Rapid oxidation of phenolic compounds by O_3 and $HO^{\bullet}$: effects of air-water interface and mineral dust in tropospheric chemical processes

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Abstract

Environmental media affect the atmospheric oxidation processes of phenolic compounds (PhCs) released from biomass burning in the troposphere. To address the gaps in experimental research, phenol (Ph), 4-hydroxybenzaldehyde (4-HBA), and vanillin (VL) are chosen as model compounds to investigate their reaction mechanism and kinetics at the air-water (A-W) interface, on TiO_2 mineral aerosols, in the gas phase, and in bulk water using a combination of molecular dynamics simulation and quantum chemical calculations. Of them, Ph was the most reactive one. The occurrence percentages of Ph, 4-HBA, and VL staying at the A-W interface are ~72%, ~68%, and ~73%, respectively. As the size of $(TiO_2)_n$ clusters increases, the adsorption capacity decreases until n > 4, and beyond this, the capacity remains stable. A-W interface and TiO_2 clusters facilitate Ph and VL reactions initiated by the O_3 and $HO^{\bullet}$, respectively. However, oxidation reactions of 4-HBA are little affected by environmental media because of its electron-withdrawing group. The O_3- and $HO^{\bullet}$-initiated reaction rate constant (*k*) values follow the order of $\text{A-W}_{\text{Ph}} > \text{TiO}_{2\ \text{VL}} > \text{A-W}_{\text{VL}} > \text{A-W}_{\text{4-HBA}} > \text{TiO}_{2\ \text{4-HBA}} > \text{TiO}_{2\ \text{Ph}}$ and $\text{TiO}_{2\ \text{VL}} > \text{A-W}_{\text{Ph}} > \text{A-W}_{\text{VL}} > \text{TiO}_{2\ \text{4-HBA}} > \text{TiO}_{2\ \text{Ph}} > \text{A-W}_{\text{4-HBA}}$, respectively. Some byproducts are more harmful than their parent compounds, so should be given special attention. This work provides key evidence for the rapid oxidation observed in the $O_3/HO^{\bullet}$ + PhCs experiments at the A-W interface.

More importantly, differences in oxidation of PhCs by different environmental media due to the impact of substituent groups were also identified.

Keywords: Air-water interface; Titanium dioxide (TiO_2); Phenolic Compounds; Adsorption mechanisms; Molecular dynamics (MD).

1. Introduction

Biomass burning, stemming from natural wildfires and human activity, significantly contributes to atmospheric particulate matter (PM). Biomass burning is a primary source of approximately 90% of the global primary organic aerosols (POA) and releases a substantial quantity of organic pollutants (Ito and Penner, 2005; Chen et al., 2017; Chen et al., 2023). Biomass burning is to blame for about 62% of total annual emissions of about 8.0 Tg of black carbon and 93% of total annual emission of about 33.9 Tg of organic carbon worldwide (Bond et al., 2004). Emissions from biomass combustion are one of the primary sources of atmospheric and particle pollutants that negatively affect human health, air quality, and climate (Reid et al., 2005; Yao et al., 2016). One of the three main types of biopolymers responsible for the formation of biomass is lignin (Sun et al., 2011), also the polymeric organic molecule most abundant in plants (Lou et al., 2010; Soongprasit et al., 2020). Pyrolysis of lignin releases phenolic compounds (PhCs) into the air, including phenols, phenolic aldehydes, and methoxyphenols. By mass, these PhCs make up between 21% and 45% of the aerosol composition (Hawthorne et al., 1989; Diehl et al., 2013; Liao et al., 2020; Soongprasit et al., 2020). Methoxyphenols are one of the potential tracers that can be found in atmospheric wood smoke pollution, with the emission rate ranging from 900 to 4200 mg kg^{-1} fuel (Hawthorne et al., 1989; Rogge et al., 1998; Simoneit, 2002; Chen et al., 2017). Evidence shows that the oxidation processes of PhCs can result in the formation of secondary organic aerosol (SOA) (Yee et al., 2013; Jiang et al., 2023). Hence, it is imperative to explore the effects of PhCs when exposed to atmospheric oxidants.

After being released into the atmosphere, PhCs will be oxidized by ozone (O_3) and hydroxyl radicals ($HO^•$). Both are significant contributors to SOA (Arciva et al., 2022). The homogenous oxidation of PhCs has been the emphasis of previous studies (Henry et al., 2008; Yee et al., 2013; Liu et al., 2019; Arciva et al., 2022). Researchers investigated the kinetics and reaction mechanisms of gas-phase interactions of PhCs with O_3 and $HO^•$ in the past decade (Kroflič et al., 2018; Smith et al., 2016; Sun et al., 2021a; Sun et al., 2021b; Liu et al., 2022). Furthermore, they investigated the hydroxylation, ring opening, and oligomerization processes of PhCs in the atmospheric liquid phase, with a focus on the potential environmental toxicity and climatic effects of these events (Ma et al., 2021; Liu et al., 2022; Arciva et al., 2022; Carena et al., 2023).

