

Review

# Review of the Mechanisms of Liquid-Phase Transformation of Atmospheric Phenolic Compounds: Implications for Air Quality and Environmental Health

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**Abstract:** Phenolic compounds (PhCs) are aromatic compounds with benzene rings that have one or more hydroxyl groups. They are found or formed in the atmosphere due to various factors such as combustion processes, industrial emissions, oxidation of volatile organic compounds (VOCs), and other photochemical reactions. Due to properties such as relatively high Henry's law constants and moderate/high water solubility, PhCs are vulnerable to reactions in atmospheric liquid phase conditions with high relative humidity, fog or cloudy conditions. PhCs can lead to the formation of secondary organic aerosols (SOAs), which can have negative effects on atmospheric conditions and human health. Changes in the optical properties of PhCs impact solar radiation absorption and scattering, potentially influencing climate. Additionally, PhCs may interact with other atmospheric constituents, potentially affecting cloud or fog formation and properties, which in turn can impact climate and precipitation patterns. Therefore, monitoring and controlling the emission of PhCs is essential. This paper discusses the transformation processes of PhCs in the atmosphere, including direct conversion of phenol, nitrate-induced and nitrite-induced reactions, hydroxylation reactions and oxidation processes involving triplet excited state organics, also providing a detailed analysis of the transformation processes. The findings lay a theoretical foundation for the future monitoring and control of atmospheric pollutants.

**Keywords:** phenolic compounds (PhCs); photoconversion; secondary organic aerosols (SOAs)



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## 1. Introduction

Observational studies reveal that organic aerosols (OAs) constitute a substantial fraction (20–90%) of global submicron particulate matter (PM<sub>1.0</sub>) concentrations [1]. Organic species directly emitted from anthropogenic or natural sources are classified as primary organic aerosols (POAs) [2]. In contrast, secondary organic aerosols (SOAs), derived from the atmospheric transformation of volatile organic compounds (VOCs), represent a significant portion of submicron atmospheric aerosols [3], and are a crucial component of PM<sub>2.5</sub> [4,5]. SOA formation primarily occurs through gas-phase oxidation reactions and liquid-phase/gas-phase transfer processes involving VOCs [6]. SOAs have significant impacts on solar radiation, atmospheric photochemistry [7], visibility [8], climate change [9,10], and human health [4]. The diverse sources, complex chemical composition, and intricate formation mechanisms of SOAs pose significant challenges in atmospheric aerosol research [9].

Phenolic compounds (PhCs) are prominent VOCs in the atmosphere, characterized by specific absorption properties in the near-ultraviolet (UV) region [11–13]. Atmospheric PhCs originate from diverse natural and anthropogenic sources, with biomass combustion being the primary anthropogenic source, accounting for 60% of total emissions [14]. The

concentrations of nitrated phenols from biomass burning range from 2.0 to 99.5  $\mu\text{g m}^{-3}$  [15]. Other significant anthropogenic sources include coal combustion, wastewater emissions, and exhaust fumes. Additionally, certain medicinal plants, which contain high concentrations of phenolics, could contribute to atmospheric PhCs [2,16]. Phenols are also present in various grains, dried orange peels, and other plants [3,17]. Field studies, laboratory experiments, and modeling results indicate that liquid-phase reactions in cloud/fog droplets or aerosol liquid water significantly increase SOA mass [14,15]. PhCs, due to their high Henry's law constants and moderate-to-high water solubility, are particularly susceptible to such transformations. Consequently, the liquid-phase transformation of phenolic compounds has attracted considerable attention. In the liquid phase, PhCs undergo reactions with free radicals and other reactive components, leading to processes such as electrophilic substitution, oxidation, and conjugate addition, which produce low-volatility and highly oxidized SOAs [18,19]. Understanding the transformation mechanisms of PhCs in the liquid phase is crucial for managing atmospheric haze pollution in China. However, current models significantly underestimate SOA mass concentrations observed in the ambient atmosphere. This underestimation is primarily due to limited knowledge of the precursors and formation mechanisms of aqueous SOAs (aqSOAs) and an incomplete understanding of liquid-phase response mechanisms under complex pollution conditions [20]. Therefore, addressing air pollution and resolving discrepancies in the predicted environmental impacts of SOAs require a precise understanding and control of the atmospheric processes involved in liquid-phase SOA transformation.

This paper summarizes several typical liquid-phase transformations of PhCs under atmospherically relevant conditions. These include direct transformations of phenolic molecules upon exposure to UV light, hydroxylation reactions involving hydroxyl radicals ( $\cdot\text{OH}$ ), nitration reactions involving nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ), and the role of organic matter's triplet state in the degradation of PhCs. Several important and widely studied phenols, such as phenol (PhOH), guaiacol (GUA), catechol (CAT), vanillin (VL), 4-nitrocatechol (4NC), and 5-nitroguaiacol (5NG), are selected to illustrate these processes. The structures and abbreviations of the phenols mentioned in the text are summarized in Table 1.

**Table 1.** Summary of physical properties of phenolic compounds [2,7,18,19].

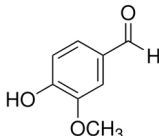
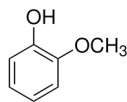
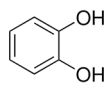
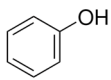
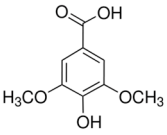
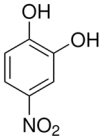
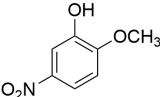
Compound	CAS	Molecular Weight (g/mol)	Molecular Formula	Structural Formula	Melting Point	Boiling Point	pKa	Solubility (g/L)
Vanillin (VL)	121-33-5	152.15	$\text{C}_8\text{H}_8\text{O}_3$		81–83 °C	170 °C	7.40 (25 °C)	10 (25 °C)
Guaiacol (GUA)	90-05-1	124.14	$\text{C}_7\text{H}_8\text{O}_2$		26–29 °C	205 °C	9.98 (25 °C)	17 (15 °C)
Catechol (CAT)	120-80-9	110.11	$\text{C}_6\text{H}_6\text{O}_2$		100–103 °C	245 °C	9.85 (20 °C)	430 (20 °C)
Phenol (PhOH)	108-95-2	94.11	$\text{C}_6\text{H}_6\text{O}$		40–43 °C	182 °C	9.89 (20 °C)	9 (20 °C)
Syringic acid (SA)	530-57-4	198.17	$\text{C}_9\text{H}_{10}\text{O}_5$		205–109 °C	193 °C	4.33 (25 °C)	5.7 (25 °C)

Table 1. Cont.

