# Kinetic Study of the Gas-Phase Reactions of Chlorine Atoms with 2-Chlorophenol, 2-Nitrophenol, and Four Methyl-2-nitrophenol Isomers

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ABSTRACT: Anthropogenic activities are the main source of nitrophenols and chlorophenols in the atmosphere. Nitro and chlorophenols have a high potential to form ozone and secondary organic aerosol, thus investigations on the major photo oxidation pathways of these compounds are important to assess their contribution to urban air pollution and human health. Presented here are rate coefficients determined at atmospheric pressure and  $(298 \pm 2)$  K using a relative kinetic method for the reactions of chlorine atoms with 2-chlorophenol (2CIP), 2nitrophenol (2NP) and four methyl-2-nitrophenol (2-nitrocresol, nM2NP (*n* = 3,4,5,6)) isomers. The following rate coefficients (in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) have been obtained:  $(5.9 \pm 1.5) \times 10^{-12}$  for 2ClP,  $(6.8 \pm 2.3) \times 10^{-12}$  for 2NP, and  $(14.0 \pm 4.9) \times 10^{-11}$ ,  $(4.3 \pm 1.5) \times 10^{-11}$ ,  $(1.94 \pm 0.67) \times 10^{-11}$  and  $(2.68 \pm 0.75) \times 10^{-11}$  for the four methyl-2-nitrophenol isomers 3M2NP, 4M2NP, 5M2NP, and 6M2NP,



respectively. This study represents the first kinetic investigation for the reaction of chlorine atoms with all the nitrophenols. In addition, to assist in the interpretation of the results, rate coefficients for the reactions of Cl atoms with the cresol ortho, meta, and para isomers have been determined for the first time. The rate coefficient for the reaction with 2CIP is in good agreement with previous data and the relative reactivity of 2NP, 4M2NP, 5M2NP, and 6M2NP can be rationalized based on known substituent effects. The rate coefficient for 3M2NP is anomalously large; the observation of significant NO<sub>2</sub> production in only this reaction suggests that an ipso substitution mechanism is the cause of the enhanced reactivity.

## 1. INTRODUCTION

Volatile organic compounds (VOCs) are ubiquitous in the troposphere and are emitted from both biogenic and anthropogenic sources. Although globally biogenic emissions are the main source of the VOCs in the atmosphere, the contribution from anthropogenic emissions is significant, particularly in urban environments. Aromatic hydrocarbons, such as benzene, toluene and the xylene isomers, commonly known as BTX, are a class of compounds for which a considerable proportion of the emissions originate from human activities. They are estimated to comprise between 17 to 25% of the total anthropogenic VOC emissions<sup>1</sup> and make a sizable contribution to photo-oxidant formation,<sup>2,3</sup> and secondary organic aerosol (SOA) formation<sup>1,4,5</sup> in urban areas.

Among the different types of aromatic hydrocarbons, nitroaromatics have been of special interest since 1987 when Rippen et al.<sup>6</sup> suggested the possible contribution of these compounds to forest decline. Prior to this suggestion, Nojima et al.<sup>7</sup> had detected nitrophenols in rainwater and in suspended particulate matter.<sup>8</sup> Nitrophenol and alkylated nitrophenols, e.g., nitrocresols, have been identified in air,<sup>9-13</sup> aerosols,<sup>14,15</sup> clouds,16,17 water,18 rain,19 soil,20 fog,21 and snow.22 Nitrophenols possess toxic properties and are highly detrimental for human health.<sup>9,13,23</sup> The concentrations of nitrophenols in urban atmospheres may be up to 60 pptv, but the concentration levels of these compounds are generally expected to be lower;<sup>11</sup> for example, Cecinato et al.<sup>24</sup> have reported 30 pptv levels of 2nitrophenol in the ambient air of Rome.

The formation of nitrophenols and nitrocresols in the combustion processes of vehicles has been reported,<sup>10</sup> and they are used in large quantities as raw materials in the manufacture of dyes, resins, explosives and pharmaceuticals which can lead to fugitive emissions.<sup>13</sup> Additionally, direct emissions of nitrophenols into the troposphere can occur from the combustion of coal and wood. Besides direct release into the atmosphere, nitrophenols and alkylated analogues can be formed in situ by the OH- and NO3-radical initiated oxidation of aromatic precursors, BTX, phenol, and cresols, etc.<sup>25-30</sup>

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Very little information on the kinetics and mechanisms of the gas-phase atmospheric photo-oxidation of nitroaromatics is available; currently 2-nitrophenol and the 2-nitrocresol isomers are the compounds which have received the most attention.<sup>31–34</sup> Atkinson et al.<sup>31</sup> found that 2-nitrophenol reacts slowly with OH radicals at room temperature ( $k = 0.9 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). However, Bejan et al.<sup>33</sup> have reported rate coefficients for the reactions of OH with methyl-2-nitrocresol isomers which are at least 1 order of magnitude faster compared to 2-nitrophenol, and have ascribed the higher reactivity to electronic resonance effects generated by the position of the CH<sub>3</sub>- group on the aromatic ring relative to the OH- group. From the available evidence, Bejan et al.<sup>33</sup> also concluded that photolysis is probably the most important atmospheric sink for 2-nitrophenol and 2-nitrocresols.