However, there is a dearth of specific data as well as explanations of the mechanisms involved in the atmospheric oxidation of PhCs at the air-water (A-W) interface. The atmosphere contains a high concentration of aqueous aerosols and water microdroplets (Zhong et al., 2019; Guzman et al., 2022). The oxidation of PhCs can rapidly occur at A-W interface (Rana and Guzman, 2022c). The term "water surface catalysis" denotes the phenomenon where chemical reactions happen at a faster rate at A-W interface compared to the bulk phase (Lee et al., 2015a; Lee et al., 2015b; Yan et al., 2016; Banerjee et al., 2017). In chemical engineering, titanium dioxide (TiO_2) is an essential photoactive component found in atmospheric mineral dust (Sakata et al., 2021; Wang et al., 2023). The interaction between PhCs and TiO_2 is continuous (Grassian, 2009; Rubasinghege et al., 2010; Shang et al., 2021), despite the relatively low prevalence of TiO_2 mineral particles (comprising 0.1% to 10% by mass). Therefore, it is essential to investigate the disparity in the oxidation reaction mechanisms and kinetics of PhCs at A-W interface and mineral dust particles.

Increasing the number of constituents on the aromatic ring would affect the reactivity and lead to complex compounds after reaction addition and/or open ring pathways. Phenol (Ph), 4-hydroxybenzaldehyde (4-HBA), and vanillin (VL) are typical lignin pyrolysis products (Jiang et al., 2010; Kibet et al., 2012) . Thus, we selected Ph, 4-HBA and VL as model compounds to present comprehensive mechanistic information at A-W interface, on TiO_2 clusters, in the gas phase, and in bulk water, using a combination of molecular dynamics simulation and quantum chemical calculations. Rate constants were calculated throughout a wide temperature range in various EM. Additionally, computational toxicology was employed to evaluate the ecotoxicological impact of PhCs and their transformation products.

2. Methods

2.1 Molecular dynamics simulation

All of the molecular-dynamics simulations were carried out by utilizing the GROMACS 2019 package, which included the AMBER force field. Parametrization of the Ph, 4-HBA, and VL was accomplished by using the GAFF force field in conjunction with RESP charge calculations performed at the M06-2X/6-311++G(3df,2p)//M06-2X/6-31+G(d,p) level. The TIP3P water model was utilized so that individual water molecules may be represented (Jämbeck and Lyubartsev, 2014).

2.1.1 Properties of Ph, 4-HBA, and VL at the A-W interface

Considering the significance of the interfacial behavior of Ph, 4-HBA, and VL at the A-W interface, the properties of these three substances were initially examined by focusing on the A-W interface. **Fig. S1 (a)** depicts a rectangular box that has dimensions of 4 × 4 × 9 nm^3 and has a Z-axis that is perpendicular to the A-W contact. This box was used for all simulations. A water box that is too small may cause the central PhCs molecules to be too close to the interface region, leading to inaccurate results. Conversely, opting for a water box that is too large can lead to unnecessary waste of computational resources. To begin the process of constructing the initial configurations, a water slab measuring 4 × 4 × 4 nm^3 was positioned at the coordinates (2 nm, 2 nm, 4.5 nm) of the center of mass (COM). Because the rest extension along the Z-axis of the box was sufficiently large (2.5 nm^3), it was possible to steer clear of the intersection of two A-W interface. Prior to the formal simulation, six Ph molecules were randomly selected position placed in a vacuum above the water box for 150 nanoseconds of NVT molecular dynamics simulation. The purpose of simulating 150 ns is to capture the fundamental molecular dynamics that occur on this time scale, such as bond formation, conformational changes, and interaction events. The results show that there are no significant π-π interactions or formation of hydrogen bonds between the Ph molecules. To simplify the model, this was followed by simulations of individual molecules. Ph, 4-HBA, or VL were each placed in their own compartment at the coordinates (2.0 nm, 2.0 nm, 7.75 nm) for each system in order to simulate the behavior of these molecules in the A-W interface region of cloud/fog drops and aerosol liquid water (ALW). To begin, the three different systems were optimized to use the least amount of energy possible. After that, NVT molecular-dynamics simulations were carried out for a total of 150 nanoseconds.

2.1.2 Umbrella sampling simulations

In **Fig. S1 (b)**, the molecule of Ph, 4-HBA, or VL was placed inside the box (their COM is (2.00 nm, 2.00 nm, 6.00 nm)), which is located directly 2.00 nm away from the COM of the water slab. The distance between the COM of Ph, 4-HBA, or VL and that of the water slab was used as the definition for the reaction coordinate (**Fig. S1**). The weighted histogram analysis approach, also known as WHAM, can be used to calculate the free energy profiles of Ph, 4-HBA, or VL when they transition from the gas phase into bulk water (Kumar et al., 1992; Hub et al., 2010) ; details about WHAM are in the Supporting Information **Text S1**.

2.1.3 Radial distribution function

Estimating the strength of hydrogen bonds (HB) between specific atoms can be done with the help of a tool known as the radial distribution function (RDF). **Text S2** has an explanation of the peculiarities of the RDF and the coordination number.