Compound	CAS	Molecular Weight (g/mol)	Molecular Formula	Structural Formula	Melting Point	Boiling Point	pKa	Solubility (g/L)
4-Nitrocatechol (4NC)	3316-09-4	155.11	C <sub>6</sub> H <sub>5</sub> NO <sub>4</sub>		173–177 °C	289 °C	6.84 (25 °C)	soluble
5-Nitroguaiacol (5NG)	636-93-1	169.13	C <sub>7</sub> H <sub>7</sub> NO <sub>4</sub>		103–107 °C	110–112 °C	8.31 (25 °C)	soluble

## 2. Direct Conversion of Phenol

Free radicals play a major role in distinguishing the two types of photolysis: direct and indirect photolysis [21]. It has been found that some phenolic compounds can undergo auto-photolytic transformation without the addition of any oxidant. Not all phenols can be converted directly; only phenols containing chromophore structures can be photoexcited and transformed to the triply excited state [22]. The most important one is VL which contains an aldehyde group structure. The light-absorbing property of the aldehyde structure is mainly reflected in its carbonyl group, in which there is a strong absorption capacity for light at specific wavelengths from the carbonyl group's carbonyl–oxygen double bond (C=O) [23]. In the infrared spectrum, the carbonyl absorption of aldehydes usually occurs around 1700 cm<sup>-1</sup>. In addition, in the UV–Vis spectrum, aldehyde groups may also exhibit absorption properties, especially in the presence of conjugated systems, which extend into the visible region. The excitation wavelength of the absorption peak of aldehydes is generally around 264 nm. The maximum absorption wavelength of VL in the UV region is usually considered to be 310 nm [24]. However, GUA lacks the aldehyde group structure compared to VL, and as the other groups are identical, GUA hardly converts itself.

## 3. Reactive Species Involved

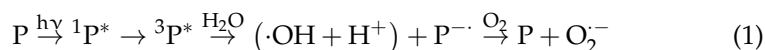
### 3.1. Reactive Nitrogen Species (RNS)

#### 3.1.1. Types and Sources of Atmospheric RNS

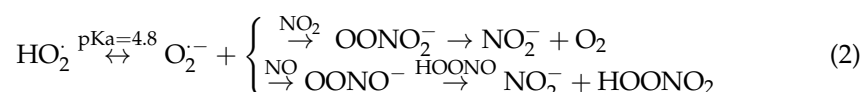
Atmospheric NO<sub>x</sub> can be converted into reactive nitrogen species (RNS), such as NO<sup>+</sup>, NO<sub>2</sub><sup>+</sup>, NO and NO<sub>2</sub><sup>-</sup> [25], in the aqueous phase of the atmosphere. The reaction of RNS with PhCs is called nitrification, which plays a critical role in the formation of light-absorbing organic matter, also known as brown carbon (BrC). Gaseous nitrite (HONO) is a significant RNS in the atmosphere and serves as a precursor to atmospheric hydroxyl radicals (·OH). One pathway for the formation of HONO is through the slow, non-homogeneous dark reaction between nitrogen dioxide (NO<sub>2</sub>) and water (H<sub>2</sub>O). Additionally, HONO can be generated through the conversion of NO<sub>2</sub> with PhCs to HONO under light conditions [26]. Under acidic conditions, NaNO<sub>2</sub> can also be transformed into HONO. However, because of the considerable volatility of HONO, the actual conversion of reactants is lower than the theoretical value when HONO is used as a nitrifier. Nitrite is another prominent nitrogen-containing oxidant in the atmosphere. The concentration of NO<sub>2</sub><sup>-</sup>/HNO<sub>2</sub> in cloud water typically ranges from 0.01 to 1000 μM, with variations based on pollution levels [27]. Nitrification can occur through free radical and photochemical reactions, with the specific mechanisms and products varying, depending on environmental conditions [28]. NO<sub>2</sub><sup>-</sup>/HNO<sub>2</sub> can be formed via two different chemical pathways: photosensitive and non-photosensitive.

1. Photosensitive reactions have two response mechanisms:

- (1) In the presence of light, PhCs are excited to the singlet state ( $^1P^*$ ), which is quickly transformed to the triplet state ( $^3P^*$ ). Phenol in the triplet state conducts electron transfer with  $H_2O$  to produce a radical anion with reducing characteristics, which then combines with dissolved oxygen (DO) to produce superoxide anion ( $O_2^{\cdot-}$ ) [29].



Subsequently, the formation of  $O_2^{\cdot-}$  which converts  $NO_2$  or  $NO$  to  $NO_2^-$  [30],

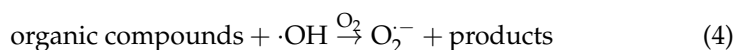


- (2) Light-excited photosensitizers generate a reducing radical intermediate, which interacts immediately with  $NO_2$  to yield HONO/ $NO_2^-$ :

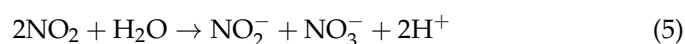


2. The two methods of producing nitrite ions under non-photosensitive condition are as follows:

- (1) Under aerobic conditions, some organic compounds containing  $\cdot OH$  form alkyl peroxy radicals ( $RO_2\cdot$ ), superoxide radicals ( $O_2^{\cdot-}$ ), or their conjugate acids ( $HO_2\cdot$ ), which react directly with nitrogen-containing oxides in the air to produce secondary products such as  $NO_2^-$  [31].