Nitrophenols and methylnitrophenols can influence the oxidizing capacity of the atmosphere in two opposing ways. Chen et al.<sup>34</sup> have investigated the near-ultraviolet absorption spectra of nitrophenols and argued that absorption by nitrophenols may lower the actinic flux and thereby retard primary photochemical processes. This approach has been made considering an unreasonable concentration of nitrophenols in the atmosphere of 1 ppbv. On the other hand, Bejan et al.<sup>32</sup> reported that 2-nitrophenol and its alkylated isomers could play an important role in enhancing the oxidative capacity of the atmosphere as photolysis of 2-nitrophenol and its alkylated isomers forms nitrous acid (HONO), the photolysis of which leads to formation of OH radicals.<sup>35</sup>

Apart from these studies, to the best of our knowledge, no other kinetic data on the reactions of the atmospherically important species OH, Cl,  $NO_3$  and  $O_3$  with nitrophenols and their methlyated derivates are currently available in the literature.

Chlorophenols are undesirable pollutants of environmental concern due to their toxicity.<sup>36</sup> Chlorophenols are emitted into the environment through their use in the production of pesticides, dyes and pharmaceuticals.<sup>37</sup> Chlorophenols have been found in wastewater, groundwater, surface water and sludge products, sewage, the atmosphere and living organisms.<sup>38,39</sup> Among the 19 different chlorophenols, the monochlorophenols have the highest vapor pressures and are consequently the most likely to be found in air.<sup>38,39</sup>

Only one gas-phase kinetic experimental study on a monochlorophenol has been reported in the literature. Platz et al.<sup>40</sup> have reported a rate coefficient of  $k = (7.32 \pm 1.30) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the reaction of chlorine atoms with 2-chlorophenol obtained at atmosphere pressure and 298 K. To the best of our knowledge, no other experimental kinetic data for the reactions of the main tropospheric oxidants with chlorophenols have been reported.

Atmospheric chlorine chemistry has generally been considered to be of importance only in the marine boundary layer and in industrial regions with chlorine emissions.<sup>41</sup> However, the detection of significant levels of photolabile nitryl chloride (ClNO<sub>2</sub>) in midcontinental regions in the United States and Europe has shown that atmospheric chlorine chemistry is potentially much more widespread and important than previously thought.<sup>42–44</sup> Both ClNO<sub>2</sub> and HCl have been shown to be significant Cl atom sources in the Los Angeles basin with Cl-atom initiated reactions calculated to account for ~25% of the alkane photo-oxidation.<sup>45</sup>

The aim of the present study is to increase the kinetic database for the reaction of chloro- and nitrophenol

compounds with atmospheric oxidants. We report here room temperature rate coefficients, determined at atmospheric pressure using a relative kinetic technique, for the reaction of chlorine atoms with 2-chlorophenol (2ClP) and 2-nitrophenol (2NP) and the methylated-2-nitrophenol isomers 3-methyl-2-nitrophenol (3M2NP), 4-methyl-2-nitrophenol (4M2NP), 5-methyl-2-nitrophenol (5M2NP), and 6-methyl-2-nitrophenol (6M2NP).

#### 2. EXPERIMENTAL SECTION

A majority of the experiments were performed at Wuppertal in a cylindrical 480 L Duran glass reactor (3 m length, 45 cm inner diameter) at (298 ± 2) K and 1000 mbar total pressure of synthetic air. The chamber has been described in detail elsewhere.<sup>46</sup> The reactor was surrounded by 20 superactinic lamps (Philips TLA 40W/05, 300 <  $\lambda$  < 450 nm,  $\lambda_{max}$  = 360 nm) for photolytic initiation of reaction mixtures. A multireflection White type mirror system (51.6 m optical path length) mounted inside the reactor was interfaced to a Fourier transform infrared (FTIR) spectrometer (Nicolet Magna 520) equipped with a KBr beam splitter and a mercury–cadmiumtelluride (MCT) detector which was used for *in situ* monitoring of reactants and products in the ppbV range.

One experiment on 2-nitrophenol was performed in a cylindrical 1080 L QUArtz glass REaction Chamber (QUAR-EC) at similar temperature and pressure conditions  $(298 \pm 2)$  K and 1000 mbar in synthetic air. The chamber, described in detail elsewhere,<sup>47</sup> has been used intensively to perform kinetic studies on the aromatic hydrocarbon systems.<sup>29,33,48</sup> Reactants and products in this chamber were also monitored in situ using FTIR spectroscopy (484.7 m path length, Nicolet NEXUS FT-IR with MCT detector).

Both chambers were equipped with inlet ports for addition of gaseous, liquid, and solid compounds into the chambers. The compounds were introduced into the chambers at low pressure in an air flow. The inlet was heated in order to ensure efficient transfer of the liquid and especially the solid compounds. Initial concentrations of the reactants in the 480 L reactor were varied in the range of 3–7 ppmV for the aromatics and up to 12 ppmV for the reference compounds. In the QUAREC chamber, the initial concentrations were approximately 5–8 times lower. The photolysis of molecular chlorine was used as the source of chlorine atoms:

$$Cl_2 + hv \rightarrow Cl + Cl$$

The chlorine atom concentrations in the experiments, estimated from the decay of the reference compounds, varied in the range  $(0.7-1.5) \times 10^7$  atom cm<sup>-3</sup>.