2.2 DFT calculations

In this work, all structural optimization and energy calculation were accomplished by utilizing the Gaussian16 program (Frisch et al., 2016). Calculated at the CCSD(T)/cc-pVDZ, CBS-QB3, B3LYP/6-311+G(d,p), MP2/6-311+G(d,p) and M06-2X/6-311+G(d,p) levels, Cao et al. (Cao et al., 2021) found that M06-2X/6-311++G(3df,2p)//M06-2X/6-31+G(d,p) is reliable for PhCs at gas phase. After analyzing the stability of the wavefunction, the method we used is reliable. Therefore, all calculations for gas-phase reactions are performed at this level. **Text S3** contains a description of the additional calculated details. The frequency correction factor (0.967) has been taken into account. Multiwfn (Lu and Chen, 2012) was used to construct the electron density map. This program integrates Visual Molecular Dynamics (version 1.9.3) (Humphrey et al., 1996) in order to conduct an analysis of the electrostatic potential (ESP) and the average local ionization energy (ALIE).

2.3 IRI analysis

Interaction Region Indicator (IRI) (Lu and Chen, 2021) was used to determine the chemical bonds and weak interactions of Ph/4-HBA/VL adsorbed to TiO_2 clusters (the details are in **Text S4**).

2.4 Kinetic calculations

Text S5 contains an explanation of the kinetic calculation methods.

3. Result and discussion

3.1 Enrichment of Ph, 4-HBA, and VL at the A-W interface

3.1.1 The uptake of gaseous PhCs at the A-W interface

Fig. S1 and **Fig. S2** illustrate the relative distributions of water, O_3, and PhCs molecules (Ph, 4-HBA, and VL) in the A-W interface system along the z-axis. $HO^{\bullet}$ are primarily situated at the A-W interface contact, with the potential to diffuse through the water slab interior (Roeselová et al., 2004). **Fig. 1(a)** displays the variation in water density along the Z-coordinate distance from 0 to 9 nm, categorizing three zones: A-W interface (2.25 to

2.79 nm and 6.21 to 6.75 nm), air (0 to 2.25 nm and 6.75 to 9 nm), and bulk water (2.79 to 6.21 nm). This method accurately determines the interfacial range (Zhang et al., 2019; Shi et al., 2020). According to location definitions, O_3 percentage distribution was as follows: 26% at the A-W interface; 72% in the air; and 2% in bulk water (**Fig. 1(b)**). **Fig. 1(c)** depicts MD trajectories of Ph diffusion through the water slab from the air region over a 150 ns period. Ph is distributed in the air (8%) and bulk water (20%), with the majority at the A-W interface (72%) (**Fig. 1 (d)**). The majority of 4-HBA and VL molecules are located at the A-W interface, constituting 68% and 73% of the total locations as presented in **Fig. S2**.

In **Fig. 2(a)**, we observe the three key processes involving PhCs (Ph, 4-HBA, or VL) diffusing into the water slab from the air region. (I) The mutual attraction of gaseous Ph, 4-HBA, or VL; (II) The uptake of PhCs (Ph, 4-HBA, or VL) at the A-W interface; (III) The hydration reaction of PhCs (Ph, 4-HBA, or VL) in the bulk water. **Fig. 2(b)** displays the free energy profile of the trajectories as Ph/4-HBA/VL transitions from the air into the bulk water (see **Text 6** for calculations details). The $\Delta G_{gas \rightarrow interface}$ values are -0.22 kcal mol $^{-1}$ for the Ph-A-W (Phenol-Air-Water) system, -0.45 kcal mol $^{-1}$ for the A-$W_{4\text{-}HBA}$ (4-hydroxybenzaldehyde at Air-Water) system, and -0.20 mol $^{-1}$ for the A-W_{VL} (Vanillin-Air-Water) system. This finding is consistent with previous studies about Per-and poly-fluoroalkyl substances (PFAS) at A-W interface (Yuan et al., 2023). These values suggest that it is thermodynamically favorable for PhCs to approach the interfacial water molecules. **Fig. S3** illustrates typical snapshots from the trajectories of PhCs (Ph, 4-HBA, or VL). Initially, one molecule of Ph, 4-HBA, or VL was placed in the center of the water box, with an equivalent COM distance of 2 nm between the PhCs and the air phase. Subsequently, the PhCs moved closer to the interface, leading to adsorption at the A-W interface. During the adsorption process, the H atom of the phenolic hydroxyl group binds to the oxygen atom of the H_2O molecules at the A-W interface, forming H bonds and preventing its return to the bulk water. This property allowed the phenolic hydroxyl groups on PhCs can effectively adhere to the A-W interface, consistent with the experimental observations using steady-state interfacial vibrational spectra (Kusaka et al., 2021) and Fourier transform infrared (FTIR) imaging micro-spectroscopy (Guzman et al., 2022) . Based on these findings, compared to the number of PhCs molecules distributed in the gas phase and in bulk water, the location where air and water meet exhibits an increased the number of PhCs molecules.

3.1.2 Interface properties of PhCs

Introducing more hydrophilic functional groups increases the characteristic angle α and β of PhCs at the interface, allowing for more secure adsorption at the water-air interface. The interaction between H_{PhCs} and O_{H_2O} is the primary factor influencing the stability of PhCs at the interface. The coordination number (N) of $H_{Ph\text{-}OH}$–O_{H_2O}, $H_{4\text{-}HBA\text{-}OH}$–$O_{H_2O}$, and $H_{VL\text{-}OH}$–O_{H_2O} are 2.68, 2.51, and 2.09 respectively. The number of functional groups attached to the benzene ring affects the N value; more functional groups lead to a lower N value. The reason is that aldehyde and methoxy are strong electron-withdrawing groups, which will reduce the conjugation effect between the benzene ring and the hydroxyl group, making the hydrogen atom on the hydroxyl group partially positively charged, thus weakening the hydrogen bonding ability with water molecules. See **Text S7** for interface properties of PhCs.

