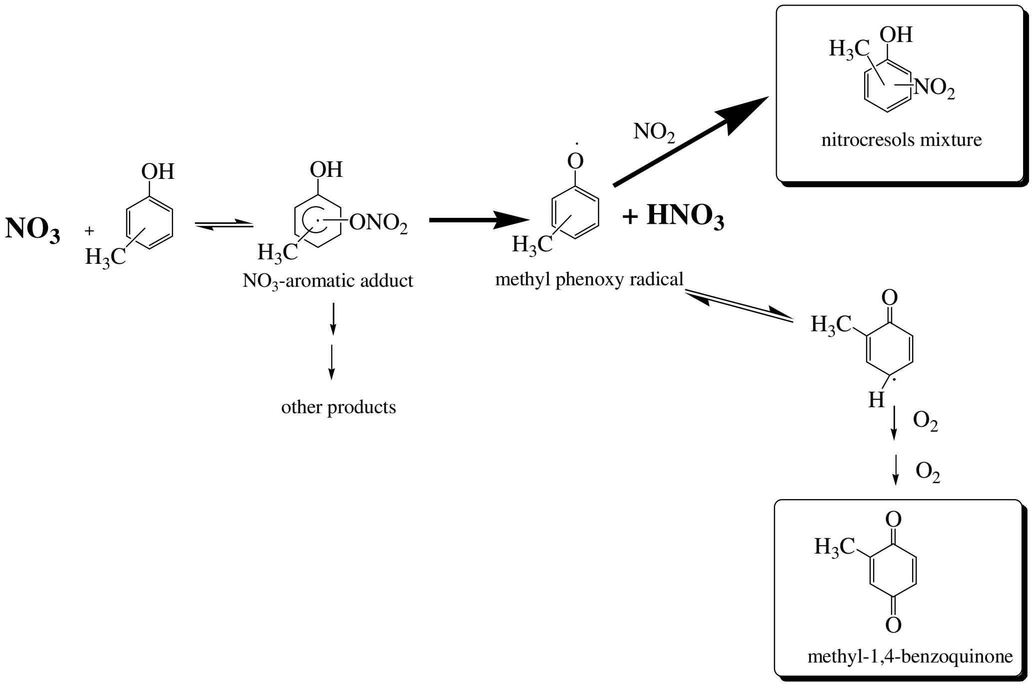


Abstract

Product analyses of the NO_3 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 O_3 with NO_2 was used for the *in situ* generation of NO_3 radicals in both QUAREC and EUPHORE. The gas-phase reaction of all three cresol isomers with NO_3 yielded nitrocresols and HNO_3. Moreover, methyl-1,4-benzoquinone was detected and quantified from the reaction of NO_3 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 NO_3 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 phenol [9-14] 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 O_3,[1,29] but they undergo rapid reactions with OH [1,30-32] and NO_3.[1,30,31,33-35] Therefore, rapid atmospheric removal is expected upon reactions with OH during the day and NO_3 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 NO_3 can be highly variable depending on NO_x levels, ranging from nearly zero to 2.0×10^9 molecule cm^{-3} or higher.[40,41] Evidence has recently emerged that NO_3 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 O_3 is large enough to produce significant NO_3.[40,42] Small daytime NO_3 mixing ratios comparable to peak OH concentrations have been observed, suggesting that VOCs reacting with NO_3 at comparable rates as with OH (*e.g.* isoprene, monoterpenes and hydroxylated aromatics) can be oxidized by NO_3 during the day. The radical NO_3 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 NO_3. Nitrophenol formation has been observed from the NO_3-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 NO_3 with phenols should proceed *via* an overall H-atom abstraction mechanism, which occurs after ring addition of NO_3.[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 NO_3 with cresols [49,50] predict that NO_3 is added to the hydroxylated carbon, followed by addition of NO_2 to a directly adjacent carbon. This pathway has the lowest energy barrier for the elimination of HNO_3 and it has the most stable transition state. Therefore, it could be energetically favorable to add both NO_3 and NO_2 before elimination of HNO_3. Such a mechanism contrasts sharply with that proposed by