- (2) Another process is the hydrolysis of airborne  $NO_2$  to produce  $NO_2^-$  and  $NO_3^-$  directly [32,33].



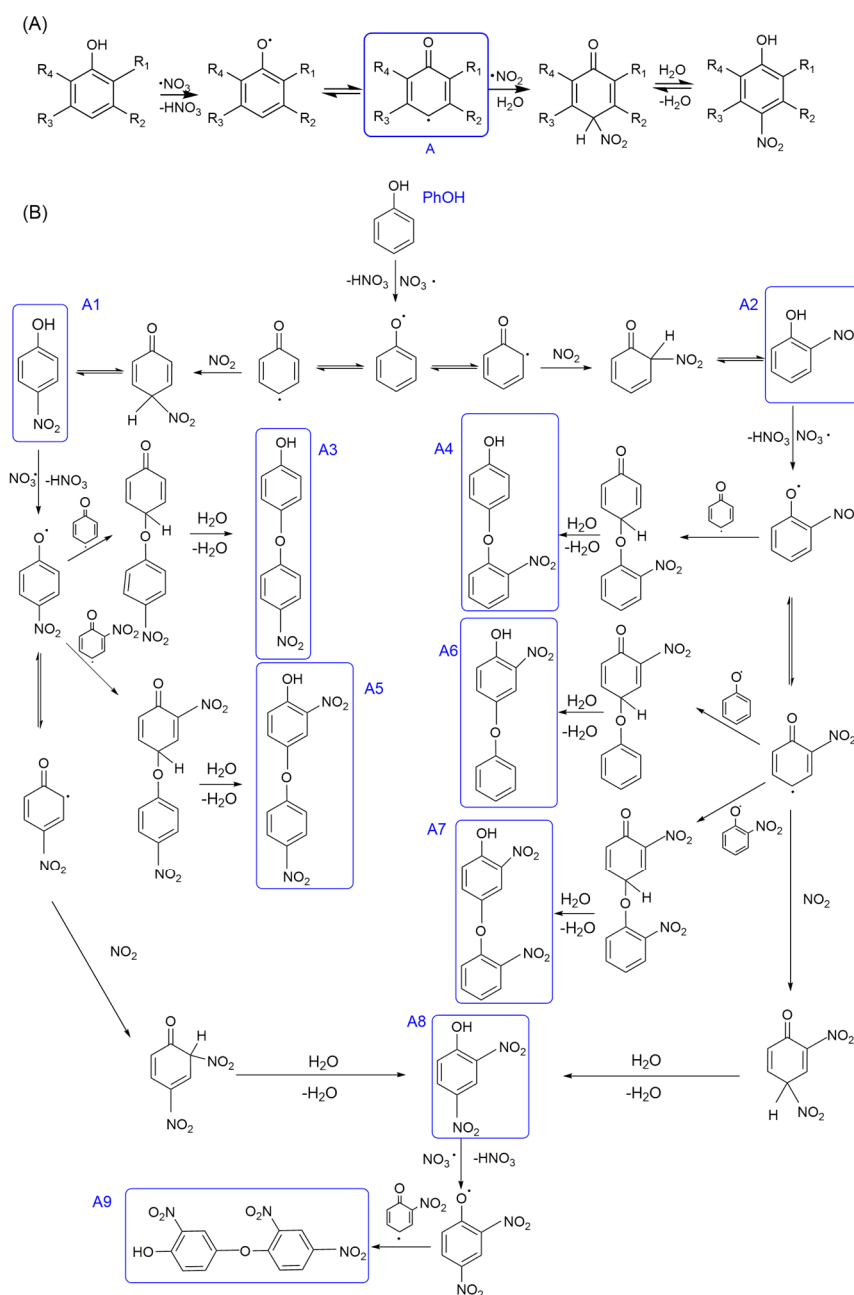
Common nitrogen-containing oxidants in the atmosphere, such as  $HNO_2$  and nitrite, can be converted to each other. In acidic aqueous solutions,  $HNO_2$  thermally decomposes to produce free radicals  $NO\cdot$  and  $NO_2\cdot$ . This decomposition process does not depend on light. Additionally,  $NO^+$  can be formed, which is only able to attack strongly activated aromatic rings.

$NO_2^+$  is formed under dark conditions in the presence of DO. Under light, both nitrite and  $HNO_2$  decompose into  $\cdot OH$  and  $NO\cdot$ , and then react with  $\cdot OH$  to form  $NO_2\cdot$  [34,35].

### 3.1.2. Nitration Mechanism of PhCs

Figure 1A below represents the general steps of nitration of PhCs to generate nitrophenol. Different R groups represent various functional groups, including -H, -OH, -OCH<sub>3</sub>, and -CH<sub>3</sub>. The structure "A" indicates the key phenyl intermediate in the mechanism, and its stability is influenced by the type, number, and position of the initial functional groups [36].

Figure 1B illustrates the oxidized process of phenol to produce the following compounds: mononitrophenol (A1, A2), dinitrophenol (A8), mononitrodimer (A3, A4, A6), dinitrodimer (A5, A7), and trinitrodimer (A9) [34,37].