3.2 Adsorption of Ph, 4-HBA, and VL by TiO_2 Clusters

The placement of PhCs on TiO_2 clusters significantly impacts adsorption energies (Bai et al., 2020). The adsorption capacity of pollutants on cluster surfaces is a key factor influencing degradation efficiency (Qu and Kroes, 2006). The primary mechanism of C atoms adsorption to $(TiO_2)_n$ (n = 1–4) clusters occurs at a range of 2.57 to 2.61 Å and involves interaction between the $H_{\text{-}OH}$ atom and the O_{TiO_2} atom, as seen in **Fig. 3(a)**. Hydrogen bonds can be formed between the $H_{\text{-}OH}$ atom and the O_{TiO_2} atom (1.80–2.61 Å), improving the adsorption capacity. In contrast, Ph adsorption to $(TiO_2)_n$ (n = 5–6) clusters, ranging from 2.08 to 2.09 Å, is primarily due to interaction between Ti atom and $O_{\text{-}OH}$ atom. For a detailed description see **Text S8**.

Adsorption energy a metric of adsorption capacity, is illustrated in **Fig. 3(b)–(d)** for Ph, 4-HBA, and VL on $(TiO_2)_n$ (n = 1–6). TiO_2 exhibits the highest adsorption capacity for Ph. ($\Delta G_{ad} = -72.35$ kcal mol $^{-1}$) (**Fig. 3(b)**). The adsorption energy values of TiO_2 and $(TiO_2)_3$ for 4-HBA and VL are −45.32 (**Fig. 3(c)**) and −102.46 kcal mol $^{-1}$ (**Fig. 3(d)**), respectively. Physisorption energy range from −1.20 to 9.56 kcal mol $^{-1}$ (Nollet et al., 2003), thus this adsorption process in this study is spontaneous chemical adsorption. However, the capacity of TiO_2 to adsorb VL is significantly higher than that to adsorb Ph and 4-HBA. **Fig. 3(b)–(d)** show that the adsorption capacity falls as the size of TiO_2 clusters increases when $n \leq 4$. In contrast, the adsorption capacity remains constant when $n > 4$. IRI measurements of Ph on the $(TiO_2)_n$ surface (**Fig. 3(e)**) reveal Ph-TiO_2 hydrogen bonds (H_{Ph}–O_{TiO_2} bonds) and their electrostatic and dispersion effects. Benzene C atom of Ph exhibits sp^2 hybridization, meaning it forms one σ-bond and one π-bond. The sp^2 hybridization of benzene for Ph explains its limited interaction with TiO_2 clusters and accounts for the substantial adsorption energy. Similar interactions occur with 4-HBA and VL (**Fig. S7**). Hydrogen bonds form between the $H_{\text{-CHO}}$ atom of 4-HBA or VL and the O_{TiO_2} atom, despite the presence of the H_{Ph} atom.

3.3 Continuous oxidation mechanisms

3.3.1 O_3- and $HO^{\bullet}$-initiated reactions

PhCs, once released into the atmosphere, undergo several processes, including adsorption on mineral aerosol surfaces, accumulation at the A-W interface, dispersion in bulk water within liquid droplets, and oxidation reactions initiated by atmospheric oxidants (Lin et al., 2017) . Reactions inside the aqueous particle have also been a hot topic of interest in recent years (Tilgner et al., 2021; Mabato et al., 2023; Zhang et al., 2024; Rana et al., 2024) , so we also focused on the process by which phenolic compounds enter the interior of the droplet. This section delves into the detailed mechanisms and characteristics of these reactions. At the M06-2X/6-311++G(3df,2p)//M06-2X/6-31+G(d,p) level, the structures with the minimum free energy for the Ph/4-HBA/VL has been determined (**Fig. S10**). In the case of VL, a significant reduction in molecular energy is observed due to the formation of a powerful intramolecular hydrogen bond with a length of 2.09 Å between the H and O atoms near the methyl group. Moreover, the lone pair electrons of oxygen atoms can form additionally p-π conjugations with the π electrons of the phenyl ring, further reducing the overall energy of VL in gas phase. The statistical charts of calculated $\Delta_r G$ and $\Delta G^{\ddagger}$ values for O_3- and $HO^{\bullet}$-initiated reactions are displayed in **Fig. 4** and **S8** and detailed data are available in **Tables 1–4**.