The time-dependent concentrations of the reactants were monitored in the spectral range  $4000-700 \text{ cm}^{-1}$  using FTIR. Infrared spectra were derived from 50, up to 90, coadded interferograms recorded with 1 cm<sup>-1</sup> resolution over 70–130 s. In typical experiments, 20–30 spectra were recorded over a period of 40–60 min. The reactants were monitored at the following infrared absorption frequencies (in cm<sup>-1</sup>): 3-methyl-2-nitrophenol 786.9 and 1608.7; 4-methyl-2-nitrophenol 827.0 and 1556.2; 5-methyl-2-nitrophenol 757.7 and 1633.4; 6methyl-2-nitrophenol 744.7 and 1553.9; chloroethane at 972.9, 1288.2 and 2943.7; 2-nitrophenol 748.2; 2-chlorophenol 747.8 and 3576.4; 2-chloropropane at 1065.9 and 2989.7; 2chlorobutane at 795.0 and 2977.4; 1,3-butadiene at 908.

Rate coefficients for the reactions of chlorine atoms with the aromatic compounds (2-chlorophenol, 2-nitrophenol, and 2-

nitrocresol isomers) have been obtained using a relative kinetic technique. With this technique, the conversion of the aromatic compounds due to reaction with chlorine atoms is measured relative to that of a reference compound, whose rate coefficient with the Cl atom is well established and is preferably of the same order of magnitude as that for the compound under investigation.

aromatic + Cl  $\rightarrow$  products  $k_1$ 

reference + Cl  $\rightarrow$  products  $k_2$ 

Tests showed that apart from reaction with Cl atoms, wall loss of the aromatic compounds also occurred in the dark and needs to be considered in the kinetic analysis.

aromatic (wall loss)  $\rightarrow$  products  $k_{wl}$ 

The dark wall losses of the aromatic compounds were measured before and after the reaction with Cl atoms in order to check that they were not modified during the reaction. No differences in the pre- and postreaction wall loss rates were observed. The dark wall loss accounted for between 15 and 20% of the overall decay of the aromatic compounds investigated. Photolytic loss of the nitrophenols<sup>32,33</sup> was negligible in comparison to both the wall loss and the loss due to reaction with chlorine atoms. Neither wall nor photolysis losses were observed for the reference hydrocarbons used in the study.

If the aromatic and reference compounds are lost in the reaction mixture solely by the reactions presented above, and neither compound is reformed by any subsequent processes in the reaction mixture, then the following relationship is valid:

$$\ln\left(\frac{[\operatorname{aromatic}]t_0}{[\operatorname{aromatic}]t}\right) - k_{wl}(t - t_0) = \frac{k_1}{k_2} \ln\left(\frac{[\operatorname{reference}]_{t_0}}{[\operatorname{reference}]_t}\right)$$
(1)

where  $[\operatorname{aromatic}]_{t_0}$   $[\operatorname{aromatic}]_{t_1}$   $[\operatorname{reference}]_{t_0}$  and  $[\operatorname{reference}]_t$ are the concentrations of the aromatic compound and reference compound, at time t = 0 and t, respectively,  $k_1$  and  $k_2$  are the rate coefficients for the reaction of the aromatic compound and reference with Cl atoms, respectively, and  $k_{wl}$  is the first-order dark wall loss rate of the aromatic compound. Plots of  $\ln([\operatorname{aromatic}]_{t_0}/[\operatorname{aromatic}]_t) - k_{wl}(t - t_0)$  versus  $\ln([\operatorname{reference}]_{t_0}/[\operatorname{reference}]_t)$  should give straight lines with zero intercept and slopes of  $k_1/k_2$ . Since  $k_2$  is known,  $k_1$  can be obtained from the slope of the plot.

The following 298 K rate coefficients (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) have been used for the reference compounds used in this study: chloroethane ( $k_{\text{Cl}} = 1.15 \times 10^{-11}$ );<sup>49</sup> 2-chloropropane ( $k_{\text{Cl}} = 2.01 \times 10^{-11}$ ); 2-chlorobutane ( $k_{\text{Cl}} = 7.01 \times 10^{-11}$ )<sup>50</sup> and 1,3butadiene ( $k_{\text{Cl}} = 25.1 \times 10^{-11}$ ).<sup>51</sup>

In addition to the experiments performed to investigate the kinetics of the reactions of Cl with nitro-, methyl nitro-, and chlorophenols, rate coefficients have also been determined for the reaction of Cl atoms with the three cresol isomers using the relative kinetic technique. These experiments were performed in two different simulation chambers, i.e., the QUAREC chamber in Wuppertal, Germany, already described in this section, and the HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry) photoreactor in Leeds, United Kingdom. The HIRAC chamber is described in detail elsewhere.<sup>52</sup> Briefly, the chamber consists of a cylindical

stainless steel container of 2.25 m<sup>3</sup>, which can be evacuated to  $10^{-2}$  mbar with a rotary pump. HIRAC contains a number of sampling and injection ports and 4 fans for reactant mixing. Photolysis was initiated by 8 blacklamps (Philips TL-D/36 W BLB; 320 nm <  $\lambda$  < 420 nm,  $\lambda_{max}$  = 365 nm) which are placed inside quartz tubes which traverse the inside of the reactor. The chamber is highly instrumented but in this study only a FTIR spectrometer has been used. Reactants were monitored using a Chernin-type multiple reflection mirror system mounted inside the chamber and coupled to a Bruker IFS/66 FTIR spectrometer with a KBr beamsplitter and a liquid nitrogencooled mercury-cadmium-telluride (MCT) detector.53 The mirror system was operated at a total optical path length of 128.52 m and IR spectra were recorded at a spectral resolution of 1 cm<sup>-1</sup> in the range 700-4000 cm<sup>-1</sup>. Typically, 100 interferograms were coadded per spectrum which equates to a time resolution of around 1 min.

