Aqueous chemical bleaching of 4-nitrophenol brown carbon by hydroxyl radicals; products, mechanism and light ~~absorptivity~~absorption

Bartłomiej Witkowski[1]*, Priyanka Jain[1]~~ and~~, Tomasz Gierczak[1]

[1]University of Warsaw, Faculty of Chemistry, al. Żwirki i Wigury 101, 02-089 Warsaw, Poland

~~*Corresponding author e-mail: ~~*Correspondence to:* Bartłomiej Witkowski (bwitk@chem.uw.edu.pl)

Abstract

. The reaction of hydroxyl radicals (OH) with 4-nitrophenol (~~4-NP~~4NP) in ~~the~~an aqueous solution was investigated at pH=2 and 9. ~~As a result, the ~~The molar yield of the phenolic products quantified was ~~measured to be ~~0.20~~ ~~±0.05 at pH=2 and 0.~~40~~39±0.~~1~~03 at pH=9. The yield of 4-~~nitrocatechol (4-NC~~nitrocatecho+l (4NC) was higher at pH=9~~;~~ ~~at~~. At the same time, a lower number of phenolic products was observed at pH=9 due to ~~the hydrolysis and other~~ irreversible reactions ~~at pH~~of some phenols formed when the pH>7. Mineralization investigated with a total organic carbon (TOC) ~~technique~~analyzer showed that after ~~4-NP~~4NP was completely consumed, approx. 85% of the organic carbon remained in the aqueous solution. ~~Hence, up to~~Moreover, as inferred from the TOC measurements and the molar yields of the phenols formed, 65% of the organic carbon that remained in the aqueous solution ~~accounted for~~was attributed to the ~~open-ring ~~non-~~phenolic~~aromatic products.

The light ~~absorptivity~~absorption of the reaction solution between 250 and 600~~-~~ nm decreased as a result of the OH reaction with ~~4-NP. At~~4NP. However, the ~~same time, 4-NP~~4NP solution showed ~~some~~a noticeable resistance to the chemical bleaching reaction investigated due to the formation of ~~the ~~light-absorbing by-products. This phenomenon effectively prolongs the time-~~scale~~scales of the chemical bleaching ~~or 4-NP via reaction with ~~of 4NP by OH by a factor of 3~~-~~–1.5 at pH 2 and 9, respectively. The experimental data acquired indicated that both photolysis and the reaction with OH can be important processes for the removal ~~processes ~~of ~~the atmospheric brown carbon~~light-absorbing organic compounds from ~~the aqueous~~cloud water particles containing ~~4-NP.~~ 4NP.

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1 Introduction

Atmospheric brown carbon (BrC) is a subfraction of organic aerosols (OA) ~~that is~~ characterized by a strong, wavelength-dependent absorption of ~~the~~ electromagnetic irradiation in the near ultraviolet (UV) and visible (~~VIS~~Vis) regions (Laskin et al., 2015; Yan et al., 2018). BrC is primarily produced by biomass burning (BB) and has a negative impact on ~~the~~ local air quality and human health (Laskin et al., 2015; ~~Yan~~Hems et al., ~~2018~~2021). Due to the high UV-Vis ~~absorptivity~~absorption, BrC greatly contributes (up to 50%) to the radiative forcing of OA (Feng et al., 2013; Wang et al., 2014; Lu et al., 2015; Cordell et al., 2016; Zhang et al., 2017; ~~Lu et al., 2015; Wang et al., 2014; Feng et al., 2013;~~ Yan et al., 2018). Numerous organic compounds contribute to ~~the~~ atmospheric BrC (Laskin et al., 2015; ~~Hettiyadura et al., 2021;~~ Li et al., ~~2020a~~2020; Fleming et al., ~~2020~~2020; Vidović et al., 2020; Hettiyadura et al., 2021); at the same time, a significant fraction of BrC chromophores ~~remains~~remain poorly characterized (Laskin et al., 2015; Bluvshtein et al., 2017~~; Laskin et al., 2015~~).

Nitrophenols are widespread nitroaromatic compounds that have been identified among the major chromophores of atmospheric BrC (Harrison et al., 2005b; Kitanovski et al., 2012; Claeys et al., 2012; Laskin et al., 2015; Frka et al., 2016; Bluvshtein et al., 2017). 4-Nitrophenol (~~4-NP~~4NP) is one of the most atmospherically abundant and environmentally widespread nitrophenols~~-~~.(Harrison et al., 2005b; Laskin et al., 2015) ~~and is characterized by very high~~4NP also exhibits strong absorption ~~cross-sections~~of electromagnetic radiation in the UV-Vis region .(Jacobson, 1999)~~.~~ For these reasons, ~~4-NP has been identified as one~~4NP was found to contribute significantly to the light absorption of ~~the major~~ambient BrC ~~chromophores~~aerosols (~~Xie et al., 2019;~~ Mohr et al., 2013; Bluvshtein et al., 2017; Kitanovski et al., 2020)~~. 4-NP is present in the air~~. 4NP was detected in the air, rain, surface waters, and snow as well as in atmospheric particulate matter (PM) ~~(2006; Mohr et al., 2013; Belloli et al., 1999; Jacobson, 1999)~~(Jaber et al., 2007; Kitanovski et al., 2012; Claeys et al., 2012; Kahnt et al., 2013; Mohr et al., 2013; Balasubramanian et al., 2019; Liang et al., 2020; Kitanovski et al., 2020)~~, rainwater~~. Large quantities of 4NP are produced by the combustion of fossil fuels and biomass (~~2006; Jaber~~Desyaterik et al., ~~2007; Nistor~~2013; Mohr et al., ~~2001; Harrison~~2013; Inomata et al., ~~2002~~2015; Xie et al., 2019)~~, surface waters and snow (Balasubramanian et al., 2019; Vanni et al., 2001), soil (Webber and Wang, 1995), as well as in the atmospheric particulate matter (PM) (Liang et al., 2020; Kahnt et al., 2013; Kitanovski et al., 2020; Vione et al., 2009). Large quantities of 4-NP are produced by the combustion of fuels, mainly biomass (Xie et al., 2019; Desyaterik et al., 2013; Mohr et al., 2013), coal (Li et al., 2020b; Liang et al., 2020), and also by diesel engines (Inomata et al., 2015). Moreover, 4-NP is introduced into the environment as an industrial waste (Aleboyeh et al., 2003; Behnajady et al., 2006; Behki and Khan, 1991). Several studies have confirmed, that 4-NP has an adverse impact on human health (Majewska~~

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~~et al., 2021; Rosenkranz and Klopman, 1990), it is a treat to aquatic organisms (Tenbrook et al., 2003; Howe et al., 1994), and contributes to the decline of forests (Natangelo et al., 1999; Rippen et al., 1987).~~

~~Formation~~. Moreover, 4NP is introduced into the environment by a number of industrial processes (Majewska et al., 2021). Several studies have confirmed that 4NP has an adverse impact on human health,(Majewska et al., 2021) is a threat to aquatic organisms (Tenbrook et al., 2003), and contributes to the decline of forests (Natangelo et al., 1999).

The formation, chemical processing and ~~decomposition~~removal (bleaching) of BrC can occur in air as well as in ~~the~~ atmospheric aqueous particles, ~~which~~and can involve direct photolysis and reactions with hydroxyl radicals (OH) (~~Hems et al., 2020;~~ Laskin et al., 2015; ~~Jiang et al., 2021; Li et al., 2020a;~~ Forrister et al., 2015; Moise et al., 2015; Hems and Abbatt, 2018; Hems et al., 2020; Li et al., 2020; Jiang et al., 2021). Due to the high value of Henry's law constant (Sander, 2015), and its high solubility in water, ~~4-NP~~4NP can readily partition into ~~the~~ atmospheric aqueous particles (~~Vione et al., 2009;~~ Harrison et al., 2005b; Vione et al., 2009)~~, Chemical~~. The chemical and photochemical reactions in the atmospheric aqueous phase contribute to the formation (Vione et al., 2003; Harrison et al., 2005a; ~~Vione et al., 2003;~~ Heal et al., 2007), ~~functionalization~~transformation (Vione et al., ~~2009~~2005; Vione et al., ~~2005~~2009) and ~~decomposition (~~removal~~)~~ (~~Braman et al., 2020;~~ Harrison et al., 2005a; Braman et al., 2020) of ~~4-NP~~4NP. The chemical and photochemical processing (aging) in the aqueous phase ~~results~~result in ~~the~~a change ~~of~~in the light ~~absorptivity~~absorption of aqueous particles containing ~~4-NP~~4NP (~~Zhao et al., 2015;~~ Zhang et al., 2003; Zhao et al., 2015; Braman et al., 2020). However, the ~~interplay~~connection between the light absorbance and chemical composition of the aqueous 4NP solution ~~of 4-NP~~ that has been subjected to photolysis and oxidation by OH is poorly characterized (~~Zhao et al., 2015;~~ Zhang et al., 2003; Zhao et al., 2015).

~~Aqueous~~The aqueous reaction of ~~4-NP~~4NP with OH (reaction ~~1~~I) is known to produce aromatic ~~compounds~~products, including hydroquinone (HH), 1,2,4-trihydroxylbenzene (1,2,4-THB), 4-nitrocatechol (~~4-NC~~4NC) and 4-nitropyrogallol (~~4-NPG~~4NPG) (Tauber et al., 2000; Oturan et al., 2000; Zhang et al., 2003; ~~Biswal et al., 2013;~~ Daneshvar et al., 2007; Biswal et al., 2013).