O_3 is a major oxidant in the atmosphere, with high concentrations in the troposphere of 9.85×10^{11} molecules cm $^{-3}$ (Tomas et al., 2003; Pillar-Little et al., 2014). Investigating the fate of PhCs in the presence of O_3 is essential (Pillar-Little et al., 2014; Rana and Guzman, 2020) . The ozonolysis of PhCs involves the synthesis of primary ozonide, the formation of active Criegee intermediate (CI), and the disintegration of CI (Rynjah et al., 2024) . The O_3-initiated reactions of Ph/4-HBA/VL involve radical adduct formation (RAF) channels on their benzene ring ($R_{O_3\text{-RAF}}$1–6), highlighted in red in **Fig. S10**. **Fig. 4(a)–(d)** depict that the ozonolysis pathways $R_{O_3\text{-RAF}}$ are exergonic, indicating their spontaneity. The average $\Delta G^{\ddagger}$ values for the ozonolysis of Ph/4-HBA/VL are ranked as Ph > VL > 4-HBA. The following is a list of the average values for the ozonolysis of Ph/4-HBA/VL, as illustrated in **Fig. 4(e)**–**5(h)**, Ph is superior to VL and 4-HBA, with the exception on TiO_2 clusters. **Fig. 4(e)** illustrates that the average value of $\Delta G^{\ddagger}$ for O_3 + Ph reactions at the A-W interface is 15.38 kcal mol^{-1}, the lowest value out of the three PhCs. The average $\Delta G^{\ddagger}$ values for the ozonolysis of Ph/4-HBA/VL are as follows: VL (13.95 kcal mol^{-1}) < Ph (24.70 kcal mol^{-1}) < 4-HBA (25.16 kcal mol^{-1}) on TiO_2 clusters (**Fig. 4(f)**). The average $\Delta G^{\ddagger}$ values for O_3 + VL reactions in gas phase are the highest among the four different EM (23.28 kcal mol^{-1}) shown in **Fig. 4(g)**). Comparing the phenolic oxidation in each of these four EM (bulk water, interface, TiO_2 clusters, and gas phase) reveals that A-W interface are more conducive to the ozonolysis of Ph, whereas TiO_2 clusters are more conducive to the ozonolysis of VL. The effect of solvation on $\Delta G^{\ddagger}$ is predominantly caused by the hydration of the phenolic OH group, as this is the part of the molecule being solvated. However, the presence of water molecules in the region around the phenyl group has been shown to have a considerable influence on the $\Delta G^{\ddagger}$ values.

$HO^{\bullet}$, known as "atmospheric detergents", is another significant atmospheric oxidant (Atkinson, 1986; Zhang et al., 2020). The worldwide mean tropospheric concentration of $HO^{\bullet}$ is roughly 11.3×10^{5} molecules cm $^{-3}$ (Lelieveld et al., 2016). For this reason, elucidating the reaction mechanism underlying $HO^{\bullet}$ + PhCs reactions in the troposphere is of the utmost importance. $HO^{\bullet}$-initiated reaction pathways of Ph/4-HBA/VL include RAF, hydrogen atom abstraction (HAA) channels from the benzene ring (R_{HAA}ben1–6) and the substituent group (R_{HAA}sub7–9). Previous research (Gao et al., 2019) has shown that the process of single electron transfer (SET) does not significantly contribute to the $HO^{\bullet}$-initiated reactions examined. Once the hydroxyl adducts or H_2O are formed, significant heats (4.21–30.28 kcal mol $^{-1}$) are released (**Fig. 4(i)–(l)**, **S8 (a)–(d) and (i)–(l)**; the detail data in **Table S3**), indicating high thermodynamic feasibility. The average $\Delta G^{\ddagger}$ values for $HO^{\bullet}$-initiated reactions (**Fig. 4(m)–(p)**, **S8 (e)–(h)** and **(m)–(p))** are lower than those for O_3-initiated reactions. Routs R_{HAA}ben make a minimal contribution to $HO^{\bullet}$-initiated reactions. At the A-W interface, VL (3.52 kcal mol $^{-1}$) < Ph (4.52 kcal mol $^{-1}$) < 4-HBA (9.50 kcal mol $^{-1}$), and the $\Delta G^{\ddagger}$ value of Ph is the lowest (-0.97 kcal mol $^{-1}$), the case for pathways $R_{RAF\text{-}HO^{\bullet}}$ **(Fig.4(m))**.

Among the three aromatic compounds, the $R_{RAF\text{-}HO}$• routes of VL on TiO_2 clusters are most likely to take place (**Fig. 4(n)**). When compared to HO$^•$-initiated reactions of aromatic compounds in the gas phase (**Fig. S9(e)**) or bulk water (**Fig. S9(f)**), the process of Ph + HO$^•$ reactions at the A-W interface is accelerated, whereas the process of VL + HO$^•$ reactions is accelerated by TiO_2 clusters. These findings are in agreement with the ozonolysis findings. The same guidelines can be used to routes R_{HAA}sub (**Fig. 4(o)**, **(p)**, **S8 (g)** and **(h)**) and R_{HAA}ben (**Fig. S8(m)–(p)**). The following is a ranking of the average $\Delta G^‡$ values for routes $R_{RAF\text{-}HO}$• in the gas phase or bulk water: Ph < 4-HBA < VL. As a result of having the lowest $\Delta G^‡$ values among all HO$^•$-initiated reaction mechanisms, routes R_{RAF} are the most advantageous of all the possible reaction mechanisms. In light of this, each and every route $R_{RAF\text{-}HO}$• and R_{HAA}sub will be dissected in detail.

Fig. 5 shows the Δ_rG and $\Delta G^‡$ values of O_3- and HO$^•$-initiated reactions at various reaction locations. These reactions are almost entirely exothermic, with a close correlation between Δ_rG values and $\Delta G^‡$ values. The $\Delta G^‡$ values for the Phe + O_3 reactions shown in **Fig. 5(a)** are the lowest among the three compounds, ranging from –0.97 to 7.86 kcal mol $^{-1}$. Exergonic and spontaneous addition reactions took place at the C1–C2 and C3–C4 locations of Ph and VL, respectively. Because of their low $\Delta G^‡$ values, the C1–C2 and C2–C3 sites of O_3-initiated reactions for 4-HBA are advantageous. Their values are 21.76 and 22.03 kcal mol $^{-1}$, respectively.