**Materials.** The following compounds were purchased from Aldrich with the stated purities and were used without further purification: 2-chlorophenol ( $\geq$ 99%), 2-nitrophenol (98%), 3-methyl-2-nitrophenol (99%), 4-methyl-2-nitrophenol, 5-methyl-nitrophenol (97%), 2-chloropropane ( $\geq$ 99%), 2-chlorobutane ( $\geq$ 99%), chloroethane ( $\geq$ 99.8%), propene (99%), and ethene (99%). 1,3-Butadiene and Cl<sub>2</sub> were purchased from Messer Griesheim with purities of 99% and >99.8%, respectively, and synthetic air was purchased from Air Liquide with a purity of 99,999%.

6-Methyl-2-nitrophenol was prepared by addition of sodium nitrite to *o*-toluidine dissolved in a concentrated solution of sulfuric acid following a method described by Winzor.<sup>54</sup> The compound was obtained with a purity >96% based on GC-FID analyses.

## 3. RESULTS

Figures 1–6 show plots of the kinetic data according to eq 1 for the reaction of Cl atoms with 2NP, 3M2NP, 4M2NP, 5M2NP, 6M2NP, and 2ClP, respectively. In all cases, linear plots are obtained with near zero intercepts. Three different reference



**Figure 1.** Plots of the kinetic data according to eq 1, obtained in the 1080 and 480 L chambers, for the reactions of 2-nitrophenol with Cl atoms using 2-chloropropane ( $\bullet$  1080L chamber;  $\bigcirc$  480L chamber), and chloroethane ( $\triangle$ ) as reference hydrocarbons.



**Figure 2.** Plots of the kinetic data according to eq 1 for the reactions of 3-methyl-2-nitrophenol (3M2NP) with Cl atoms using 2-chloropropane  $(\bigcirc)$ , 2-chlorobutane  $(\blacksquare)$ , and 1,3-butadiene  $(\diamondsuit)$  as reference hydrocarbons.



**Figure 3.** Plots of the kinetic data according to eq 1 for the reactions of 4-methyl-2-nitrophenol (4M2NP) with Cl atoms using 2-chloropropane  $(\bigcirc)$ , 2-chlorobutane ( $\blacksquare$ ), and 1,3-butadiene ( $\diamondsuit$ ) as reference hydrocarbons.

hydrocarbons have been used in the determination of the rate coefficients for the reactions of Cl atoms with 2NP, 3M2NP, 4M2NP, and 5M2NP and two reference compounds in the cases of 6M2NP and 2ClP. A minimum of three experiments have been performed for each aromatic compound/reference compound combination.

The rate coefficient ratios  $k_1/k_2$  obtained from the slopes of the plots in Figures 1 to 6 for each aromatic and reference compound combination are listed in Table 1. The corresponding rate coefficients  $k_1$  obtained from the slopes, using the appropriate value for the reference compound rate coefficient, are also listed in Table 1. In the majority of cases, there is a good agreement between the values of the rate coefficients obtained using different reference compounds, the only exception being the values obtained with 1,3-butadiene as



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**Figure 4.** Plots of the kinetic data according to eq 1 for the reactions of 5-methyl-2-nitrophenol (5M2NP) with Cl atoms using 2-chloropropane ( $\bigcirc$ ), 2-chlorobutane ( $\blacksquare$ ), and chloroethane ( $\triangle$ ) as reference hydrocarbons.



**Figure 5.** Plots of the kinetic data according to eq 1 for the reactions of 6-methyl-2-nitrophenol (6M2NP) with Cl atoms using 2-chloropropane ( $\bigcirc$ ) and 2-chlorobutane ( $\blacksquare$ ) as reference hydrocarbons.

reference for the reactions of Cl with 3M2NP (Figure 2) and 4M2NP (Figure 3). The values obtained with 1,3-butadiene as a reference are around 24% lower than the values obtained with the other reference compounds (2-chlorobutane and 2-chloropropane). We can find no apparent reason for this discrepancy. In the case of 4M2NP, the difference between its rate coefficient with Cl and that of the 1,3-butadiene reference compound may simply be too large and give rise to uncertainties in the spectral analysis.

The rate coefficients obtained for 2NP using same reference hydrocarbon in two different reaction chambers show very good reproducibility  $(k_1/k_2 = 0.31 \pm 0.01$  in 1080 l quartz glass chamber and  $k_1/k_2 = 0.32 \pm 0.01$  in Duran glass chamber), despite different surface:volume ratios of the chambers, different wall material, and different wall loss contributions



**Figure 6.** Plots of the kinetic data according to eq 1 for the reactions of 2-chlorophenol with Cl atoms using 2-chloropropane ( $\bullet$ ), and chloroethane ( $\triangle$ ) as reference hydrocarbons.

for 2NP, suggesting that the measurements are reliable and free of experimental artifacts. The reactions of nitrophenols are known to produce SOA, which may potentially affect the rate coefficient determinations.<sup>55</sup> However, Sorensen et al.<sup>56</sup> have investigated the impact of aerosol on rate coefficient determinations for a number of aromatic compounds, e.g., phenol and xylenes, and found no indication that SOA affected their kinetic investigations. We, therefore, assume that aerosol formation will not affect the present investigations on the kinetics of the reactions of Cl atoms with nitroaromatics.