4NP+OH ~~+ 4-NP~~ → products ~~(1~~(I)

However, the yields of the substituted phenols ~~produced by~~from reaction (~~1~~I) remain ambiguous (Tauber et al., 2000; Oturan et al., 2000; Zhang et al., 2003; ~~Oturan et al., 2000;~~ Daneshvar et al., 2007; Ding et al., 2016). Reaction (~~1~~I) was previously investigated ~~on~~at a molecular level but almost exclusively in the context of wastewater treatment via advanced oxidation processes (AOP) (Tauber et al., 2000; Oturan et al., 2000; Zhang et

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al., 2003; ~~Oturan et al., 2000; ~~Ding et al., 2016) where the reaction conditions cannot be considered as atmospherically-relevant (Tauber et al., 2000; Zhang et al., 2003; Daneshvar et al., 2007; ~~Zhang et al., 2003; Tauber et al., 2000; ~~Ding et al., 2016). Consequently, it is currently difficult to evaluate whether or not reaction (~~1~~I) is a relevant source of atmospheric BrC (~~Xiong et al., 2015; ~~Oturan et al., 2000; ~~Biswal et al., 2013; ~~Tauber et al., 2000; Kavitha and Palanivelu, 2005; Biswal et al., 2013; Xiong et al., 2015).

~~In the atmospheric aqueous particles, which are characterized by a broad pH-range~~In some clouds and fogs (Herrmann et al., 2015), ~~4-NP~~4NP (pKa≈7.2)~~ can exist in both protonated and deprotonated forms~~ (Rived et al., 1998) can exist in both protonated and deprotonated forms (Fig. S1).~~.~~ At the same time, little information is available about the ~~pH ~~impact of pH on the ~~products ~~distribution of the products of reaction (~~1~~I) (Tauber et al., 2000; Oturan et al., 2000). ~~There is no data available about~~Also, little information exists regarding the pH-dependence of the light absorbance of ~~4-NP~~a 4NP solution that has been subjected to ~~the ~~oxidation by OH (~~Zhao et al., 2015; ~~Biswal et al., 2013; Zhao et al., 2015). It should be also noted that the UV-Vis ~~absorptivity~~absorption of ~~4-NP~~4NP and its oxidation products is strongly pH-dependent (Biswal et al., 2013; Braman et al., 2020~~; Biswal et al., 2013~~).

The goal of this ~~work~~study was to investigate the mechanism of OH ~~reaction~~reactions with ~~4-NP~~4NP in the aqueous phase in the context of atmospheric BrC formation and processing. Hence, ~~the ~~reaction (~~1~~I) was investigated at 298 K in ~~the~~an aqueous ~~phase~~solution under acidic (pH=2) and basic (pH=9) conditions using the photoreactor developed in ~~our~~the host laboratory~~:~~ (Witkowski et al., 2019). Additionally, the phenolic products of reaction (~~1~~I) were analyzed together with the changes in the UV-Vis ~~absorptivity of the reaction solution (Witkowski et al., 2019). Phenols under investigation were ~~absorption of the reaction solution. The phenols under investigation were quantified using gas chromatography coupled to mass spectrometry (GC/MS). ~~A~~The possible mineralization of 4NP and the formation of volatile products ~~was~~were monitored with ~~the~~a total organic carbon (TOC) analyzer. The UV-Vis ~~absorptivity~~absorption of the reaction solution as well as the molar ~~absorptivity (base-e ~~absorption (ε, mol^{-1}×L×cm^{-3}) of the phenols under investigation were measured between pH 2 and 9.

2~~-~~. Experimental section

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~~Materials~~The materials and reagents used are listed in section S1 of the electronic ~~Supplementary Information~~supplementary information (SI). All solutions were prepared using deionized (DI) water (18 MΩ×cm^{-1}).

2.1 Aqueous phase photoreactor

The aqueous ~~phase~~ photoreactor was described previously (Witkowski et al., 2019)~~, and~~; more details are provided in section S4.1. The reaction vessel ~~was~~is a quartz jacketed ~~reaction~~ flask with ~~100 ml~~an internal volume~~.~~ of 100 ml, surrounded by eight 4W lamps. All experiments were carried out at 298 K; the temperature of the reaction solution was maintained ~~with~~by a circulating water bath (SC100-A10, Thermo Fisher Scientific). Two 4W lamps (TUV ~~TL 4W~~, peak emission 254 nm) and six 4W lamps (33-640, emission >400 nm, Philips) were used to irradiate the reaction solution.

2.2 Experimental procedure

The reaction mixture was a 100~~ ml~~–250 µM aqueous solution of ~~4-NP (concentration~~4NP; total volume 100~~-250 µM) in deionized (DI) water.~~ ml. The pH of ~~the~~this solution was not adjusted (unbuffered, no acids or buffers added) or it was adjusted to pH 2 or 9 ~~using~~with HCl, $HClO_4$ ~~and~~or Na_2HPO_4 (50 mM) to investigate ~~oxidation~~the reaction of fully protonated and deprotonated ~~4-NP (section S2).~~forms of 4NP (Fig. S1). Hydrogen peroxide (H_2O_2, concentration 5 mM) was photolyzed with UV irradiation (~~254nm~~254 nm) to generate OH~~, the~~ with an estimated steady-state concentration~~ of OH was~~ = 1.4×10^{-9} M (section S3) (Tan et al., 2009). Under these conditions ~~4-NP~~, the 4NP was almost completely consumed ~~by OH within~~after ca. 1h. Aliquots of the reaction mixture were sampled every 5 min and analyzed ~~by~~with GC/MS, a UV-Vis ~~spectroscopy~~spectrophotometer and a TOC analyzer. The experimental procedure is described in detail in section S4.1.

2.3 ~~Gas~~ Quantification of the phenolic products with gas chromatography coupled ~~with~~to mass spectrometry

Analyses were carried out using a GC-MS-QP2010Ultra gas chromatograph ~~(Shimadzu)~~ coupled with ~~the~~a single quadrupole ~~QP-5000~~ mass spectrometer ~~(Shimadzu), the instrument was~~ and equipped with an AOC-5000 autosampler~~.~~ (Shimadzu). Analytes were separated using a capillary column ZB-5MSPlus (Phenomenex). The mass spectrometer was equipped with ~~the~~an electron ionization source (EI, 70 eV) ~~and was operating~~which operated in the selected ion monitoring (SIM) mode. ~~For quantitative analyses GC/MS~~The instrument was calibrated with the standard solutions of ~~4-NP~~4NP, HH, 1,2,4-THB, ~~4-NC~~and 4NC that were identified as products of ~~4-NP~~ reaction ~~with OH.~~(I). 2-Nitrophloroglucinol was used as a surrogate standard for the quantification of 4-nitropyrogallol (~~4-NPG~~4NPG) and 5-nitropyrogallol (~~5-NPG)~~5NPG), both identified among the products of reaction ~~products. Phloroglucinol~~(I). Because phloroglucinol was not identified ~~among the~~as product of reaction (~~1~~I) (Zhao et al., 2013; Xiong et al., 2015~~; Zhao et al., 2013~~) ~~hence,~~ it was used, therefore, as an internal standard

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(IS). ~~Phenols~~The phenols were derivatized with acetic anhydrite (AA) and analyzed ~~via~~with GC/MS (Regueiro et al., 2009). ~~Detailed~~A detailed description of the analytical procedure is provided in section S4.2.

The yields of the phenols formed from reaction (I) were derived using eq. (I).

$$[Product]_t = Yield \times \Delta[4NP]_t \ (I)$$

In eq. (I), [Product]$_t$ is the concentration (or the sum of the concentrations) of the products at a given time (t) from the onset of the reaction (mM). [4NP] is the amount of the precursor which reacted at a given time (t) from the onset of the reaction (mM). The yield (molar) is derived as the slope of the initial, linear portion of the plot obtained using eq. (I) (Gierczak et al., 2021).

2.4 UV-Vis spectrophotometry

UV-Vis measurements were carried out ~~with~~by an i8 dual-beam spectrophotometer (Envisense) in 4~~-~~ml cuvettes with a 1~~-~~cm absorption pathlength~~. The~~; the spectral range was 230 to 600 nm. Absorbance of the aliquots of the reaction solution was initially measured at pH=2 or 9, which was the pH of the reaction mixture (section 2.2). Afterward, a small amount of NaOH or H_3PO_3 was added to each sample taken from the reactor, the pH was adjusted by 1 unit and the absorbance was measured again. This procedure was repeated until the absorbance of each aliquot of the reaction solution was ~~measured~~recorded between ~~wavelengths 230 and 600 nm. The pH of each sample taken from the reactor was adjusted between~~pH 2 and 9 (~~by intervals of 1, see~~ section S4.3~~) by adding a small amount of NaOH or H_3PO_4 solution in DI water. In a separate set of experiments~~). Separately, the wavelength-dependent absorption cross sections, ε, (~~base-e;~~ mol^{-1} × L × cm^{-1}) were measured (Fig. S4) for ~~4-NP~~4NP, HH, 1,2,4-BT, ~~4-NC~~4NC and 2-NPG ~~between~~ using the commercially available standards and are ~~reported~~listed in ~~appendix~~Appendix 1 ~~(Fig. S5).~~.

2.5 –Total organic carbon ~~analysis~~analyses

Non-purgeable organic carbon (NPOC) was ~~quantify~~quantified with a TOC-5050A analyzer (Shimadzu) ~~connected to the~~ equipped with an ASI-5000A autosampler (Shimadzu). The 1.5~~-~~ml of the reaction solution was diluted with the ~~1.5 ml of DI water.~~same volume of water, filtered through a 0.22 µm PTFE membrane and placed in the TOC autosampler vial. Then, 50~~-~~µl of 2M HCl was added ~~via~~by the ~~TOC~~ autosampler and each sample was ~~sparged~~purged with ~~oxygen~~O_2 for 2~~-~~min before being injected to remove the CO_2 and the sparingly soluble, volatile organic compounds. The injection~~. The injection~~ volume was ca. 20~~-~~µl and each sample was injected into the instrument three times. The TOC analyzer was calibrated with the standard solutions of ~~4-NP in DI water with~~

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~~concentrations between 3 and 35 mg$_{TOC}$ × L^{-1}; the squared linear coefficient of determination for calibration curve (R^2)=0.9995 was obtained.~~4NP (section S4.4).