The C1–C2 location of 4-HBA is activated to a greater extent at the A-W interface in comparison to the gas phase and bulk water. However, the $\Delta G^{\ddagger}$ values of O_3 + Ph reactions on TiO_2 clusters are significantly greater than those of the A-W interface (12.86–18.10 kcal mol $^{-1}$) than 24.30–25.34 kcal mol $^{-1}$. The VL + O_3 reactions on TiO_2 clusters are favorable at the C2–C3 and C4–C5 locations (the $\Delta G^{\ddagger}$ values are 11.42 and 11.14 kcal mol $^{-1}$, respectively, **Fig. 5(b)**). This can be explained by the fact that the electron cloud has a greater propensity to congregate in the places C2–C3 and C4–C5, respectively. In addition, the p orbitals of the methoxy and hydroxy groups are conjugated to the benzene ring, which offers a powerful electron-donating conjugation effect (Aracri et al., 2013). Because of this, the oxidation of aromatic molecules is thermodynamically more favorable than the oxidation of the aldehyde group. This is consistent with previous studies that electron density influences the oxidative activity of PhCs (Rana and Guzman, 2022a). Clearly, the $\Delta G^{\ddagger}$ values of $HO^{\bullet}$-initiated reactions (–0.97~13.46 kcal mol $^{-1}$) in **Fig. 5(c)–(f)** are lower than those of O_3-initiated processes (11.14~27.83 kcal mol $^{-1}$) at different points in A-W interface and TiO_2 clusters. This can be seen by comparing the values to each other. At the A-W interface, the most advantageous position for the phenol hydroxyl group to be in for Ph/4-HBA/VL + $HO^{\bullet}$ reactions are the ortho position (**Fig. 5(c)**). OESI-MS, which stands for online electrospray ionization mass spectrometry, was also able to identify the hydroxylation product known as 3,4-dihydroxybenzaldehyde (Rana and Guzman, 2020). In **Fig. 5(d)**, the ortho- and meta-sites of phenol hydroxyl are, respectively, the most favorable positions for Ph/4-HBA + $HO^{\bullet}$ reactions on the TiO_2 clusters. On the other hand, all of the VL sites on the TiO_2 clusters are advantageous. At the A-W interface and on the TiO_2 clusters, the abstraction of hydrogen atoms follows the order of H_{-CHO} atom > H_{-OCH_3} atom > H_{-OH} atom in **Fig. 5(e) and (f)**. This can also be explained by the ALIE values of these atoms listed in the same order of H_{-CHO} atom (11.67–11.74 eV) > H_{-OCH_3} atom (14.06 eV) > H_{-OH} atom (15.46 eV), as shown in **Fig. S8**.

3.3.2 Generation and degradation of key products

For the purposes of this discussion, the primary atmospheric fate of the selected aromatics was considered to be their reactions with O_2 (typically mediated by reactive intermediates or catalytic processes) and O_3. **Fig. 6** and **S10** illustrate the subsequent reaction mechanisms of IMs, respectively. IM_{1-2} was produced using the pathway that offered the best conditions for the $HO^{\bullet}$-initiated reaction of Ph. As can be seen in **Fig. 6(a)**, the addition of O_2 to the C3 sites of the C_6H_5O radicals results in the formation of C_6H_5O-OO radicals with no barriers in either the gas phase or the bulk water. This is a desirable outcome. For the transformation of the $C_6H_5O_2$-OO radicals that were created, the ring closure reaction to form $C_6H_5O_2$-OO-d is attractive option. However, it must overcome an energy barrier of

18.83 kcal mol $^{-1}$ in the gas phase or 13.67 kcal mol $^{-1}$ in bulk water. The $C_6H_5O_2$-OO-d_1 radical, which was produced by the $C_6H_5O_2$-OO-d reaction, interacts once more with O_2. In the atmosphere, these Criegee intermediates also may undergo bimolecular reactions with NOx (Sun et al., 2020). Malealdehyde (P1) is what should mostly result from the reaction of the $C_6H_5O_2$-OO-d_1 radical with NO. However, during this process, it still needs to overcome an energy barrier of 49.5 (in the gas phase) or 50.83 kcal mol $^{-1}$ (in the bulk water) to generate $C_6H_5O_2$-OO-d_3 radical; as a result, the further transformation of the formed $C_6H_5O_2$-OO-d_2 should continue very slowly. Pyrocatechol (P2) is the primary product generated in the gas phase and bulk water when the H atom of the $C_6H_5O_2$-OO radical is displaced. P2 generates o-semiquinone radicals via pathways R_{HAA} by $HO^\bullet$ or O_3, which in turn generate oligomers (Guzman et al., 2022). This results in the formation of brown organic carbon in atmospheric aerosols. At the A-W interface, a sequence of hydroxylation products, including pyrocatechol (P2), benzene-1,2,3-triol (P3), and benzene-1,2,3,4,5-pentaol (P4), are generated through hydroxylation processes rather than by a single SET ($\Delta G^\ddagger$ = 111.79 kcal mol $^{-1}$). It is difficult for P4 to form benzene-1,2,3,4,5,6-hexaol because hydrogen transfer reactions are difficult to occur ($\Delta G^\ddagger$ = 34.32 kcal mol $^{-1}$). These hydroxylation products have been detected by experimental means (Pillar-Little et al., 2014; Pillar-Little and Guzman, 2017; Rana and Guzman, 2020). The $HO^\bullet$