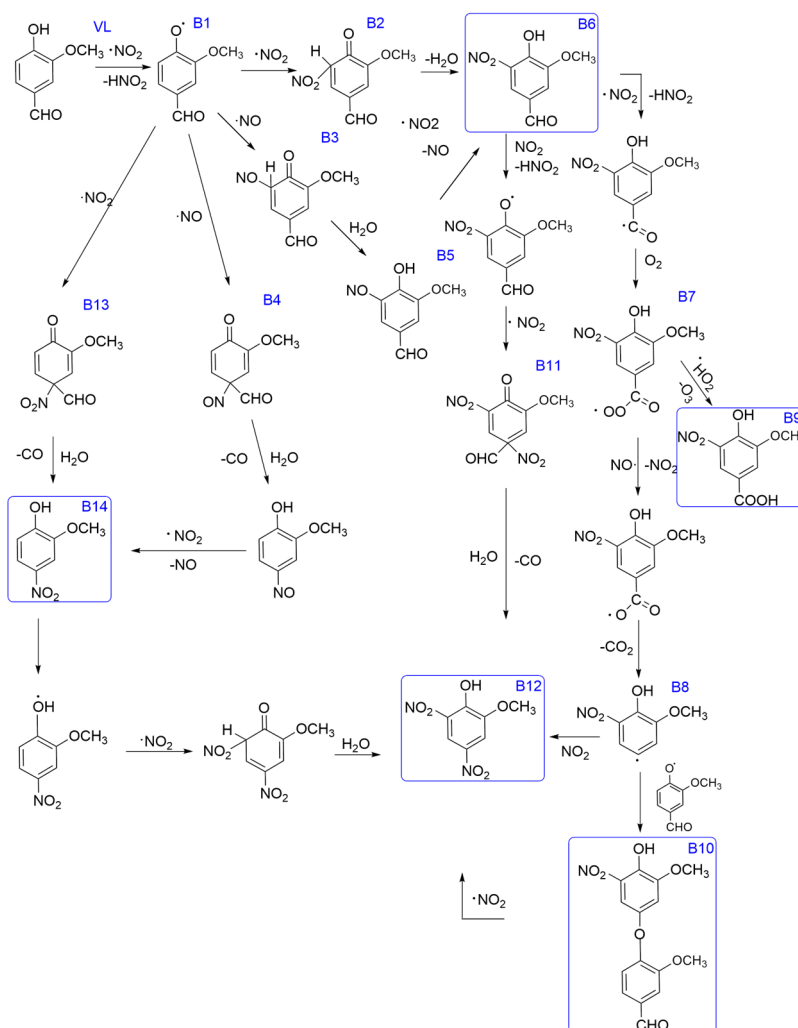


**Figure 1.** General steps for the nitration of PhCs (A) and phenol (B) to produce nitrophenol [37].

### 3.1.3. Reaction Pathways and Products

There are three main pathways for the chemical transformation of SOAs: functionalisation, fragmentation, and polymerisation. Functionalisation adds polar oxygen-containing functional groups to the molecule, decreasing volatility. Fragmentation breaks covalent bonds, increasing volatility. Polymerisation combines molecules to produce substances of greater molecular weight, and a less volatile molecule [38]. Figure 2 shows the main pathways of VL photornitration in aqueous solutions, the solution mixture containing a 10:1 molar ratio of  $\text{NO}_2^-/\text{VL}$  at pH 5 after 3 h of photoreaction. The structure in the box represents the main products, which are detected by HRMS coupled with UPLC [27]. First,  $\text{NO}_2\cdot$  extracts a hydrogen atom from the hydroxyl group of VL to form a phenoxyl radical (B1); in this way, the aromaticity of the phenol is destroyed and the second  $\text{NO}_2\cdot$  is added and forms an intermediate (B2) [39]. Then B2 undergoes hydrogen rearrangement with the participation of water molecules to produce 5-nitrovanillin (5NV) (B6) in this step, the water molecule serves as a bridge to transport hydrogen atoms. B1 reacts with  $\text{NO}\cdot$  to

form B3 and B4, B3 experiences hydrogen rearrangement again to form 5-nitrovanillin (B5) [40]. But this product is very unstable, and once formed, it is prone to undergo further oxidation by  $\text{NO}_2\cdot$  to form B6. B6, as one of the most abundant products, can continue to be converted to other products. Hydrogen is extracted from the hydroxyl group and the  $\text{NO}_2\cdot$  is added to the position where the aldehyde group is located, producing an intermediate (B11) [41]. The rearomatization of B11 gives 4,6-dinitroguaiacol (B12) through a  $\text{H}_2\text{O}$ -assisted rearrangement of a hydrogen atom in the aldehyde group to the quinonic oxygen of B11 and a CO elimination [42]. The  $\text{NO}_2\cdot$  extracts hydrogen from the aldehyde group of the intermediate, and the subsequent addition of oxygen results in the formation of peroxy radicals (B7) [43]. After that, there are two possible reactions: one is to interact with  $\text{HO}_2\cdot$  to form 5NV acid (B9) [44], another is reduced by  $\text{NO}\cdot$  to alkoxy radicals [45], subsequent undergoing decarboxylation to give the aryl species (B8). This transition state can combine with phenoxy radicals to form dimers (B10), and can also generate B12 under the action of  $\text{NO}_2\cdot$ . A  $\text{NO}_2\cdot$  is added to the aldehyde position of B13, and a hydrogen rearrangement and CO elimination in the presence of  $\text{H}_2\text{O}$  generates 4NG (B14) [46].



**Figure 2.** Specific reaction processes and products of vanillin nitration [27].

### 3.2. Hydroxyl Radicals ( $\cdot\text{OH}$ )

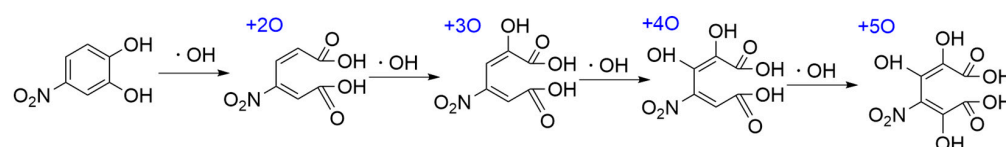
#### 3.2.1. The Generation Pathway of $\cdot\text{OH}$ in the Atmosphere

Research indicates that the concentration of  $\cdot\text{OH}$  in clouds and fog typically ranges around  $10^{-13}$  M, with the cloud condensation–evaporation period lasting between 0.5 and 3 h. As a result, it is commonly believed that the initial 40–60 min of a simulation experiment are closely linked to environmental cloud conditions [47].