2.6 Light ~~absorptivity~~absorption and atmospheric lifetimes

~~Production~~The production of light-absorbing compounds following reaction (I) was evaluated ~~via~~using eq. ~~I.~~(II).

$$\frac{\cancel{\left(\int_{250nm}^{600nm} A_{R.mix}(pH)\right)_t d\lambda}\left(\int_{250nm}^{600nm} A_{10}^{R.mix}(pH)\right)_t d\lambda}{\cancel{\left(\int_{250nm}^{600nm} A_{4-NP}(pH)\right)_t d\lambda}\left(\int_{250nm}^{600nm} A_{10}^{4NP}(pH)\right)_t d\lambda} = \left(\frac{[4-NP]_0}{[4-NP]_t}\right)^{K_{abs}} \quad (\cancel{I}II)$$

~~Where: A$_{R.mix}$~~In eq. (II), $A_{10}^{R.mix}$ and ~~A$_{4-NP}$~~A_{10}^{4NP} are integrated absorbance peak areas between 250 and 600 nm (dλ) for the reaction mixture measured between pH 2 and 9 at different time intervals (t), [~~4-NP~~4NP]$_0$ and [~~4-NP~~4NP]$_t$ are the initial (0) and intermediate (t) concentrations of ~~4-NP~~4NP measured with GC/MS, and the absorbance (~~A$_{4-NP}$~~A$_{4NP}$) of ~~4-NP~~4NP was calculated ~~with~~by the Beer-Lambert law using the ε measured in this ~~work~~study between pH 2 and 9. The expression described ~~using~~by eq. ~~I follows the~~(II) followed function $y = A \times x^K$ (section S8 and Fig. S9).

The atmospheric ~~lifetimes~~lifetime of BrC was evaluated by deriving the empirical k$_{bleaching}$ rate ~~coefficients~~constant (M^{-1}s^{-1}) – eq. ~~II.~~(III).

$$k_{bleaching=}\ k_{OH}\cancel{(4-NP)\times\frac{K_{A.rmix}}{K_{A.4-NP}}}\ (\cancel{II}(4-NP)\times\frac{k_{A.rmix}}{k_{A.4-NP}}\ (III)$$

In eq. (III),~~In eq. (II) the~~ k$_{OH}$ is the ~~bimolecular reaction~~ second-order rate ~~coefficient~~constant (M^{-1}s^{-1}) for the reaction of ~~4-NP~~4NP or 4-nitrophenolate (4NPT) with OH (~~Biswal et al., 2013;~~ García Einschlag et al., 2003; Biswal et al., 2013), k$_A$~~,~~ and k$_{A.rmix}$ are the first-order disappearance rate constants (min^{-1}) of the integrated absorbance peak for the ~~4-NP~~4NP and for the reaction mixture, respectively (Fig. ~~S9~~S8). The k$_{A.rmix}$ values derived showed little dependence on the pH at which the absorbance was measured, thus average values were used.

The ~~organic carbon based~~TOC-normalized mass~~-~~ absorption coefficients (~~MAC$_{Int}$~~MAC$_{TOC}$) of the reaction mixture were calculated ~~with~~using eq. ~~III~~(IV) (~~Jiang~~Laskin et al., ~~2021~~2015; Bluvshtein et al., 2017; Jiang et al., 2021).

$$\cancel{MAC_{Int}}MAC_{TOC}(\mathrm{cm}^2 \times g_{TOC}^{-1}) = \cancel{\frac{\ln(10)\times\int_{250nm}^{600nm}\alpha_\lambda \times d\lambda}{TOC}}\frac{\ln(10)\left(\int_{250nm}^{600nm} A_{10}^{R.mix}\times l_{solution}^{-1}\right)_t d\lambda}{NPOC} \times 10^{-6}\ (\cancel{III}IV)$$

In eq. ~~III, α$_\lambda$~~(IV), l is the ~~base-10 absorbance of the reaction mixture derived by the~~ optical ~~pathway length~~pathlength (cm^{-1}), ~~TOC~~NPOC is the concentration of non-purgeable organic carbon (mg × L^{-1}).

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The TOC-normalized rate of ~~absorption of~~ sunlight absorption (R_{abs}) by the reaction solution was ~~calculated with~~estimated using eq. ~~IV~~(V) (Jiang et al., 2021).

$$R_{abs}(\text{photons}\times s^{-1}\times mg_{TOC}^{-1}) = \cancel{\left(\frac{\ln(10)\times\int_{250nm}^{600nm}\alpha_\lambda\times I_\lambda\times d\lambda}{TOC}\right)\times 10^{-3}\ (IV}\left(\frac{\ln(10)\times\left(\int_{250nm}^{600nm}A_{10}^{R.mix}\times l_{solution}^{-1}\times I_\lambda\right)d\lambda}{NPOC}\right)\times 10^{-3}\ (V)$$

In eq. (V), I_λ is the actinic flux (photons× s^{-1}× cm^{-2}×nm^{-1}) estimated by the TUV calculator for zenith angles 0-50° (Ncar, 2016).

~~In eq. (IV), I_λ is the actinic flux (photons× s^{-1}× cm^{-2}×nm^{-1}) estimated with TUV calculator for zenith angles 0-50° (Ncar, 2016).~~

2.7 Control experiments and uncertainty

The stability of the phenols under investigation in the presence of H_2O_2 ~~and~~or UV-Vis irradiation ~~only~~alone was studied ~~by carrying~~in control experiments (section S6). Also, for the experiments at pH=2~~-~~, HCl or $HClO_4$ was used to confirm that the buffering agent used did not ~~affected~~affect the distribution of the detected products. ~~Control~~The control experiments revealed that all the phenols under investigation were stable at pH≤7, within the time-scale of the experiments, but 1,2,4-THB, ~~4-NPG, 5-NPG~~4NPG, 5NPG and HH underwent irreversible dark reactions at pH>7.

Experimental uncertainties are reported as 2σ from triplicate measurements, other uncertainties were calculated with the exact differential method, unless ~~noted~~ otherwise noted.

3~~-~~. Results and discussion

3.1 Products and reaction mechanism

~~As presented~~The products of reaction (I) formed under acidic pH conditions are shown in Fig. ~~S4,~~ 1.

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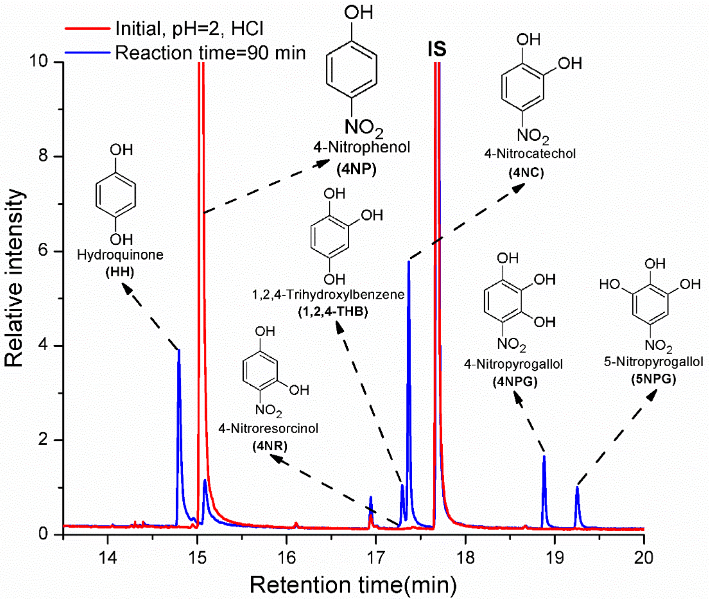
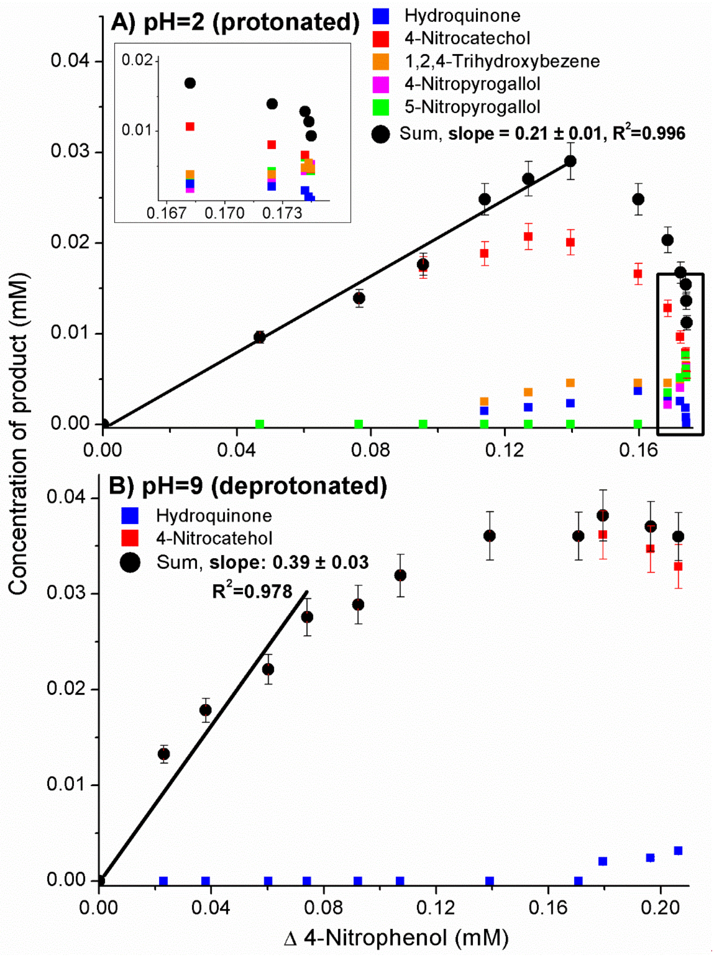


Figure 1: GC/MS chromatogram illustrating the formation of phenols from reaction (I) at pH=2.