Since the values of the rate coefficients obtained for the aromatic compounds with different reference compounds are in good agreement, we prefer to give final rate coefficients for the reactions which are averages of all the determinations. The final rate coefficients for the reactions of Cl atoms with the aromatic compounds are listed as  $k_{\text{average}}$  in Table 1. The errors quoted in Table 1 for the  $k_1/k_2$  ratios are the  $2\sigma$  statistical errors resulting from the linear regression analyses of the plots. The errors quoted for absolute rate coefficient values  $k_{\text{average}}$  includes an additional 20% contribution to cover possible errors in the reference compound Cl rate coefficients.

## 4. DISCUSSION

This work represents the first kinetic study on the reactions of Cl atoms with 2-nitrophenol and the four *n*-methyl-2nitrophenol isomers (n = 3, 4, 5 or 6). Accordingly, no comparison with literature data is possible. To help with the following discussion on the kinetic measurements presented in this work, rate coeffcients for the reactions of Cl atoms with various substituted aromatic hydrocarbons are listed in Table 2.

**2-Chlorophenol (2CIP).** The value of  $(5.9 \pm 1.5) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the rate coefficient of the reaction of Cl with 2-chlorophenol is, within the error limits, in agreement with the value of  $(7.32 \pm 1.3) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> obtained by Platz et al.<sup>40</sup> using a relative kinetic technique. Altarawneh et al.,<sup>63</sup> using transition state theory, calculated a rate coefficient for the reaction of Cl with 2-chlorophenol of  $5.60 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which is in very good agreement with the value obtained in this study.

From Table 2 one can see that, of the chlorophenols, it is only the reaction of Cl with 2ClP that is significantly reduced compared to the rate coefficient for Cl with phenol ( $1.9 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). The latter reaction is proposed to proceed via H atom abstraction from the OH group,<sup>40</sup> suggesting, as proposed by Platz et al., that hydrogen bonding between the two substituents rather than inductive effects, is responsible for the relatively slow reaction of Cl with 2chlorophenol.

In the study of the reaction of Cl with phenol, no evidence was found for a displacement reaction producing chlorobenzene,<sup>41</sup> and we assume that displacement of OH with Cl in the reaction of Cl with 2-chlorophenol is also negligible and that the reaction proceeds entirely by H atom abstraction from the OH group. In a preliminary product study on the reaction of Cl with 2-chlorophenol,<sup>64</sup> no evidence was found for the formation of 1,2-dichlorobenzene, which supports these assumptions.

**2-Nitrophenol (2NP).** The rate coefficient for the reaction of Cl atoms with 2NP is similar to that of 2ClP, and one would expect hydrogen bonding to again be significant, supported by observations of significantly lower boiling points for 2NP compared to 3 and 4NP.<sup>65</sup> However, the nitrogrouping is strongly deactivating and hence one might not expect a full recovery in the reactivity, as with chlorosubstitution, particularly for the 4NP where the radical of the phenoxy species can be delocalized to the *para* position. Unfortunately, kinetic data on Cl reactivity with 3NP and 4NP are not available for comparison.

The rate coefficient for the reaction of Cl with nitrobenzene is nearly 4 orders of magnitude higher than that of Cl with benzene. In a kinetic and product study on the reaction of Cl with nitrobenzene, Frosig et al.<sup>60</sup> have shown that the reaction produces chlorobenzene in essentially 100% yield and proceeds via a displacement mechanism probably involving Cl-atom ipso addition to the substituent NO2 site followed by NO2 elimination. We have performed a product study on the reaction of Cl with 2-nitrophenol in the 1080 L reactor<sup>64</sup> using FTIR to monitor reactants and products. The products detected include 2-chlorophenol, HCl, NO<sub>2</sub> and ClNO<sub>2</sub> formed from the reaction of Cl with NO<sub>2</sub>. After subtraction of the absorptions due to 2-chlorophenol and the identified products, IR absorptions remained, which could not be unequivocally attributed to any specfic compound. An analysis of the data gave molar yields of 56  $\pm$  8% for 2-chlorophenol, 41  $\pm$  3% for HCl and 50  $\pm$  10% for the combined yields of NO<sub>2</sub> and ClNO<sub>2</sub>. These results support that the reaction of Cl with 2nitrophenol is probably proceeding via a two-channel mechanism with an approximate 40% contribution from H atom abstraction by Cl from the OH group and a 60% contribution from displacement of NO<sub>2</sub> by Cl. This mechanism would imply a rate coefficient contribution of approximately 2.6  $\times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for H atom abstraction from the OH group. This is approximately a factor of 74 lower than the rate coefficient for H atom abstraction by Cl in phenol and illustrates the very strong hydrogen bonding existing between OH and NO<sub>2</sub> substituents in 2-nitrophenol.