As the most significant active oxidative species in the atmosphere, the hydroxyl radical ( $\cdot\text{OH}$ ) has a variety of sources.  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  are the primary sources of  $\cdot\text{OH}$  in aerosol liquid water, with the presence of  $\text{H}_2\text{O}_2$  also playing a role in the generation of  $\cdot\text{OH}$  [48]. The reaction of Fe (II) with unsaturated hydroxyl hydroperoxide (ISOPHOH) can also lead to the production of hydroxyl radicals  $\cdot\text{OH}$  [49]. Additionally, oxalic acid and Fe (II) can combine to form an iron oxalate complex, which has the ability to generate hydroxyl radicals ( $\cdot\text{OH}$ ) when exposed to light [50]. Lastly, the photolysis of nitrite and nitrate serves as another significant source of  $\cdot\text{OH}$  in the environment, with the simultaneous production of  $\text{NO}_2$  [22].

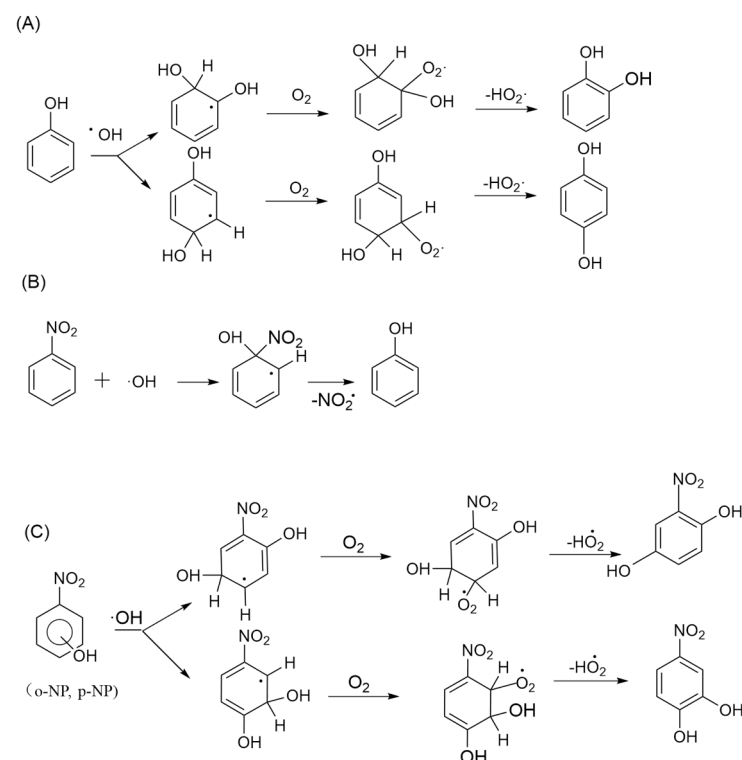
### 3.2.2. PhCs Oxidation Mechanism Involving $\cdot\text{OH}$

Taking nitrocatechol as an example, proposed structures for the functionalized products are shown in Figure 3. The ring-opened products cannot be differentiated from the ring-closed structures of the same molecular formula. The presence of  $\cdot\text{OH}$  leads to a conjugated molecule with two carboxylic acid functional groups where the carbon–carbon bond is broken [51].



**Figure 3.** Hydroxylation mechanism of nitrocatechol [51].

According to the general steps of hydroxylation, the hydroxylation mechanism is speculated to occur when benzene rings contain only hydroxyl groups, only nitro groups, or both; the detailed process is shown in Figure 4 [52].

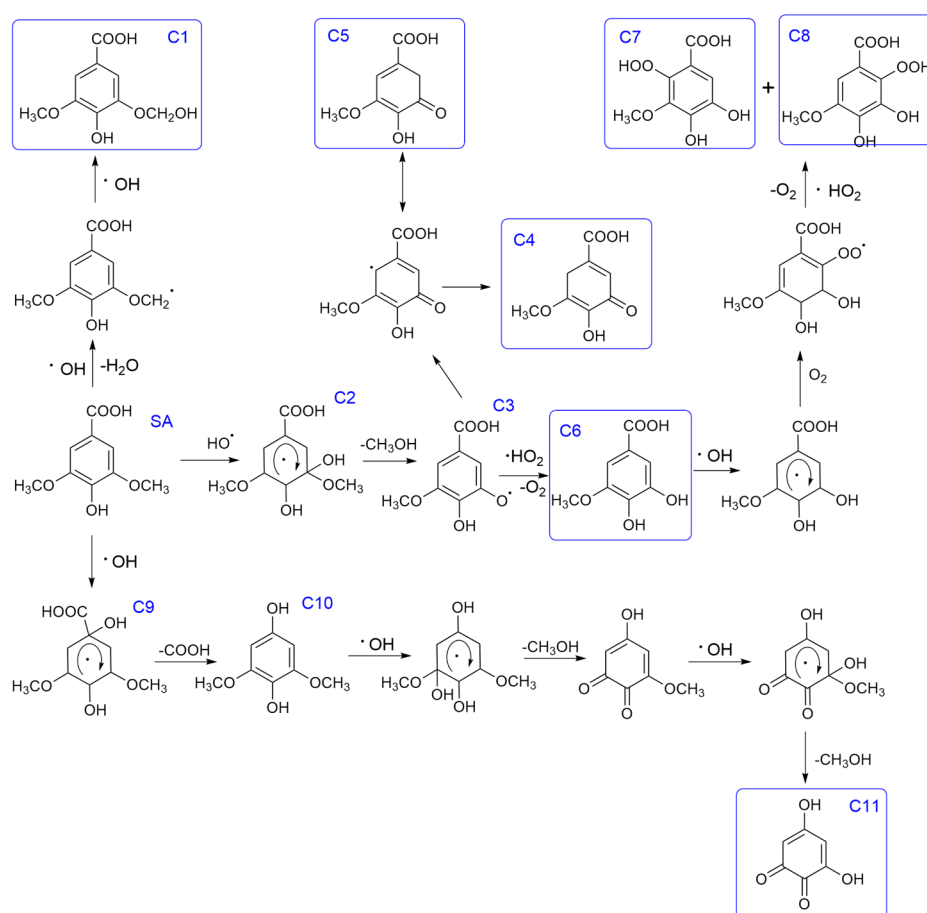


**Figure 4.** Hydroxylation process of hydroxyl group (A), nitro group (B), hydroxyl group and nitro group (C) at the same time [52].