HH, 1,2,4-THB, ~~4-NC~~4NC and ~~5-NPG~~5NPG were formed following reaction (~~1~~I) under acidic pH conditions~~,~~ (Fig.1), which is in ~~a~~ good agreement with the previously published results (~~Xiong et al., 2015;~~ Oturan et al., 2000; Tauber et al., 2000; Liu et al., 2010; Xiong et al., 2015; Du et al., 2017; Chen et al., 2018). ~~4-Nitroresorcinol (4-NR) was also tentatively identified among the products. Isomers of 4-NC~~Previously, two unknown isomers of 4NC were ~~previously reported~~detected as products of ~~4-NP oxidation by OH but the exact structures were not proposed for these compounds~~reaction (I) (Zhao et al., 2013).

~~To our knowledge~~Here, 4-nitroresorcinol (4NR), a structural isomer of 4NC, was also tentatively identified among the products for the first time. Moreover, this ~~work~~study is first to report the formation of ~~4-NPG~~4NPG from reaction (~~1).~~I) (Xiong et al., 2015). Previously, detection of ~~isomeric~~these two products (~~4-NR~~4NR and ~~4-NPG~~4NPG) might have been difficult to observe due to the lack of standards and the absence of ~~the~~an MS detector (Tauber et al., 2000; ~~Liu et al., 2010;~~ Daneshvar et al., 2007; Liu et al., 2010). Also, the insufficient resolving power of the HPLC used to ~~investigate~~study the ~~composition of~~ products of reaction (I) likely contributed to the fact that the formation of ~~4-NR~~4NR and ~~4-NPG~~4NPG was not previously ~~observed~~reported (Lipczynska-Kochany, 1991; Oturan et al., 2000; Tauber et al., 2000; ~~Liu et al., 2010;~~ Daneshvar et al., 2007; ~~Lipczynska-Kochany, 1991~~Liu et al., 2010).

The phenolic products from reaction (~~1~~I) were quantified with GC/MS; the results are presented in Fig. ~~1~~2.


A) pH=2 (protonated)
🟦 Hydroquinone
🟥 4-Nitrocatechol
🟧 1,2,4-Trihydroxybezene
🟪 4-Nitropyrogallol
🟩 5-Nitropyrogallol
● Sum, slope = 0.21 ± 0.01, R²=0.996
0.02
0.01
0.167
0.170
0.173
0.00
0.01
0.02
0.03
0.04
0.00
0.04
0.08
0.12
0.16
B) pH=9 (deprotonated)
🟦 Hydroquinone
🟥 4-Nitrocatehol
● Sum, slope: 0.39 ± 0.03
R²=0.978
0.00
0.01
0.02
0.03
0.04
0.00
0.04
0.08
0.12
0.16
0.20
Concentration of product (mM)
Δ 4-Nitrophenol (mM)

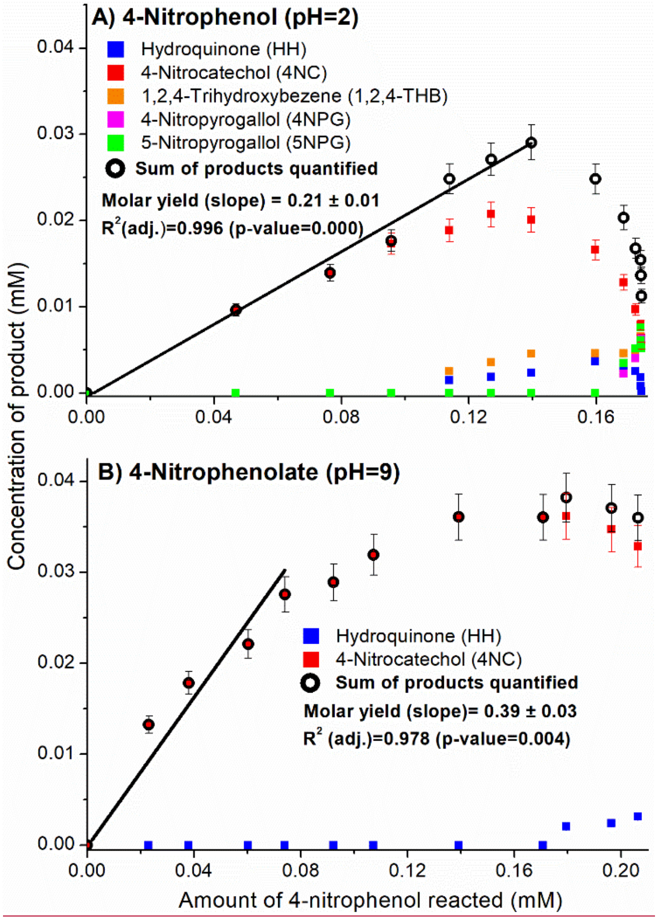


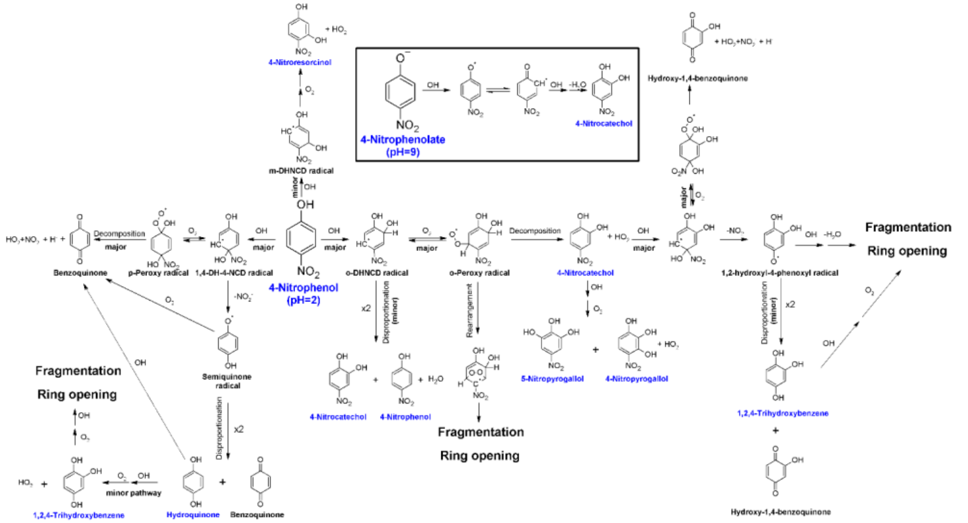
Figure ~~1: Formation~~2: The formation of phenolic products ~~following the~~from the 4-nitrophenol (A, pH=2) and 4-nitrophenolate (B, pH=9) + OH reaction ~~with protonated (A) and deprotonated (B) forms of 4-NP. The slopes were derived from the linear regression analysis of the initial section of the plots, linear coefficients of determination (R^2)≥0.97 were obtained.~~. Uncertainties of the yields obtained from eq. (I) are standard errors from the linear regression analysis.

~~Results of the experiments carried out in unbuffered solution are not included in Fig. 1. Due to the formation of nitrite (NO_2^-) and nitrate (NO_3^-) ions (Kotronarou et al., 1991; Lipczynska-Kochany, 1991; Liu et al., 2010; Kavitha and Palanivelu, 2005), pH of the reaction solution quickly decreased to about 3.5 (Di Paola et al., 2003). Hence, the distribution of products in the acidic and unbuffered solutions was the same.~~

~~4-NC~~ Adjusted linear coefficients of the determination (R2) >0.97 and p-values <0.05 were obtained, confirming that the linear correlation was statistically significant. The values of the standardized residuals from the linear regression analyses were all <3, confirming that none of the data points included in the regression analysis should be classified as an outlier (Table S2).

The results of the experiments carried out in pure water (no acids or buffers added) are not included in Fig. 2. The pH of the reaction solution quickly decreased to ca. 3.5 (Di Paola et al., 2003), likely due to the formation of nitrite (NO_2^-) and nitrate (NO_3^-) (Kotronarou et al., 1991; Lipczynska-Kochany, 1991; Kavitha and Palanivelu, 2005; Liu et al., 2010). For this reason, the distribution of products in the acidic reaction solution and in pure water was the same.

As presented in Fig. 2, 4NC was the major product ~~detected (Fig. S4),~~formed in both the acidic ~~solution, the~~ and basic reaction solutions. The other products detected were HH, 1,2,4-THB, ~~4-NPG~~4NPG and ~~5-NPG~~5NPG. The proposed mechanism of reaction (~~1~~I) is ~~shown~~presented in Fig. ~~2~~3.