**Cl Reactions with Cresols.** When checking the literature for rate coeffcients for the reactions of Cl atoms with aromatic compounds, we could find no reports on determinations for the reactions of Cl with the cresol isomers, which would be interesting to know and compare with the rate coeffcients for Cl with the methyl-nitrophenol isomers since their structures Table 1. Rate Coefficient Ratios  $k_1/k_2$  and Rate Coefficients  $k_1$  Obtained for the Reactions of Cl Atoms with 2-Chlorophenol, 2-Nitrophenol, and 2-Nitrocresol Isomers

	roforonco		<b>k</b> 1	<b>k</b> average
aromatic	compound	<b>k</b> <sub>1</sub> / <b>k</b> <sub>2</sub>	(10 <sup>-11</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	(10 <sup>-11</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
OH NO <sub>2</sub>	2-chloropropane <sup>a</sup>	0.32±0.01	0.65±0.13	
	2-chloropropane <sup>a</sup>	0.31±0.01	0.63±0.13	0.68±0.23
2NP	(1080L chamber)			
	chloroethane <sup>b</sup>	0.65±0.02	0.75±0.15	
OH NO <sub>2</sub>	2-chlorobutane <sup>c</sup>	2.13±0.03	14.9±3.0	
	2-chloropropane <sup>a</sup>	7.72±0.10	15.5±3.1	14.0±4.9
3M2NP	1,3-butadiene <sup>d</sup>	0.46±0.01	11.5±2.3	
OH NO <sub>2</sub>	2-chlorobutane <sup>c</sup>	0.65±0.01	4.55±0.91	
	2-chloropropane <sup>a</sup>	2.47±0.04	4.96±0.99	4.3±1.5
<sub>сн</sub> , 4M2NP	1,3-butadiene <sup>d</sup>	0.14±0.01	3.50±0.74	
OH NO <sub>2</sub>	2-chlorobutane <sup>c</sup>	0.24±0.01	1.68±0.34	
H.C.	2-chloropropane <sup>a</sup>	1.02±0.01	2.05±0.41	1.94±0.67
5M2NP	chloroethane <sup>b</sup>	1.82±0.03	2.09±0.42	
H <sub>3</sub> C NO <sub>2</sub>	2-chlorobutane <sup>c</sup>	0.39±0.01	2.73±0.55	2 69±0 75
6M2NP	2-chloropropane <sup>a</sup>	1.31±0.02	2.63±0.52	2.0010.75
OH CI	2-chloropropane <sup>a</sup>	0.29±0.01	0.58±0.11	0 59+0 15
2CIP	chloroethane <sup>b</sup>	0.51±0.01	0.59±0.11	0.55±0.15

 ${}^{a}k_{\text{Cl+2-chloropropane}} = 2.01 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}; {}^{50} {}^{b}k_{\text{Cl+chloroethane}} = 1.15 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}; {}^{49} {}^{c}k_{\text{Cl+2-chlorobutane}} = 7.01 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}; {}^{50} {}^{d}k_{\text{Cl+1,3-butadiene}} = 25.1 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}; {}^{51}$ 

possess cresol elements. We have, therefore, made a few relative kinetic measurements on the reactions of Cl with the three cresol isomers. The following rate coefficients values have been obtained (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for each chamber: in the QUAREC,  $k_{Cl+ortho-cresol} = (1.1 \pm 0.23) \times 10^{-10}$ ;  $k_{Cl+meta-cresol} = (2.9 \pm 0.58) \times 10^{-10}$ ;  $k_{Cl+para-cresol} = (2.8 \pm 0.57) \times 10^{-10}$  and in the HIRAC  $k_{Cl+ortho-cresol} = (1.1 \pm 0.24) \times 10^{-10}$ ;  $k_{Cl+meta-cresol} = (3.2 \pm 0.65) \times 10^{-10}$ ;  $k_{Cl+para-cresol} = (3.4 \pm 0.77) \times 10^{-10}$ . Very good agreement has been obtained between the rate coefficient values determined from each chamber. The measurements were made relative to the reaction of Cl with ethene ( $k = 1.0 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, Stutz et al.)<sup>66</sup> in the QUAREC chamber and relative to the reaction of Cl with propene ( $k = 2.23 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, Ceacero-Vega et al.)<sup>67</sup> in the HIRAC chamber and the average results are listed in Table 2. The

errors are the average error of the values obtained in both simultation chambers involved in this study. They consist of the  $2\sigma$  errors from the analysis of the kinetic plots, examples of which are shown in Figure 7, and an additional 20% to account for the uncertainty in the rate coefficient for the reference compound.

Lauraguais et al.<sup>61</sup> found that the rate coefficients for many di- and higher substituted benzenes with Cl could be estimated to a good approximation by summing the individual rate coefficients for H atom abstraction by Cl from all of the H atom containing substituents attached to the aromatic ring. As can be seen from Table 2, the rate coefficients for the reactions of Cl with *meta-* and *para-*cresol are only modestly higher than the sum of the rate coefficients for the reactions of Cl with phenol and toluene  $(25.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ , while the rate

Table 2. Comparison of the Rate Coefficients for the Reactions of Cl Atoms with a Range of Substituted Aromatic Compounds

	$k (10^{-11} \text{ cm}^3 \text{ molecule}^{-1})$		
compound	s <sup>-1</sup> )	reference	
benzene	$1.76 \times 10^{-5}$	Alecu et al., 2007 <sup>57</sup>	
toluene	6.2	Wang et al., 2005 <sup>58</sup>	
phenol	19.3	Jenkin et al., 2010 <sup>59</sup>	
nitrobenzene	0.09	Frosig et al., 2000 <sup>60</sup>	
dimethylbenzenes (xylenes)	~14.0 <sup>ª</sup>	Wang et al., 2005 <sup>58</sup>	
ortho-cresol	$11.3 \pm 3.3$	this study (see text)	
meta-cresol	$30.3 \pm 8.7$	this study (see text)	
para-cresol	31.3 ± 9.6	this study (see text)	
methoxyphenols	~27.0 <sup><i>a</i></sup>	Lauraguais et al., 2014 <sup>61</sup>	
2-methoxy-4- methylphenol	33.4	Lauraguais et al., 2014 <sup>61</sup>	
1.2-dihydroxybenzenes	$\sim 64.0^{b}$	Bejan et al., 2010 <sup>62</sup>	
2-nitrophenol	0.65	this study	
3-methyl-2-nitrophenol	14.0	this study	
4-methyl-2-nitrophenol	4.32	this study	
5-methyl-2-nitrophenol	1.94	this study	
6-methyl-2-nitrophenol	2.69	this study	
2-chlorophenol	0.59	this study	
3-chlorophenol	15.6	Platz et al., 1998 <sup>40</sup>	
4-chlorophenol	23.7	Platz et al., 1998 <sup>40</sup>	