### 3.2.3. The Oxidation Pathways of Syringate by HO·

In general, there are three pathways for HO· reacting with organic compounds: electrophilic addition, hydrogen atom abstraction and electron transfer. In the presence of ·OH, which we can see in Figure 5, the methoxy group in syringic acid (SA) provides the active site for hydrogen atom extraction, and subsequently, another ·OH is added to ·OCH<sub>2</sub> to form a hemiacetal (C1) [53]. In addition, the ·OH undergoes electrophilic addition to SA to form carbon-centered radicals, and the ·OH is added to the position where the carboxyl or methoxy group is located, which are C2 and C9, separately. Then C2 undergoes demethylation to form the radical C3; this is due to the fact that the addition of hydroxyl groups to the methoxy group increases the electrophilicity of the aryl ring [54]. C3 transfers the electron to form the C4, C5 and C6 (5-Hydroxyvanillic acid). The C6 also forms carbon-centered radicals after hydroxyl attacks, following the addition of oxygen molecules to generate peroxy radicals C8 and C7 [55]. In addition, the carboxyl group in C9 will fall off, due to the occupancy of the hydroxyl group. In the process, intermediate 1,4-dihydroxy-2,6-dimethoxybenzene (C10) is generated, and then C10 undergoes two hydroxyl radical oxidations and two demethylations, to form the C11 [48].



**Figure 5.** Specific reaction processes and products of hydroxylation of syringic acid [48].

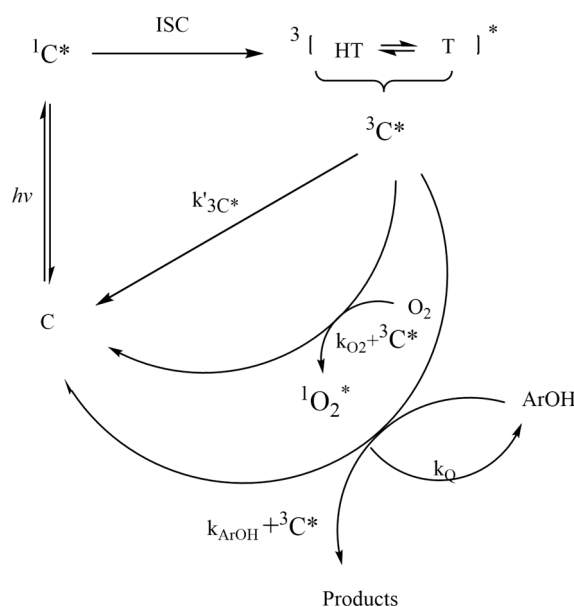
### 3.3. Triplet State Organic Matter (<sup>3</sup>C\*)

#### 3.3.1. Generation of Triplet Compounds

In the atmosphere, the triplet state of organic compounds (<sup>3</sup>C\*) serves as a common oxidant for oxidizing PhCs [56], which is generated from the excitation of chromophoric dissolved organic matters (the donors or photosensitizers) under solar irradiation. Subsequently, it can undergo quenching reactions with other species (the acceptors or quenchers) via electron or energy transfer [34].



The ground state of a common chromophore (C) absorbs light to form a single excited state ( $^1C^*$ ), which can return to the ground state or undergo an inter-system crossing (ISC) to the triplet state ( $^3C^*$ ). The reaction mechanism is shown in Figure 6. The triplet pool contains protonated (HT) and neutral (T) molecules. The  $^3C^*$  has three pathways: reaction with  $O_2$ , relaxation of a single molecule to the ground state, and reactions with phenol, which result in phenol losing reactivity. This can result in loss of reactivity of phenol ( $k_{ArOH+^3C^*}$ ) or non-destructive physical quenching ( $k_Q$ ) [57].

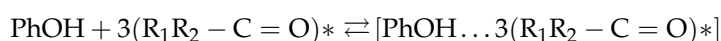


**Figure 6.** Program for the formation and reaction of three excited states [57].

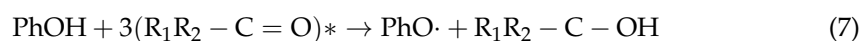
Under simulated sunlight, VL underwent direct oxidation or oxidation processes in the presence of ammonium nitrate. Initially, VL absorbs light and transitions to its excited singlet state ( $^1VL^*$ ), which is then followed by ISC transitioning to its excited triplet state ( $^3VL^*$ ) [58]. Furthermore, the decay-rate constant of the photosensitizer VL under air-saturated conditions was determined to be four times higher than that under  $N_2$ -saturated conditions. The increased reaction rate constant observed under air-saturated conditions can be attributed to the combined effect of  $^1O_2$  and  $^3C^*$  generated in the presence of  $O_2$ . Additionally, the decay-rate constant of VL under air-saturated conditions was found to be four times higher than that under  $N_2$ -saturated conditions [2].

### 3.3.2. Reaction Mechanism of PhCs and $^3C^*$

Electrons are transferred from phenol to the excited triplet state of the carbonyl compound [22], producing protonated phenoxy ( $PhOH^{\cdot+}$ ) and deprotonated carbonyl ( $R_1R_2-C\cdot-O^-$ ). Within the framework of various kinetic theories, the intermolecular electron transfer reaction is commonly explained through the following mechanisms: (a) formation of precursor complexes, (b) electron transfer, leading to the formation of charge transfer (CT) complexes, and (c) the separation of oxidized donors and reduced acceptors, as illustrated in Equation (6) [59].



The second transfer mechanism is hydrogen atom transfer, which is less likely to occur.