abstracts a hydrogen atom from the hydroxyl group of catechol, forming $C_6H_5O_2$ radical and a water molecule. Due to the widespread presence of NO_2 in the environment, it adds to the $C_6H_5O_2$ radical at the ortho position of the extracted hydrogen atom through an addition reaction. Subsequently, a hydrogen transfer reaction occurs, resulting in the formation of 4-nitrobenzene-1,2-diol ($P_{2\text{-}a}$). This computational result validates the previous experimental hypothesis by Finewax et al (Finewax et al., 2018). The $P_{2\text{-}a}$ subsequently transform into benzoquinone, maleic acid, fumaric acid, acetic anhydride, acetic acid, and formic acid, or are directly mineralized into carbon dioxide and water (Chen et al., 2015). In order to gain a more comprehensive understanding of the reaction mechanism at the A-W interface, the major product (the $C_7H_5O_2$ radical) for pathways R_{HAA} of 4-HBA was also taken into consideration. According to **Fig. S11 (a)**, the addition of $HO^{\bullet}$ to the C7 sites of the $C_7H_5O_2$ radical can occur without any obstructions. The overpowering of the 18 kcal mol $^{-1}$ barrier resulted in the formation of the hydroxylation products (4-hydroxybenzoic acid (P5), 3,4-dihydroxybenzoic acid (P6), 2,3,4-trihydroxybenzoic acid (P7), and 2,3,4,5,6-pentahydroxybenzoic acid (P8)). There was found to be one transition route for the continued ozonolysis of the hydroxylation products that were produced in P6. The C2–C3 site of P6 to create P6-$5O_3$ ($\Delta G^{\ddagger}$ = 16.59 kcal mol $^{-1}$) has the lowest activation energy of all the available paths for the relevant reactions (**Fig. S11(b)**). This corresponds to a value of 16.59 kcal mol $^{-1}$. When the $\Delta G^{\ddagger}$ values of the breakage of five-membered rings created by ozonolysis pathways are compared, one can get the conclusion that the formation of IM_{P6}-5O_3-a is the most favored pathway. All of the hydrogen abstraction processes involving H_2O and IM_{P6}-5O_3-a have rather high energy barriers (32.93 kcal mol $^{-1}$). On the other hand, in **Fig. S10(a)**, the very low $\Delta G^{\ddagger}$ values (19.74 ~ 22.89 kcal mol $^{-1}$) of the -NO-O abstraction make it a desirable choice. Following a chain of ozonolysis reactions, the following products were obtained (**Fig.S11(c)**) : ((2E,4Z)-2-formyl-4,5-dihydroxy-6-oxohexa-2,4-dienoic acid (P9); 2,3-dihydroxymalealdehyde (P10); and 2,3-dioxpropanoic acid (P11). Therefore, the product that was created, P10, may also be the product that was discovered through experimentation (mass to charge ratios (m/z) = 115) (Rana and Guzman, 2020). The VL subsequent reaction mechanism is demonstrated in **Fig. S11(d)**. The final oxidation products of VL are P12 ((2E,4E)-4-formyl-2-methoxy-6-oxohexa-2,4-dienoic acid), P13 (ethene-1,1,2-tricarbaldehyde), P14 (2-methoxy-2-oxoacetic acid), P15 (oxalaldehyde) and P16 ((E)-2-methoxy-4,5-dioxopent-2-enoic acid). The formation of these products could explain the biomass burning material for the formation of SOA (Rana and Guzman, 2022b).