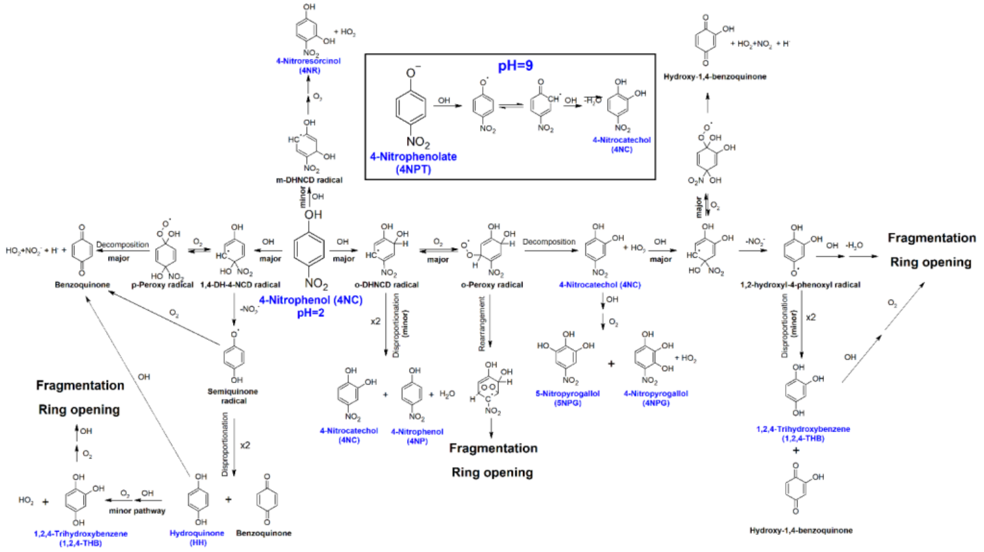


Figure ~~2~~3: The proposed mechanism for the reaction of OH with 4-nitrophenol in ~~the~~an aqueous solution. ~~Names~~The names of the compounds detected ~~in this work~~with GC/MS are shown in blue.

~~**As presented in Fig. 2, the electrophilic addition of OH to 4-NP yields dihydroxynitrocyclohexadienyl (DHNCD) radicals (Kotronarou et al., 1991; Di Paola et al., 2003; Kavitha and Palanivelu, 2005). Due to the combined directing effects of -OH (electron-donating) and -NO₂ (electron-withdrawing) substituents, OH preferentially adds in the ortho position, resulting in 1,2-dihydroxy-4-nitrocyclohexadienyl radical (ortho-DHNCD radical) (Zhao et al., 2013; Gonzalez et al., 2004; Tauber et al., 2000). Two o-DHNCD radicals can undergo disproportionation reaction to produce 4-NP and 4-NC (Gonzalez et al., 2004; Tauber et al., 2000; Liu et al., 2010) or react with molecular oxygen (Gonzalez et al., 2004; Di Paola et al., 2003; Oturan et al., 2000). Reaction of o-DHNCD radical with O₂ produces the o-peroxy radical which can rearrange, yielding a non-phenolic products, or decompose to produce 4-NC and a hydroperoxyl radical (Di Paola et al., 2003; Kotronarou et al., 1991; Gonzalez et al., 2004; Oturan et al., 2000; Liu et al., 2010). Due to the measured yield of 4-NC of 0.21 (Fig. 1) it is reasonable to assume that the o-peroxyradicals preferentially decompose to ring-opening products. Alternatively, the decomposition of the o-peroxyradicals yields 4-NC, a major phenolic product detected (Di Paola et al., 2003; Xiong et al., 2015; Ding et al., 2016; Oturan et al., 2000; Liu et al., 2010). OH addition in meta position results in the formation of meta-DHNCD radical; this minor pathway leads to the formation of 4-NR (Fig. 2).**~~ **Note that~~,~~ for clarity, ~~the~~all possible fragmentation and reaction pathways~~, leading to~~ of the ~~formation of ring-opening~~ radical by-products~~,~~ are not shown ~~in Fig. 2 for all peroxyradicals.~~**

~~4-NPG and 5-NPG are likely formed from 4-NC via analogous mechanism, OH addition to the aromatic ring followed by reaction with molecular oxygen~~ Reaction (I) is initiated by the electrophilic addition of OH, primarily in the ortho and para positions of 4NP, yielding dihydroxynitrocyclohexadienyl (DHNCD) radicals – Fig. 3 (~~Du~~Kotronarou et al., ~~2017; Ding et al., 2016; Xiong et al., 2015; Zhang~~1991; Di Paola et al., 2003; ~~Oturan et al., 2000~~Kavitha and Palanivelu, 2005)~~. This was also confirmed by the experimental data reported in section S7. Interestingly, only trace amounts of 1,2,4-THB were formed from OH+4-NC reaction (Fig. S6). When the 4-NC was oxidized in the unbuffered solution (DI water), the initial pH was approx.~~

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~~6.3 but quickly decreased to 3.3 thereby excluding the potential hydrolysis reaction of 1,2,4-THB under these experimental conditions (Table~~ . Two ortho-DHNCD radicals can then disproportionate to form 4NC and regenerate 4NP.~~S1).~~

~~It was previously proposed that 1,2,4-THB is formed by the addition of OH in para position of 4-NC (ipso attack) followed by elimination of $NO_2^{\bullet}$~~ (~~Daneshvar~~Tauber et al., ~~2007; Zhang~~2000; Gonzalez et al., ~~2003; Kavitha and Palanivelu, 2005~~2004; Liu et al., 2010; Zhao et al., 2013)~~, but this assumption was never confirmed experimentally. It is still unclear whether or not the 1,4-hydroxy-4-nitrocyclohexadienyl type radicals primarily eliminate $NO_2^{\bullet}$ to yield stable phenolic products or decompose to phenoxyl radicals and NO_2^-~~ Alternatively, 4NC is formed by reaction of o-DHNCD with O_2 and decomposition of the resulting o-peroxy radical (~~O'neill~~Oturan et al., ~~1978; Kotronarou et al., 1991; Xiong et al., 2015;~~ 2000; Di Paola et al., 2003; Liu et al., 2010; Xiong et al., 2015; Ding et al., 2016)~~. The limited literature data available indicate that the elimination of NO_2^- is more likely~~ . Due to the low molar yield of phenols at pH=2 (0.21), the ortho-addition primarily yields ring-opening products. The addition of OH in the meta position of 4NP (minor pathway) leads to the formation of 4-NR (Fig. 1). Likewise, 4NPG and 5NPG (second-generation products) are most likely formed following the 4NC+OH reaction, which also involves the formation of a peroxy-type radical.

Moreover, only trace amounts of 1,2,4-THB were formed from 4NC+OH under acidic conditions – see also section S7 and Fig. S5 (~~O'neill~~Oturan et al., ~~1978; Kotronarou~~2000; Zhang et al., ~~1991~~2003; Xiong et al., 2015; Ding et al., 2016; Du et al., 2017)~~, which would also explain the fast decrease in pH observed during OH+4-NC reaction and the absence of 1,2,4-THB among the major products (Fig. S6). The trace amounts of 1,2,4-THB formed from OH+4-NC reaction are likely due to minor disproportionation reaction of the two phenoxy radicals (Liu et al., 2010). It was previously reported that 4-NC was quantitatively converted into 1,2,4-THB in the absence of O_2, which effectively promoted the disproportionation reaction between two 1,2-hydroxyl-4-phenoxyl radicals (Gonzalez et al., 2004; Liu et al., 2010; Di Paola et al., 2003). These results are in a good agreement with the experimental data acquired in this work.~~

~~Ipso addition of OH to 4-NP results in the formation of 1,4-dihydroxy-4-nitrocyclohexadienyl (1,4-DH-4-NCD) radical (Fig. 2)~~ . As previously reported, 4NC was quantitatively converted into 1,2,4-THB in the absence of O_2, which promotes the disproportionation reaction between the two 1,2-hydroxyl-4-phenoxyl radicals formed by the ipso addition of OH to 4NC (Di Paola et al., 2003; Gonzalez et al., 2004; Liu et al., 2010). Hence, in the presence of O_2, the formation of 1,2,4-THB from the 4NC+OH reaction is expected to be a minor process (Liu et al., 2010), which is consistent with the experimental data reported in section S7. Consequently, it is proposed that 1,2,4-THB is likely formed following the ipso addition of OH to 4NP (~~O'neill~~Zhang et al., ~~1978~~2003; Kavitha and Palanivelu, 2005; Daneshvar et al., 2007~~; Kotronarou et al., 1991~~). ~~This~~The resulting 1,4-hydroxy-4-nitrocyclohexadienyl (1,4-DH-4-NCD) type radical ~~likely eliminates~~can then eliminate NO_2^- ~~to produce benzoquinone (BQ), thereby contributing to~~, producing HH and 1,2,4-THB by the ~~observed decrease in pH in the unbuffered reaction mixture~~disproportionation mechanism (~~Al-Suhybani and Hughes, 1985; Gonzalez~~O'neill et al., ~~2004~~1978; Kotronarou et al., 1991)~~. Consequently, HH is likely produced via disproportionation of two semiquinone radicals, which is evidently a more favorable reaction than the analogous reaction between the two 1,2-hydroxyl-4-phenoxyl radicals~~ . The formation of NO_2^- is also consistent with the observed rapid decrease in the pH of the unbuffered reaction solution.

Previously, the formation of 1,2,4-THB from the reaction of OH with HH was observed (~~Kotronarou~~Niessen et al., ~~1991~~1988; Barzaghi and Herrmann, 2002; Sobczyński et al., 2004)~~. Previously, the formation of 1,2,4-THB from the reaction of OH with HH was observed~~ . Therefore, under the experimental conditions used in this study, the low yield of HH is likely due to its rapid oxidation to 1,2,4-THB and BQ (not quantified) (~~Barzaghi and Herrmann, 2002; Niessen~~Kotronarou et al., ~~1988~~1991; Oturan et al., 2000; Di Paola et al., 2003; Sobczyński et al., 2004; Gonzalez et al., 2004)~~. Evidently, under the experimental conditions used in this work, HH is rapidly oxidized to 1,2,4-THB and BQ resulting in the low yield measured for this product (Fig. 1A)~~ .