Atkinson et al.,[30] where HNO_3 is eliminated prior to addition of NO_2. 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 NO_3 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 NO_3 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 NO_3 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 NO_3 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 m^3. 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 O_3 with NO_2 was used for the *in situ* generation of NO_3 in both chambers.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (1)$$

$$NO_3 + NO_2 \leftrightarrows N_2O_5 \qquad (2)$$

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 NO_2 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, O_3 produced by a commercial generator (corona discharge in O_2) 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 $(4.4\text{-}5.9)\times10^{-5}$ 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 CH_3CN. NO_2 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 O_2 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-NO_2-O_3 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 SF_6 as inert tracer gas: the dilution loss was typically 3% h^{-1}. Apart from reaction with NO_3 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 O_3 and NO_2. 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 O_3 and NO_3 and thus terminate any ongoing oxidation.

The initial and final concentrations of cresols, O_3 and NO_2 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-NO_2-O_3 experiments at EUPHORE (see SI, Figure SI-7) showed the formation 4-methyl-2-nitrophenol and HNO_3, 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 NO_3-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 NO_3) need to be considered to determine reaction yields. Rate coefficients between NO_3 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 NO_3 reacts slowly with nitrocresols with rate constants around 1×10^{-14} cm^3 $molecule^{-1}$ s^{-1}.[56] With average NO_3 concentration around $(6\text{-}10)\times10^6$ molecule cm^{-3}, one would obtain a nitrocresol loss of ~2% under QUAREC conditions. Based on rate coefficients between NO_3 and other unsaturated compounds,[33,38] it is reasonable to assume that reaction of NO_3 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 NO_3 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 HNO_3 formed from the reaction of NO_3 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 HNO_3 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 HNO_3 yields were about 20% higher in EUPHORE for *ortho*-cresol and *meta*-cresol, while there was good agreement for *para*-cresol. The HNO_3 yields from cresols + NO_3 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*-cresol [30] 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 GC [30] 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/NO_2/O_3 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 NO_3 + *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 NO_3-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/NO_2/O_3/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 NO_3-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 NO_2 in the experiments was much larger than that of the cresol (see Tables SI-2 and SI-3).

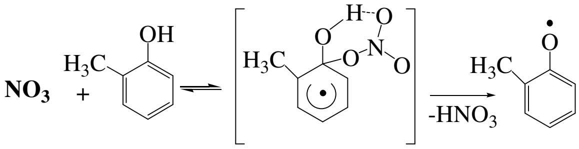
Formation of HNO_3

We found HNO_3 as an important product of the reaction of NO_3 with cresols. The formation yield of HNO_3 was calculated using literature cross sections.[58] Nitric acid can be formed in the gas phase through several reactions: *(i)* NO_3 + cresols; *(ii)* N_2O_5 + water vapor, and *(iii)* heterogeneous reactions of NO_2 and N_2O_5 on the reactor surface. The fast reaction of NO_3 with cresols and the experimental procedure used to generate NO_3 ensure that formation of N_2O_5 is minimized. Moreover, no spectral features characteristic of N_2O_5 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 HNO_3 formation from N_2O_5 + H_2O. In blank experiments performed in EUPHORE with N_2O_5/air mixtures, dark formation of HNO_3 was found to be negligible. Finally, HNO_3 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 HNO_3. Hence, in the present work the formation of HNO_3 can be largely attributed to reaction between cresols and NO_3. In EUPHORE the HNO_3 yield was ~90% with all the three cresol isomers. In QUAREC the HNO_3 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 HNO_3 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 HNO_3 observed in this study suggest that the NO_3 + cresol reaction is largely proceeding via an overall mechanism involving H-atom abstraction.