<sup>*a*</sup>Rate coefficient is the average of the values reported for the three isomers. <sup>*b*</sup>Rate coefficient is the average of the reported values for 1,2-dihydroxybenzene, 3-methyl-1,2-dihydroxybenzene and 4-methyl-1,2-dihydroxybenzene.



**Figure 7.** Plots of the kinetic data for the reactions of Cl with *ortho*. ( $\blacklozenge$ ), *meta*- ( $\blacklozenge$ ) and *para*-cresol ( $\bigstar$ ) measured relative to Cl with ethene in QUAREC chamber (filled symbols) and relative to Cl with propene in HIRAC chamber (open symbols) at 298 K and atmospheric pressure. Plots obtained from QUAREC chamber shifted vertically for clarity.

coeffcient for Cl with *ortho*-cresol is around a factor of 2 lower. The much lower rate coeffcient for the reaction of Cl with *ortho*-cresol is attributed to hydrogen bonding between the CH<sub>3</sub> and OH substituents, which can not occur in *meta*- and *para*-cresol. It is interesting to note that, contrary to the case for the cresol isomers, the rate coefficients for reactions of Cl with the three isomers of methoxyphenol are all very similar,<sup>61</sup> i.e.,

the relative positions of the substituents on the ring to one another has little effect on the rate coefficient. The positive inductive (+*I*) effect of the CH<sub>3</sub> in the methoxy group would appear to counteract any hydrogen bonding that may occur between the OH and methoxy substituents in 2-methoxyphenol. From the above observations on the reactivity of Cl toward aromatic compounds, we speculate that the strong electron withdrawing effect of the NO<sub>2</sub> group will be the main factor determining the very different reactivities of the individual methyl-2-nitrophenol isomers toward Cl.

CI + n-Methyl-2-nitrophenols (3M2NP, 4M2NP, 5M2NP, 6M2NP). The primary focus of this study were the methyl-2-nitrophenols. The rate coefficients for the cresols  $((1-3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$  are close to the sum of the rate coefficients for the reaction of Cl with phenol  $(1.9 \times 10^{-10}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)<sup>59</sup> and toluene  $(6.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1})$  $s^{-1}$ ),<sup>58</sup> with the rate coefficient for *ortho*-cresol being slightly lower  $(1.13 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$  presumably due to either hydrogen bonding or steric hindrance. The measurements for 2NP suggest that the combined steric hindrance, hydrogen bonding and deactivating effect of the nitrogroup reduces the reactivity of 2NP to approximately a factor of 10 lower than that of toluene ( $6.8 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> vs  $6.2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-158</sup>), suggesting that the observed reactivity for the *n*-methyl-2-nitrophenols (n = 4, 5, 6) is due to abstraction from the methyl group. The rate coefficients, 1.9- $4.3 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, are ~31-69% of the toluene value, consistent with some overall deactivation of the ring by the nitrogrouping. For 4M2NP and 6M2NP, the OH and CH<sub>3</sub> groupings are ortho or para to each other, enhancing stabilization effects on phenyl product radicals. In 6M2NP, the methyl group is ortho to phenol, and the slightly lower rate coefficient compared to 4M2NP would be consistent with OH-CH<sub>3</sub> hydrogen bonding or steric hindrance. For 5M2NP, the nitrogroup is para to the methyl group and would therefore destabilize the resulting phenyl radical, consistent with this isomer having the lowest rate coefficient of the three methyl-2nitrophenols discussed so far.

The relative and absolute reactivities of the nM2NPs (n = 4, 5, 6) can be rationalized by conventional arguments, but the result for 3M2NP stands out as being anomalous. From the arguments presented above, the deactivating effect of the nitrogroup ortho to the methyl group (and hence to the phenyl radical formed from abstraction) plus any steric hindrance or hydrogen bonding, should result in a significantly lower rate coefficient compared to Cl + toluene. In fact, a factor of 2 enhancement compared to reaction with toluene is observed. One possible explanation would be a reduction in OH-NO<sub>2</sub> hydrogen bonding, allowing for abstraction from the OH group; however, the bidentate nature of NO2 should allow for hydrogen bonding to both OH and CH<sub>3</sub> groupings. Preliminary product studies with the observation of NO<sub>2</sub> production, suggest that ipso substitution is the explanation. Figure 8 shows the production of NO<sub>2</sub> from the reaction of Cl with 3M2NP, whereas no significant NO<sub>2</sub> is observed from the reactions of Cl with the other methyl-2-nitrophenols. While quantitative yields and mechanistic studies are subject to ongoing investigation, qualitatively the NO2 yield is substantive. Further product studies and theoretical calculations would be very beneficial to explain why only the 3N2NP isomer demonstrates this particular reaction pathway.