Due to the irreversible reactions of some phenols under investigation at pH=9 (Table S3), only 4NC and HH were detected as products of reaction (I) from 4-NPT – Fig. 2B. At the same time, the total yield of phenols produced (mainly 4NC) increased from 0.21 (pH=2) to 0.39. At pH=9, reaction (I) can proceed by addition as well as by one-electron oxidation mechanisms, as shown in the inset in Fig. 3 (~~Sobczyński~~Biswal et al., ~~2004; Kotronarou~~2013; Zhao et al., ~~1991; Di Paola et al., 2003; Gonzalez et al., 2004; Oturan et al., 2000~~2013).

~~Lower number of products was observed at pH=9, likely due to hydrolysis or other~~ The reactions of ~~HH, 1,2,4-THB, 4-NPG and 5-NPG. Additionally,~~ the ~~yield of 4-NC was increased (Fig. 1B) at pH=9. The 4-nitrophenolate (Fig. S1) is expected to react via mixed mechanism:~~4-nitrophenolxyl radicals formed following the one-electron oxidation ~~and~~of 4NPT by OH ~~addition – Fig. 2~~are unclear (~~Biswal~~Gonzalez et al., ~~2013~~2004; Wojnárovits and Takács, 2008; Liu et al., 2010; Zhao et al., 2013)~~. The subsequent reactions of 4-nitrophenolxyl radicals formed following the one-electron oxidation are unclear~~ . It was proposed (~~Gonzalez~~Niessen et al., ~~2004; Liu et al., 2010; Zhao et al., 2013; Wojnárovits~~1988; Barzaghi and ~~Takács, 2008~~Herrmann, 2002)~~. Similar, semiquinone radicals were shown to react with~~ ~~O_2~~ ~~or disproportionate (Valgimigli et al., 2008; Gonzalez et al., 2004). However, these reactions cannot explain the much higher yield of 4-NC in basic solution (Fig 1B). It was proposed that the resonance forms of phenoxyl radicals may react directly with OH and~~ ~~NO_2~~~~, which leads to the formation of stable phenolic products (Fig. 2) (Barzaghi and Herrmann, 2002; Niessen et al., 1988). This mechanism would explain factor of 2 higher yield of 4-NC in basic solution (Fig. 1B). Analogous reaction of 1,2-hydroxyl-4-phenoxyl radical likely leads to ring-opening products, as previously reported (Liu et al., 2010).~~

~~In a concentrated (160 mM) basic solutions, 1,2,4-THB was shown to generate stable aromatic oligomers with the absorbance between 400-700 nm (Randolph et al., 2018). Detecting such oligomers with GC/MS is unlikely due to their lower volatility, insufficient thermal stability or low reactivity towards AA (section 2.3). However, at pH>7 the integrated absorbance of the reaction solution in this spectral range is lower as compared with the acidic solution, as discussed in more detail in section 3.2. Hence, the formation of "brown" phenolic oligomers from 1,2,4-THB is evidently suppressed in a more diluted solution and in the presence of nitrated phenols,~~ ~~NO_2^-~~ ~~and~~ ~~NO_3^-~~ ~~ions.~~

that such radicals can exist in two resonance forms; in the case of 4NP, one of these resonance forms may directly react with OH to produce 4NC. This mechanism would explain the higher yield of 4NC from reaction (I) under basic pH conditions.

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3.2 Light ~~absorptivity~~absorption and the time-evolution of brown-carbon chromophores

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~~A continuous decrease of the~~The absorbance of the reaction solution ~~was observed~~ decreased during the course of the reaction (section S8~~). On the other hand~~) for both 4NP and 4NPT. Previously, an initial~~,~~ small increase in the absorbance at 420~~-~~ nm of the ~~4-NP~~reaction 4NP solution ~~during reaction with OH~~(pH=5) was ~~previously~~ reported, followed by a rapid bleaching (Zhao et al., 2015); ~~such~~these differences can be caused by the slightly different reaction conditions used. Also, in this ~~work, an~~study, integrated absorbance values were used ~~(~~[eq. ~~I~~(II) and ~~II)~~(III)] which may be a more adequate approach due to the shifting of the ~~absorption~~ maximum absorbance (A_{max}) ~~-~~of the reaction solution (Fig. ~~S8~~S7) (Zhao et al., 2015; Hems and Abbatt, 2018). The contribution of the light-absorbing products of reaction (~~1~~I) to the ~~overall light absorptivity~~ absorption of the reaction solution was evaluated ~~via~~with eq. ~~I. Results presented~~ (II) – the results are shown in Fig. ~~S10 show~~4.

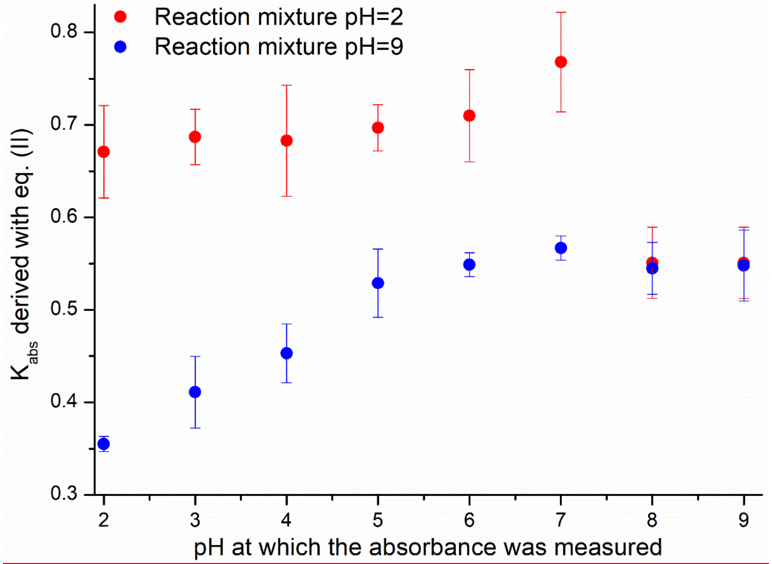
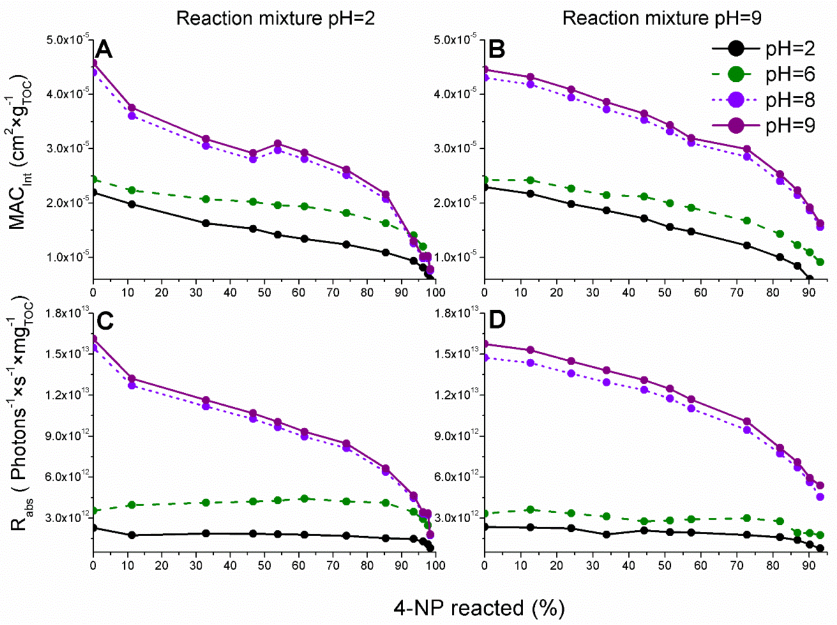


Figure 4: The ability of 4NP to generate products with an absorbance between 250 and 600 nm evaluated with Kabs factors derived using eq. (II). Uncertainties are precisions from the regression analysis.

The results presented in Fig.4 indicate that when the reaction was carried out under basic pH conditions the relative absorbance of the products~~ (eq. I)~~ was lower and increased more slowly. ~~This points out that~~ The absorbance of the products generated from 4NP (pH=2) decrease sharply when the pH of the solution before the UV-Vis measurement was adjusted to 8 and 9. Such a result indicates that the light-absorbing compounds are not stable at pH>7 which is in a good agreement with the results ~~discussed~~presented in ~~section~~sections 3.1 and S6 (Randolph et al., 2018). The observed increase in the light absorption of the reaction solution (pH=9) between pH=2 and 9 could be due to the pH-dependence of the absorbance of the substituted carboxylic acids; aromatic ring-opening products (Oturan et al., 2000; Zhang et al., 2003; Kavitha and Palanivelu, 2005; Hems and Abbatt, 2018) with pK_a values likely falling between 3 and 6 (Rapf et al., 2017).

The values of ~~MAC_{init}~~MAC_{TOC} and R_{abs} calculated ~~with~~using eq. ~~III~~(IV) and ~~IV~~(V) are presented in Fig. ~~3~~5.