Proposed formation mechanism of nitrocresols

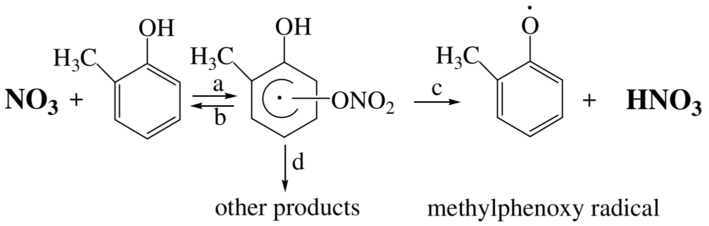
It has been postulated that the gas-phase reactions of NO_3 with phenolic compounds proceed via an overall H-atom abstraction mechanism through the intermediacy of a six-membered transition state, as shown below for *o*-cresol (reaction 3).[30] This is in agreement with the concentration-time behavior of HNO_3 formation and the high HNO_3 yields observed in this study.



ortho-cresol methylphenoxy radical (3)

The methylphenoxy radicals thus formed have been postulated to react further with NO_2 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 NO_2. 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 NO_2 and would explain the experimental results of this study. As an example, the possible electron resonance structures for the methylphenoxy radical formed from NO_3 + *meta*-cresol and the subsequent reactions with NO_2 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 NO_3 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 NO_3, which takes into account the occurrence of other possible reaction pathways (see reaction (4) of NO_3 with *ortho*-cresol).[30]



(4)

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>> 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 5.0×10^{-21} cm^3 $molecule^{-1}s^{-1}$ 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 O_2 to give methyl-1,4-benzoquinone and HO_2. The presence of high concentrations of NO_2 could result in the intermediate formation of a labile cyclic peroxynitrate. 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 NO_2 to give nitrocresols.

Atmospheric implications

This work shows for the first time that the reaction of NO_3 with cresols results in near-unity yield of HNO_3, 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, NO_3 and O_3, wet and dry deposition and photolysis. Reactions with O_3 are unlikely to be important, as inferred from the behavior of similar compounds: nitrophenols react very slowly with O_3, cresols have O_3 rate coefficients in the range of $2\text{-}5\times10^{-19}$ cm^3 molecule^{-1} s^{-1}, and in the case of nitrobenzene one has $< 7\times10^{-21}$ cm^3 molecule^{-1} s^{-1}.[1]

2-Nitrophenol reacts slowly with OH (9.0×10^{-13} cm^3 molecule^{-1} 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 CH_3- group on the aromatic ring relative to the OH- group.[60]

The rate coefficients for the reactions of NO_3 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 NO_3 + nitrocresols are ~1×10^{-14} cm^3 molecule^{-1} 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 Dawson [62] has been used successfully to estimate the wet deposition rate of oxidation products of hydroxyl-nitrate isoprene [63] and of first-generation products formed from NO_3 + 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 NO_2- 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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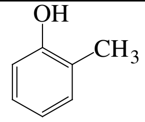
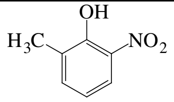
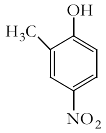
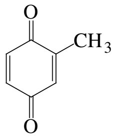
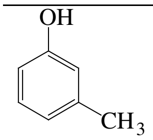
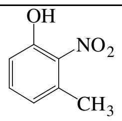
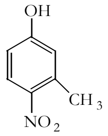
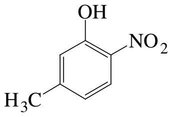
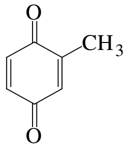
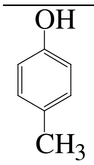
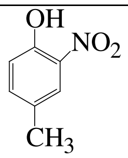
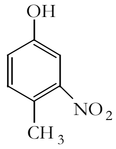
Table 1. Formation yields of the products observed in the gas-phase reactions of cresol isomers with NO_3 radicals.

Reagent	Products		Yield (%) (this work)		Yield (%) (literature)
			QUAREC	EUPHORE	
		6-Methyl-2-nitrophenol	11.5±0.8	n.d.[a]	12.8±2.8[b] 2.4-23.0[c]
ortho-Cresol		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	-
		3-Methyl-2-nitrophenol	21.2±1.4	22.3±1.6	16.8±2.9[b]
meta-Cresol		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	-
		4-Methyl-2-nitrophenol	41.3±3.7	44.3±3.3	74±16[b]
para-Cresol		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).