**Atmospheric Implications.** The rate coefficients for the Cl-atom initiated oxidation of the 2-nitrophenol, 2-chlorophe-



**Figure 8.** Qualitative indication of NO<sub>2</sub> formation from the reaction of the 3M2NP, 4M2NP, and 5M2NP, respectively, with chlorine atoms in the presence of reference hydrocarbon as have been used in the relative kinetic studies. (A) reference spectrum of NO<sub>2</sub>; (B–D) residual IR spectra of the reaction mixture of *n*M2NP (n = 3, 4, 5) with Cl atoms in the typical NO<sub>2</sub> IR absorption range (1680–1550 cm<sup>-1</sup>) after the subtraction of *n*M2NP (n = 3, 4, 5), H<sub>2</sub>O and reference compound. Qualitatively similar residuals to 4M2NP were observed for 6M2NP and 2-NP, but have been omitted to keep the figure clear.

nol, and the methyl-2-nitrophenol isomers can be used to calculate the tropospheric lifetimes of these compounds with respect to reaction with Cl. The estimated lifetimes of the methyl-2-nitrophenol isomers with respect to reaction with Cl, OH, and photolysis are presented in Table 3. Bejan et al.<sup>33</sup> have reported atmospheric photolysis frequencies and OH rate coefficients for methyl-2-nitrophenol isomers, and these have been used to calculate the lifetimes of the compounds with respect to photolysis. The photolysis frequencies were obtained from photolysis frequencies measured in the QUAREC reactor and scaled to atmospheric conditions through multiplication by the ratio of the NO<sub>2</sub> photolysis frequency measured in the atmosphere (40° N for July 1st) to that measured for NO<sub>2</sub> in the reactor.

As can be observed from the values in Table 3, even though the photolysis frequencies for the nitrophenols are associated with quite large uncertainties, photolysis is undoubtedly the main loss process for the methyl-2-nitrophenol isomers. Even in the early morning in coastal regions where elevated Cl atom levels can prevail ( $\sim 10^5$  molecule cm<sup>-3</sup>),<sup>45,68</sup> the reaction of chlorine atoms with 2-nitrophenol and the methylated-2nitrophenols is still only a very minor sink for these compounds.

Besides the loss of the methyl-2-nitrophenol isomers by reaction with different atmospheric oxidants, these compounds may also partition between the gas and liquid phase. The transfer of a gas to the liquid involves a number of processes and parameters including diffusion to and absorption on the surface, mass accommodation, Henry's law solubility and diffusion and reaction in the liquid. Except for 2-nitrophenol, Henry's law coefficients are not known for the other phenolic compounds investigated in this study. For 2-nitrophenol at 298 K, the Henry's law coefficient is reasonably large, 84 M atm $^{-1}$ , $^{71}$ and increases with decreasing temperature. Leyssens et al.<sup>72</sup> have measured a mass accommodation coefficient of  $8.3 \times 10^{-4}$ at 298 K for 2-nitrophenol, which leads to an estimated accommodation time for 2-nitrophenol of approximately 20 min. Therefore, if the methylated-2-nitrophenols have fairly similar mass accommodation coefficients, it is possible that mass accommodation is a fast process for these compounds and may compete with photolysis as an effective atmospheric removal process for the methyl-2-nitrophenols.

The ozone-forming potentials of nitrobenzene, nitrotoluene, and methylated nitrophenols are all fairly high in the incremental scale of Carter  $(1994)^{73}$  and have MIR (Maximum Incremental Reactivity) values of between 120 and 130 g O<sub>3</sub>/g VOC. The cresol isomers have an MIR of 108. It is, therefore, quite probable that the methyl-2-nitrophenol isomers investigated in this study will also have high ozone forming potentials and will contribute to tropospheric ozone formation on a local scale.

	2NP	3M2NP	4M2NP	5M2NP	6M2NP	2CIP
compound	OH NO2	OH NO <sub>2</sub> CH <sub>3</sub>	OH NO <sub>2</sub>	H <sub>3</sub> C	H <sub>3</sub> C NO <sub>2</sub>	OH CI
τ <sub>hν</sub> <sup>a</sup> (h)	4.41 <sup>d</sup>	0.40	0.75	0.60	0.85	-
τ <sub>он</sub> <sup>а,b</sup> (h)	193 <sup>e</sup>	47	50	24	64	-
τ <sub>Cl</sub> <sup>c</sup> (days)	35	1.6	5.4	12	8.6	39

Table 3. Comparison of the Atmospheric Lifetimes for Substituted Phenolic Aromatic Compounds with Respect to Photolysis and Reaction with OH Radicals and Cl Atoms

<sup>*a*</sup>Calculated using atmospheric photolysis frequencies taken from Bejan et al.;<sup>33</sup> see text. <sup>*b*</sup>Daily average [OH] =  $1.6 \times 10^6$  cm<sup>-3</sup> from Prinn et al., (1995).<sup>69</sup> <sup>*c*</sup>Daily average [Cl] =  $5 \times 10^4$  cm<sup>-3</sup> from Spicer et al., (1998).<sup>68</sup> <sup>*d*</sup>Calculated from the photolysis frequency measured by Bardini (2006)<sup>70</sup> and quoted in Chen et al. (2011).<sup>34</sup> <sup>*e*</sup>Based on the rate coefficient  $k_{(2-nitrophenol+OH)} = 0.9 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> reported by Atkinson et al. (1992).<sup>31</sup>

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#### Notes

The authors declare no competing financial interest.

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