### 3.3.3. Specific Reaction Processes and Products of Phenol with $^3\text{C}^*$

PhCs and  $^3\text{C}^*$  produce different types of products through multiple pathways. Next, we discuss the detailed reaction mechanism and products using phenol as an example, as shown in Figure 7. Phenol and the  $^3\text{C}^*$  form HOOH in the presence of oxygen, which is one of the important sources of  $\cdot\text{OH}$  in the atmosphere. The free radicals obtained by photolysis bind to phenol and subsequently form a hydroxylation product (D1) with the addition of oxygen and the elimination of  $\text{HO}_2\cdot$ . In the meantime, the  $\cdot\text{OH}$ -phenol adduct can undergo unimolecular elimination of  $\text{H}_2\text{O}$  to form a phenoxy radical (D2), or  $^3\text{C}^*$  via electron transfer coupled with proton transfer from the phenoxy radical cation. D2 and semiquinone radicals (D3) can be transformed into each other. Both D2 and D3 then combine with another radical to form dimer and higher oligomers (D4 and D5). Phenol reacts with  $^3\text{C}^*$  combined with an organic acid to form an ester (D6) [60]. In exploring six highly substituted phenols reacted with  $\cdot\text{OH}$  and  $^3\text{C}^*$ , the higher absorbance of the reaction of phenol with the  $^3\text{C}^*$  indicates that more polymer is produced [57]. Moreover, lower O/C was detected in the product of the reaction of the  $^3\text{C}^*$  with phenol compared to the product of the reaction of the hydroxyl radical with phenol [38].

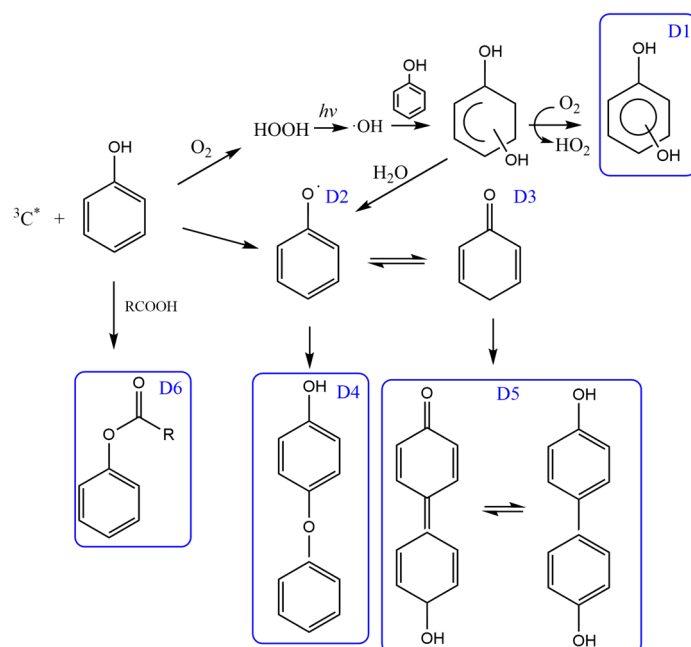


Figure 7. Specific reaction processes and products of  $^3\text{C}^*$  of Phenol [38].

## 4. Factors Affecting the Liquid-Phase Conversion of PhCs in the Atmosphere

The formation of the BrC aqueous phase is a complex process. PhCs prefer to form stable intermediates, and their structures will influence the formation of phenyl intermediates. Environmental factors such as reactant concentration, pH value, temperature, and light can also have a significant impact on the conversion mechanism and resulting products.

### 4.1. Effect of pH on the Transformation of PhCs

pH plays a crucial role in influencing the conversion of PhCs. The decay-rate constant of VL decreases approximately 1.5-fold when the pH is lowered from 4 to 2.5. The normalised abundance of products, especially polymeric and functionalised products, increases as the pH decreases. This is likely due to the increased formation of  $\cdot\text{OH}$  and  $\text{NO}_2\cdot$  groups in lower-pH conditions [2].

The rate constants for both GUA and CAT during photolysis were observed to be higher at pH 3.5 in comparison to pH 6, indicating that these compounds are more susceptible to direct photolysis under acidic conditions. Interestingly, the rate constants of 5NG

showed no significant difference between pH 6 and pH 3.5, while the 4NC were higher at pH 6 than at pH 3.5. This difference can be attributed to the susceptibility of p-nitrophenols like 4-nitrocatechol to releasing nitro groups, such as photolytic  $\text{NO}_2$  and  $\text{HNO}_2$ , with low spatial resistance when exposed to light in aqueous solutions. Furthermore, the yield of  $\text{NO}_2$  and  $\text{HNO}_2$  increases with pH levels [61].

Non-p-nitrophenols, like 5NG, are less affected by this process, due to the significant spatial hindrance of the  $-\text{NO}_2$  group. Photolytically released  $\text{NO}_2$  and  $\text{HNO}_2$  can readily form free radicals, such as  $\cdot\text{OH}$ ,  $\text{NO}_2\cdot$  and  $\text{NO}\cdot$ , which can quickly react with the remaining phenol in the solution, thus speeding up the reaction rate [62,63].

#### 4.2. Effect of Reactant Concentration on the Conversion of PhCs

The pH was set at 4 to investigate the rate and product formation under different concentration ratios of VL and ammonium nitrate (AN). The reactant concentrations were standardized as follows: VL (0.01 mM), VL/AN (0.01 mM VL + 0.01 mM AN), and VL/AN (0.01 mM VL + 1 mM AN). Polymerization becomes the primary pathway at high [VL], and the phenoxy radicals increase, interacting with carbon-centered cyclohexadienyl radicals to facilitate radical–radical polymerization and enhance oligomer production, while at lower [VL] levels, products with  $m/z$  300 show the opposite trend. This suggests that functionalized products are the predominant outcomes at low [VL] [51].

At the VL/AN ratio of 1:1, VL may compete with  $\text{NO}_2^-$  for  $\cdot\text{OH}$  produced from the photolysis of nitrate or nitrite, which indirectly reduces the concentration of  $\text{NO}_2\cdot$  [2]. A study on the liquid-phase formation of 3-methylcatechol (3MC) under simulated sunlight revealed that the absorption near 350 nm increased over time when the ratio of nitrite ions to 3MC concentration was 1:1. Additionally, as the concentration of phenol increased, the absorption also increased, particularly above 400 nm [64].