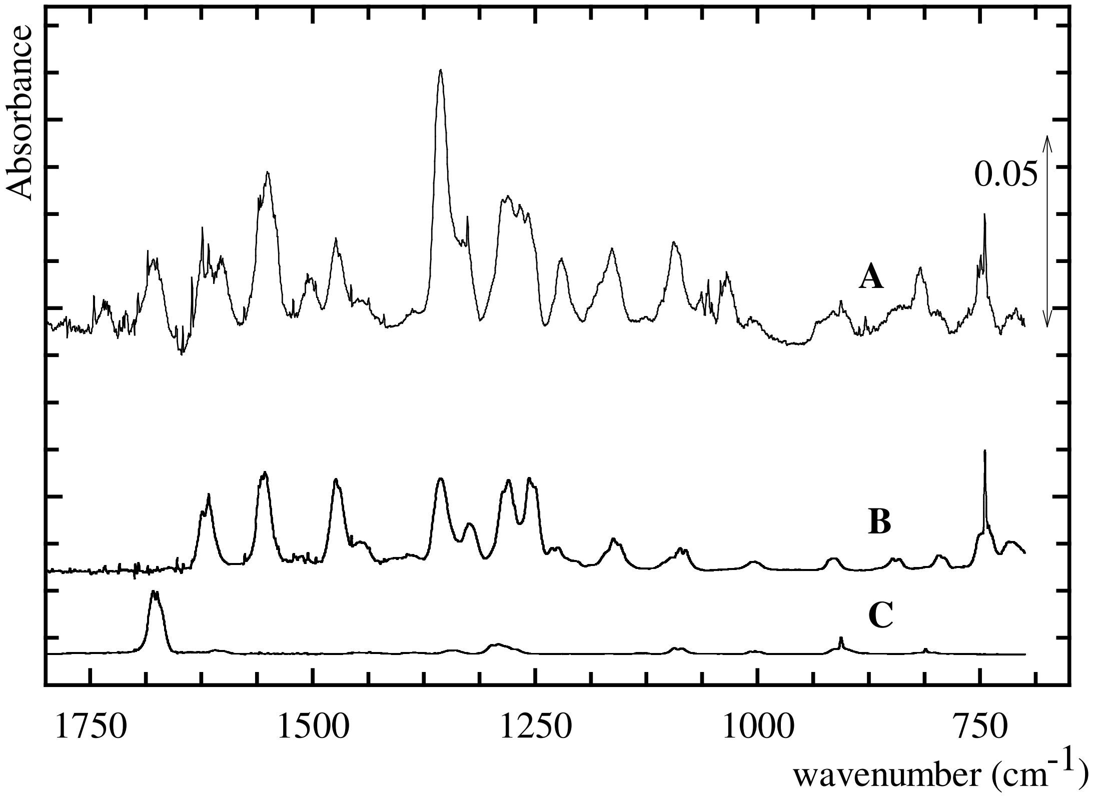


Figure 1. Infrared spectra from the NO_3 radical initiated oxidation of *ortho*-cresol in the QUAREC reactor: (A) product spectrum after subtraction of reactants; (B) reference spectrum of methyl-1,4-benzoquinone; (C) reference spectrum of 6-methyl-2-nitrophenol.