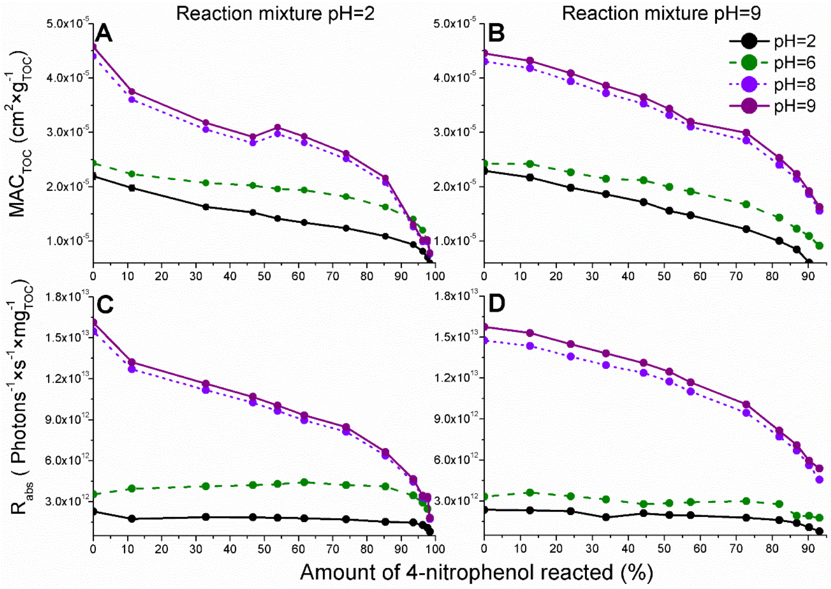


Figure ~~3~~5: The pH~~-~~-dependent organic carbon-~~based~~normalized mass absorption coefficients (~~MACint~~MACTOC) derived using the integrated absorbance peak for the reaction mixture ~~absorptivity~~absorption measured for the reaction of ~~4-NP~~4NP (A, pH=2) and ~~4-nitrophenolate~~4NPT (B, pH=9) and the corresponding TOC-normalized rates of sunlight absorption (Rabs) for ~~of 4-NP~~4NP (C) and ~~4-nitrophenolate~~4NPT (D). Only the data for pH =2, 6, 8, 9 is shown for clarity and the complete data is presented in Fig. ~~S12. Experimental data is~~ S10. The colors refer to the pH at which the absorbance was measured (section 2.4). The experimental data are represented by points, with the lines ~~are~~ provided to guide the eye.

As ~~expected, MACint decreased steadily~~presented in Fig. 5, a decrease in the calculated MAC_{TOC} was observed during the course of reaction (I). Moreover, the experimental data acquired shows an increase of MAC_{TOC} following the ~~oxidation of the precursor. The experimental data acquired (Fig. 3) show a clear increase in absorptivity following the~~ increase in pH at which the absorbance was measured (2, 6, 8 or 9). Such a result is likely due to ~~pH-depended~~the higher ε values for ~~the light-absorbing phenols present in the reaction solution.~~ 4NP and 4NC under basic pH conditions (Fig. S4).

In Fig. ~~3A~~5A and ~~B~~5B, the disappearance ~~rates~~rate constants of ~~MACint~~MAC_{TOC} are of a similar order ~~(Table S3).~~. This is most likely due to the formation of a higher number of light-absorbing phenols (second-generation products) at pH=2 and also due to the higher yield of ~~4-NC (~~4NC, which ~~is characterized by~~has high ε values~~, Fig. S5)~~ at pH=9~~, respectively.~~. Consequently, the ~~rates of~~ disappearance rate constants of the overall light ~~absorptivity~~absorption of ~~4-NC~~4NC following reaction (~~1~~I) are mostly independent on the pH of the reaction solution and primarily depend on the pH at which the absorbance is measured. The ~~MACInt~~MAC_{TOC} values calculated were slightly higher ~~as~~ compared with the values measured for the

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previously investigated aromatic BrC chromophores (~~for~~derived from the non-nitrated precursors) (Jiang et al., 2019; Jiang et al., 2021), likely due to the high ε values of ~~4-NP~~4NP and the nitrated phenols ~~formed following~~generated by reaction (~~1~~I). The R_{abs} values (Fig. ~~3C~~5C and ~~D~~5D) decrease ~~more slowly as~~slower compared with the values of ~~MAC_{Int}, which is caused by~~MAC_{TOC} and become stable when the pH at which the absorbance was measured is less than 7 (see also Fig. S10). This is likely due to a red-shift of the A_{max} of the reaction solution ~~combined with the pH – dependence of ε values of the 4-NP and phenolic products (for instance,~~, likely connected to the red-shift of ~~A_{max}~~the 4NP and 4NCs absorbance following the increase ~~of~~in the pH ~~observed for 4-NC, (~~(Fig. S4). As presented in Fig. ~~S5). Also, because of~~S12, the actinic flux exhibits a significant increase ~~in the actinic flux at λ>400 nm (Fig. S14), any “brown” products formed efficiently stabilize the~~when λ>400 nm. Consequently, the BrC chromophores – products of reaction (I) – characterized by a strong absorbance above 400 nm, will contribute to the observed stabilization of the estimated R_{abs} ~~values thought the course of the reaction when pH<7 - see also Fig. S12~~at pH<7.

~~4. Conclusions~~3.3. Atmospheric implications

The average measured Henry’s law constant~~,~~ – 5×10^4 ($M\times atm^{-1}$~~),~~) – indicates that ~~4-NP resides~~4NP exists entirely in the aqueous~~-~~ phase in clouds but not in “wet” aerosols (Fig. ~~S13) where it can undergo chemical and photochemical processing~~S11) (Herrmann et al., 2015). Once dissolved in cloud water, 4NP can undergo chemical and photochemical processing; thus, the rates of the bleaching of the 4NP solution due to the reaction with OH were evaluated – Table 1.

Table 1. The pH-dependent second-order rate constants, empirical bleaching rate constants and the effective quantum yields of photolysis used to estimate the lifetimes of 4NPs and the corresponding BrC

Reactive species	**$K_{A.4NP}$ (min^{-1})**	**$K_{A.rmix}$ (min^{-1})**	**$k_{OH}\times10^{-9}$ ($M^{-1}s^{-1}$)**	**Reference**	**$k_{bleaching}\times10^{-9}$ ($M^{-1}s^{-1}$) (this work)**	**Lifetime of BrC relative to the lifetime of 4NP**
			Reaction with OH			
4NP (pH<3)	0.047	0.016	6.2 4.1 3.8 4.7	(Biswal et al., 2013) (García Einschlag et al., 2003) Average literature value	1.6	3
4NPT (pH>8)	0.029	0.019	8.7	(Biswal et al., 2013)	6.0	1.5

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Photolysis

Reactive species	ϕ (molecules ×photon^{-1}) × 10^6	Reference
4NP (pH<3)	110.0[a]	(Lemaire et al., 1985; Braman et al., 2020)
4NPT (pH>8)	5.5	(Lemaire et al., 1985)

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[a] The average quantum yields measured in the presence of photorecalcitrant *α*-pinene SOA used as a scavenger of the secondary OH formed following the photolysis of HONO formed during the photolysis of 4NP.

Presented in Table 1, the first-order $k_{bleaching}$ ~~coefficients~~ rate constants were derived ~~via~~with eq. (II~~(~~) using the experimental data acquired in this study and the lifetimes due to the reaction with OH were estimated with eq. SIII. The data summarized in Table ~~S3) show~~1 shows that the lifetimes of BrC chromophores are 3 and 1.5-times longer than the lifetime of ~~4-NP~~4NP (precursor) under acidic and basic pH conditions, respectively, due to the formation of light-absorbing products. ~~The rates of bleaching of 4-NP solution due to reaction with OH and due to direct photolysis were compared (Fig. 4) using the $k_{bleaching}$ values derived in this work and the~~

The previously reported~~,~~ average quantum yields (ϕ, molecules×photon^{-1}) ~~—see Table S3 and eq. SIII and IV~~ (~~Braman et al., 2020;~~ Lemaire et al., 1985; ~~Biswal et al., 2013;~~ García Einschlag et al., 2003; Biswal et al., 2013; Braman et al., 2020) were used to derive the lifetimes of 4NP due to photolysis using eq. SIV.~~. The~~ The literature ϕ values listed in Table ~~S3~~1 were derived by measuring the decrease in the absorbance of ~~4-NP~~the 4NP solution, hence can be regarded as effective ϕ for the bleaching of ~~4-NP and 4-nitrophenolate-derived BrC.~~chromophores in aqueous solutions of 4NP and 4NPT.(Lemaire et al., 1985; Braman et al., 2020) To our knowledge, the wavelength-dependent ϕ values for ~~4-NP and 4-nitrophenolate are not available.~~4NP and 4NPT are not available. The estimated lifetimes of light-absorbing compounds in the cloud water particles containing 4NP due to direct photolysis and due reaction with the OH were compared (Fig. 6).

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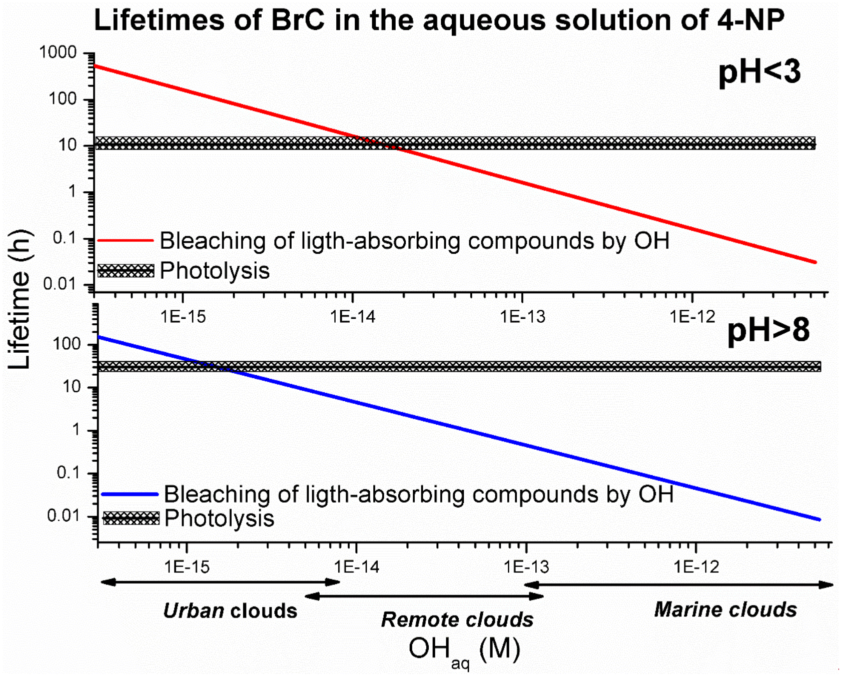
Lifetimes of BrC in the aqueous solution of 4-NP
pH<3
pH>8
Lifetime (h)
1000
100
10
1
0.1
0.01
Bleaching of ligth-absorbing compounds by OH
Photolysis
1E-15
1E-14
1E-13
1E-12
Urban clouds
Remote clouds
Marine clouds
OH$_{aq}$ (M)