#### 4.3. Effect of Transition Metal Ions on the Transformation of PhCs

The interaction between common transition metal ions (TMs) in the atmosphere, like  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$ , with soluble organic matter leads to the formation of organism–metal complexes and reactive species (ROS) like  $\cdot\text{OH}$ .  $\text{Zn}^{2+}$  is less likely to form complexes with organic matter easily compared to  $\text{Cu}^{2+}$ , due to the lack of d-d electron transition.  $\text{Cu}^{2+}$  complexes are more significant, followed by  $\text{Fe}^{2+}$  and then  $\text{Mn}^{2+}$ , which exhibits the weakest synergistic effect. This difference in complex formation may be attributed to the higher ease with which  $\text{Cu}^{2+}$  binds to the benzene ring through  $\pi$ - $\pi$  electron transfer in comparison to  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  [65].

$\text{Fe}^{3+}$  can form organic trilinear state- $\text{Fe}^{3+}$  complexes with aromatic chromophores that possess visible-light trapping ability and appropriate excited-state energy levels. This can be followed by processes such as energy transfer, electron transfer, or non-radiative transitions to the ground state, leading to the generation of reactive oxygen species like  $^1\text{O}_2$  and  $\cdot\text{OH}$ . Additionally,  $\text{Fe}^{3+}$  has the capability to directly form complexes with organic matter [66].

The primary sources of atmospheric iron include windblown mineral dust particles, mineral dust, and soil [67]. Additionally, iron can come from potentially available sources such as hydrotalcite colloids, nanoparticles, and aqueous materials [68]. Iron (II) may also be produced through the photolysis of iron–oxygen (hydroxide) compounds in a non-homogeneous photo-Fenton reaction [22].

Considering factors such as ionic abundance and the stability of the complexes formed, the iron oxalate system is the most common [50,69,70]. It also serves as a major source of atmospheric  $\text{H}_2\text{O}_2$ ,  $\text{O}_2^{\cdot-}$ ,  $\text{HO}_2$ , and  $\cdot\text{OH}$  [71,72]. The pH and inorganic anions also play a significant role in influencing the formation of Fe (III) species and BrC [73]. As the Fenton reaction consumes hydrogen ions, the rate of  $\cdot\text{OH}$  generation slows down, making higher pH levels detrimental to  $\cdot\text{OH}$  generation [71]. CAT and GUA react with trivalent iron under dark conditions, where dissolved  $\text{O}_2$  acts as an oxidizing agent and Fe (III) acts as a

catalyst. Numerous experiments have demonstrated maximum photoreactivity for organic degradation of iron at pH 3 [74].

The measured secondary rate constants ( $k$ ) of PhCs mentioned in the text with  $\cdot\text{OH}$ ,  $\text{NO}_2\cdot$  and  ${}^3\text{C}^*$  in the aqueous phase are summarized in Table 2, and this will help our understanding of the different reactions. We find that the  $k$  are different for different compounds under different reaction paths, as well as the reaction conditions, such as temperature and pH. In addition, the  $k$  for the same compound reacting with  $\cdot\text{OH}$  under similar reaction conditions will be higher than with  $\text{NO}_2\cdot$  or  ${}^3\text{C}^*$ , but there is no such pattern for CAT.

**Table 2.** The measured reaction rate constants of PhCs mentioned in the text.

Compound	PhOH	VL	GUA	CAT	SA	
$\cdot\text{OH}$	Experimental conditions	293 K pH = 5	298 K pH = 5	293 K pH = 5	293 K pH = 5.5	313 K pH = 5.5
	$k$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$1.5 \pm 0.5 \times 10^{10}$	$4 \times 10^8$	$1.6 \pm 0.5 \times 10^{10}$	$6.9 \pm 2.4 \times 10^7$	$1.66 \times 10^{10}$
	Reference	[75]	[25]	[75]	[75]	[48]
$\text{NO}_2\cdot$	Experimental conditions	298 K pH = 5	-	298 K pH = 4.5	313 K pH = 5	-
	$k$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$2.7 \pm 0.04 \times 10^8$	-	$4.01 \pm 0.04 \times 10^9$	$1.9 \times 10^9$	-
	Reference	[22]	-	[35]	[28]	-
${}^3\text{C}^*$	Experimental conditions	293 K pH = 5	-	293 K pH = 5	293 K pH = 5	293 K pH = 2
	$k$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$1.3 \pm 0.9 \times 10^8$	-	$2.5 \pm 0.6 \times 10^9$	$5.8 \pm 2.0 \times 10^8$	$1.1 \pm 0.3 \times 10^{10}$
	Reference	[29]	-	[75]	[75]	[56]

$\cdot\text{OH}$ ,  $\text{NO}_2\cdot$  and  ${}^3\text{C}^*$  in the aqueous phase.

## 5. Summary

This review primarily discusses key transformation processes of volatile organic phenols in the liquid phase. The first process is the direct conversion of phenol: some phenolic compounds, such phenol and halogenated hydrocarbons, can break down in the presence of light to create free radicals, which are then utilized in the subsequent conversion. The second process is the nitration reaction, with common nitration reagents such as HONO,  $\text{NO}_2^-$ , and  $\text{NO}\cdot$ , which can interconvert under specific conditions. The third process involves the oxidation of  $\cdot\text{OH}$ , which has a wide range of sources. The fourth important reaction is the formation of triplet states in organic matter through light excitation.

The transformation of phenol in atmospheric liquid-phase water is influenced by factors including light intensity, temperature, atmospheric composition, reaction conditions, and the structural characteristics of PhCs. The mechanism of phenol's liquid-phase transformation is complex.

Since VOCs are some of the most significant volatile organic compounds in the atmosphere, studying and controlling their transformation processes will be crucial for both the future of the environment and humankind. VOC properties have the potential to pollute the environment and have an adverse effect on ecosystems.

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