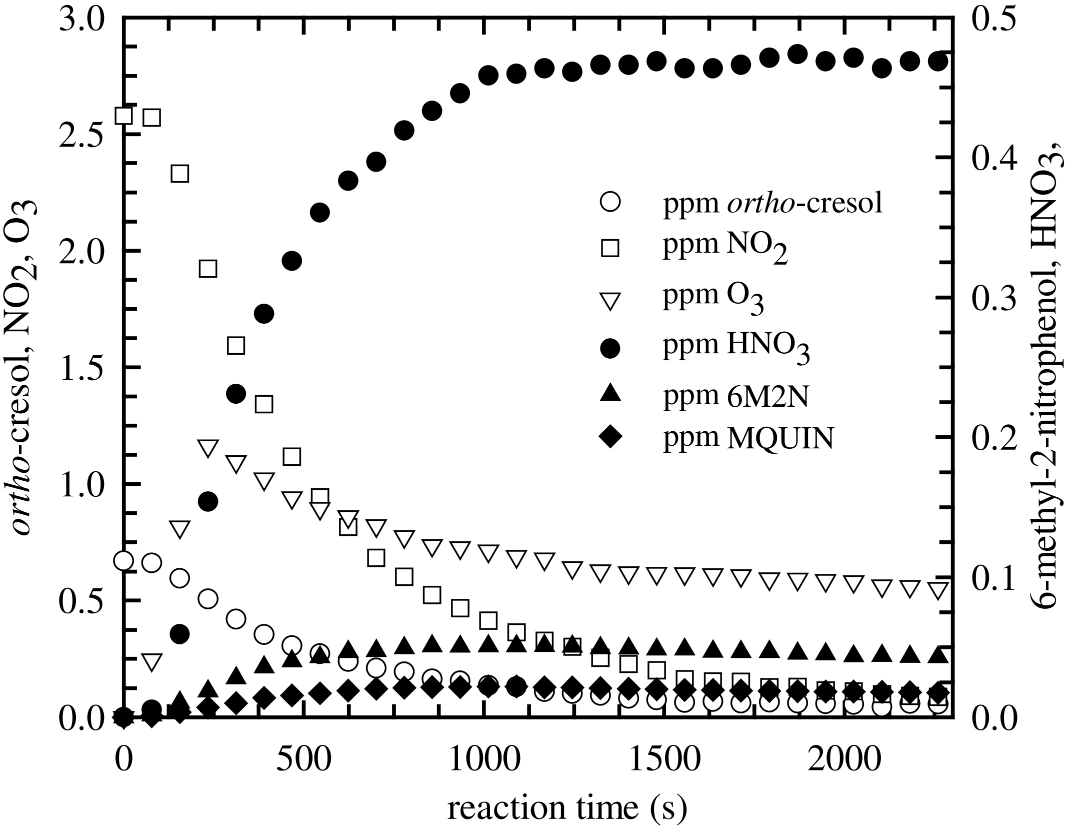


Figure 2. Concentration-time profile of the reactants and products identified in the NO_3-initiated oxidation of *ortho*-cresol in the QUAREC reactor.