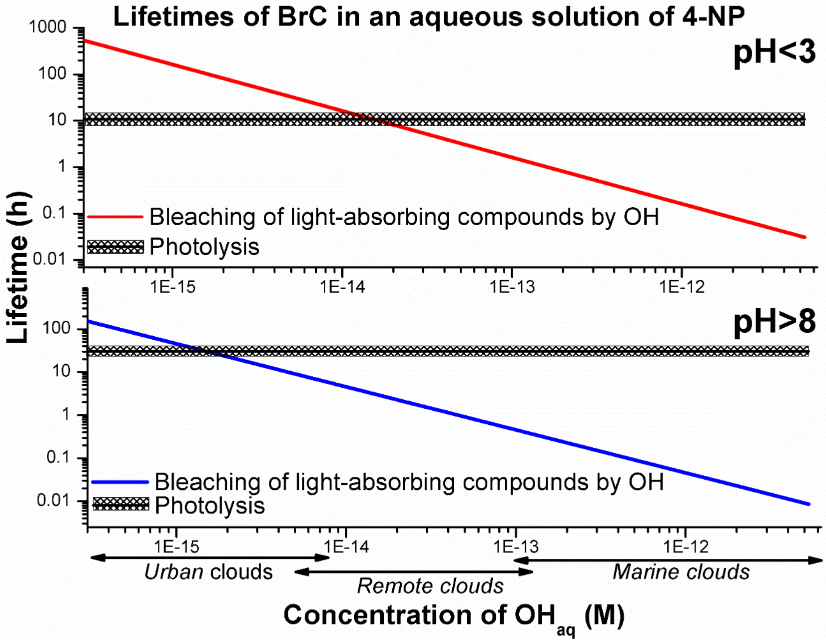

Figure ~~4~~6: The estimated aqueous-phase lifetimes of light-absorbing compounds in ~~the~~ solutions of ~~4-NP~~4NP and ~~4-nitrophenolate~~4NPT due to the reaction with OH and direct photolysis. The lifetimes due to the reaction with OH were calculated with $k_{bleaching}$ ~~coefficients~~rate constants derived ~~via eq. II~~ with eq. (III) using the experimental data acquired in this ~~work~~study. The average lifetime due to photolysis is shown ~~for zenith angles 0–50°,~~, shaded ~~area is~~areas are 2σ values, representing the range of photolysis lifetimes calculated ~~via eq.~~ for the solar zenith angles 0–50°. ~~SIV.~~

As presented in Fig. ~~4, both bleaching mechanisms can~~6, the photolysis of 4NP BrC may be relevant under realistic atmospheric conditions~~, depending from [OH].~~ in urban and remote clouds, with the estimated concentration of OH_{aq} lower than 1×10^{-13} M (Herrmann et al., 2010). Bleaching by OH is expected to be a more ~~dominant pathway~~efficient removal mechanism for ~~4-nitrophenolate~~4NPT, due to its lower reported quantum yields (ϕ) combined with the higher OH reactivity of the precursor at pH>8 (Lemaire et al., 1985; Braman et al., 2020).

A low degree of mineralization of the precursor (ca. 15%) was observed for both 4NP and 4NPT, as presented in Fig. 7.

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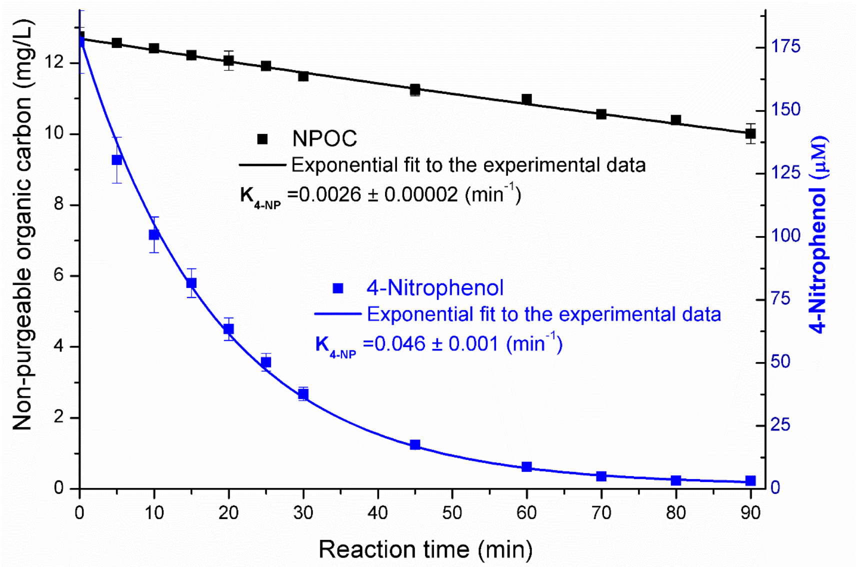

Figure 7: The concentrations of 4NP and non-purgeable organic carbon during the reaction in pure water (the results obtained for pH=2 and 9 reaction solutions were very similar – section S11). The uncertainties for the first-order decay rates (K, min-1) are standard errors from the regression analysis.

Due to the low degree of mineralization of 4NP (Fig. 7) combined with the yields of phenolic products calculated as ~0.2 (pH=2) and ~0.4 (pH=9), it is estimated that the yield of non-aromatic products from reaction (I) was between 0.45 and 0.65. These aromatic ring-opening products may include functionalized carboxylic acid, as previously proposed (Oturan et al., 2000; Zhang et al., 2003; Kavitha and Palanivelu, 2005; Hems and Abbatt, 2018).

4. Conclusions

The results acquired in this study show that the reaction of OH with 4NP in cloud water leads to the bleaching of light-absorbing compounds. Previously, the reaction with ~~the~~ OH was concluded to be ~~the~~a major removal ~~mechanisms~~mechanism for a number of nitrophenols in the atmospheric aqueous phase (~~Zhao et al., 2015;~~ Vione et al., 2009; Albinet et al., 2010; Zhao et al., 2015)~~. In the context of the formation and processing of the atmospheric BrC, reaction of OH with 4-NP leads to the removal of light-absorbing compounds. At the same time, it was previously concluded that~~ . As previously reported, the reaction of OH with 5-nitroguaiacol, ~~4-NC~~4NC and dinitrophenol initially ~~lead~~leads to ~~the~~a small increase in the light-~~absorptivity~~ absorption followed by ~~a~~ rapid bleaching ~~of the reaction solution~~ (Zhao et al., 2015; Hems and Abbatt, 2018~~; Zhao~~

~~et al., 2015~~)~~. The results described~~ but such behavior was not observed for 4NP in this ~~work and~~study. By comparing the results obtained in this study with the literature data (Zhao et al., 2015; Hems and Abbatt, 2018~~; Zhao et al., 2015~~) ~~indicate~~, it can also be concluded that more substituted nitrophenols initially yield higher amounts of light-absorbing products ~~as~~ compared with ~~4-NP~~4NP. Moreover, the atmospheric lifetimes of BrC chromophores due to the reaction with OH are expected to be significantly longer than the lifetimes of the parent nitrophenols (precursors) due to the formation of ~~aromatic,~~ light-absorbing by-products (Zhao et al., 2015; Hems and Abbatt, 2018~~; Zhao et al., 2015~~).

~~Based on GC/MS quantitative~~The results obtained here and the literature data ~~it was estimated~~also indicate that ~~in~~the aqueous reaction ~~(1) ca. 20 to 40%~~ of ~~4-NP, depending on pH, was converted into phenolic products. A low degree of mineralization of the precursor (ca. 15% - section S15) and up to 40% yield of phenolic products indicates that reaction (1) generates a substantial amount, between 45 to 65%, of non-aromatic products, like for instance functionalized carboxylic acid (Hems and Abbatt, 2018; Kavitha and Palanivelu, 2005; Zhang et al., 2003; Oturan et al., 2000). Consequently, reaction (1) and reaction of other~~ nitrophenols with OH can potentially contribute to cloud water acidity ~~of atmospheric aqueous particles via~~due to the formation of NO_2^-~~–;~~, NO_3^- and organic ~~(nitrated)~~nitro carboxylic acids (Tilgner et al., 2021). Additionally, the aqueous oxidation of nitrophenols ~~via~~by OH may be ~~a~~an important source of potentially toxic and harmful aqueous SOAs ~~($_{aq}$SOAs).~~due to the formation of nitrogen-containing organic compounds combined with the low degree of mineralization of such precursors.

Data availability. The raw data can be obtained by contacting the corresponding author.

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Author contributions. BW designed the study, developed the methodology, analyzed the data and wrote the paper. PJ carried out the experiments, optimized the methodology and processed the raw data~~;~~. TG supervised the experiments, analyzed the data and contributed to the final manuscript. All authors contributed to the interpretation of the results.

*Competing interests***.** The authors declare that they have no ~~conflict~~conflicts of interest

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measurements possible. We thank ~~dr Marcin Wilczek~~the anonymous reviewers for the ~~NMR measurements.~~ very insightful comments and suggestions.

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