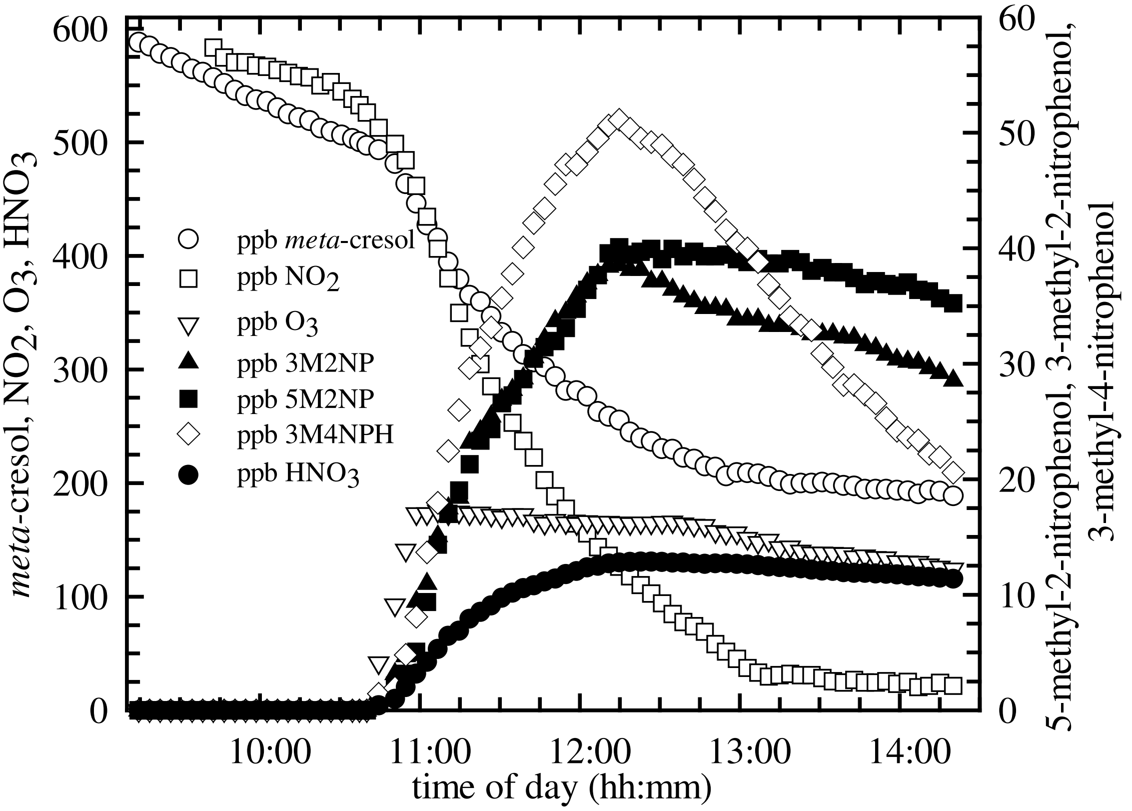
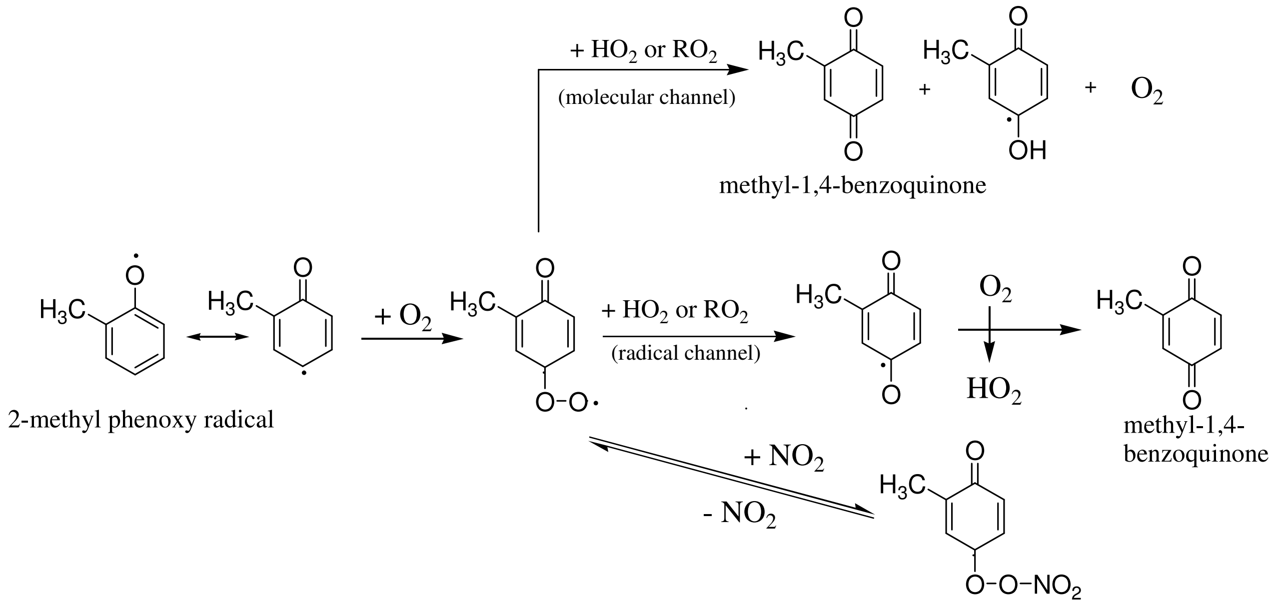


Figure 3. Concentration-time profiles of reactants and identified products in a *meta*-cresol/NO_2/O_3 oxidation EUPHORE experiment.



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 NO_3 with *ortho*-cresol in *ortho*-cresol/NO_2/O_3/air reaction mixtures.