3.4 Comparison with available experimental results

The rate constants (*k*) of the overall reaction under the temperature range of 278–318 K were computed based on acquired potential energy surfaces for the O_3-initiated and $HO^•$-initiated reactions of selected compounds. The results of these calculations are listed in **Table S5** and **S6**, respectively. The temperature dependences of the various *k* values for Ph, 4-HBA, and VL at the A-W interface and in bulk water are depicted in **Fig. 7**. At low values of *k*, there is a positive dependence on temperature. When the *k* values are raised to a certain degree, the temperature dependency seems to lose any significance it may have had before. The following is an order of the *k* values for O_3-initiated reactions: $\text{A-W}_{\text{Ph}} > \text{TiO}_{2\ \text{VL}} > \text{A-W}_{\text{VL}} > \text{A-W}_{\text{4-HBA}} > \text{TiO}_{2\ \text{4-HBA}} > \text{TiO}_{2\ \text{Ph}}$ (**Fig. 7(a)**). According to **Fig. 7(b)**, the *k* values of $HO^•$-initiated reactions go as follows: $\text{TiO}_{2\ \text{VL}} > \text{A-W}_{\text{Ph}} > \text{A-W}_{\text{VL}} > \text{TiO}_{2\ \text{4-HBA}} > \text{TiO}_{2\ \text{Ph}} > \text{A-W}_{\text{4-HBA}}$. In **Fig. 7(a)** and **Fig. 7(b)**, the *k* values of $HO^•$-initiated reactions are one hundred times greater than those of O_3-initiated reactions. **Table 1** is a listing of the experimental and estimated *k* values that are available for O_3-initiated and $HO^•$-initiated reactions at 298 K. According to the findings, the ozonolysis of Ph was promoted by the water-gas interface as well as by TiO_2 clusters, and the $HO^•$ initiated reactions of VL were promoted by TiO_2 clusters. However, the $O_3/HO^•$ + 4-HBA reactions have the lowest *k* values among the three molecules when tested in a variety of environmental environments. The estimated $k_{O_3\text{+Ph}}$ values at the A-W interface are 11 orders of magnitude greater than those of catechol under dry conditions in gas phase (Zein et al., 2015), when compared with the experimental data. Because it has a higher k_{O_3} value, catechol, which is one of the main products of Ph's oxidation in the atmosphere, has a higher degree of reactivity than its parent compound (**Table 1**). The estimated value of VL is lower than the experimentally determined value of k_{O_3} for guaiacol under dry conditions, which is (0.40 ± 0.31) × 10^{-18} cm^3 $molecule^{-1}$ s^{-1} in the gas phase (Zein et al., 2015). The difference between the predicted value of $k_{HO^\bullet+VL}$ is 1.14 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} and the average experimental value of $k_{HO^\bullet}$ for methoxyphenols is just an order of magnitude. As a consequence, the findings of our calculations are reliable. Previous studies measured the second order rate constants of guaiacylacetone + $HO^\bullet$ reaction to be (14–25) × 10^9 M^{-1} s^{-1} at pH 5 and 6 at aqueous secondary organic aerosol, which is lower than our results (Arciva et al., 2022). This is because galactose reduces the steady-state concentration of $HO^\bullet$. The reaction rate constants of PhCs increase with increasing pH and we calculated the rate constants at pH 7 in bulk water (Ma et al., 2021). This study summarizes the O_3- and $HO^\bullet$-initiated reaction sequences of three PhCs in different environmental media. The reaction sequences for O_3- and $HO^\bullet$-initiated reactions of Ph and 4-HBA are identical in different environmental media, while VL shows slight variations. For O_3-initiated reactions, the reaction sequences are as follows: Ph: A-W interface > Bulk water > Gas phase > TiO_2 clusters; 4-HBA: Bulk water > A-W interface > TiO_2 clusters > Gas phase; VL: Bulk water > TiO_2 clusters > A-W interface > Gas phase. For $HO^\bullet$-initiated reactions, the sequences are: Ph: A-W interface ≈ Bulk water > Gas phase > TiO_2 clusters; 4-HBA: Bulk water > A-W interface > TiO_2 clusters > Gas phase; VL: TiO_2 clusters > Bulk water > A-W interface > Gas phase. According to the atmospheric concentration of O_3, the atmospheric lifetime of Ph is the shortest (< 1s) of the three PhCs at the gas-water interface or bulk water, whereas 4-HBA and VL were oxidized more slowly than Ph (Smith et al., 2016). See **Fig. S12** and **Text S9** for ecotoxicity assessment.

4. Conclusions

Combining molecular dynamic simulations (with the AMBER force field) and quantum chemical calculations (at the M06–2X/6–311++G(3df,2p)//M06–2X/6-31+G(d,p) level) methods has provided comprehensive insights into the surface properties of Ph, 4-HBA, and VL, as well as their reactions induced by O_3 and $HO^\bullet$, both in homogeneous and heterogeneous environments. Here are some key findings from this research:

(1) Free energy well of Ph, 4-HBA, and VL favor the A-W interface as their preferred location, with the occurrence percentages of approximately ~72%, ~68%, and ~73% respectively. Ph and 4-HBA show a preference for the A-W interface over the air, with energy difference of around 0.22 and 0.45 kcal mol $^{-1}$. The VL adsorbed on the TiO_2 clusters has a higher likelihood of remaining compared to VL adsorbed at the A-W interface. (2) The adsorption capacity of TiO_2 clusters decreases with increasing cluster

size until n > 4. After that point, the adsorption capacity remains constant. Strong electrostatic attractive interactions and attractive dispersion effects occur between the benzene of the Ph and Ti atoms. Hydrogen bonds form between the atom of O_{TiO_2} and the H_{-CHO} group of 4-HBA or VL. (3) The O_3- and $HO^•$-initiated reactions for Ph and VL are facilitated by the A-W interface and TiO_2 clusters, respectively, For O_3-initiated reactions at the A-W interface, the C1–C2 position on the benzene ring is most favorable. In both the A-W interface and on TiO_2 clusters, the total branching ratio for routes R_{RAF} and R_{HAA}sub is 72.68% ~ 100%. For route R_{HAA}sub, the order is H_{-CHO} atom > H_{-OCH_3} atom > H_{-OH} atom. (4) The *k* values (in molecules·cm $^{-3}$ s $^{-1}$, at 298K and 1 atm) of O_3-initiated reactions follow the order of A-W_{Ph} (5.98×10^{-7}) > TiO_2 $_{VL}$ (3.30×10^{-15}) > A-W_{VL} (1.27×10^{-17}) > A-$W_{4\text{-}HBA}$ (6.79×10^{-23}) > TiO_2 $_{4\text{-}HBA}$ (5.32×10^{-24}) > TiO_2 $_{Ph}$ (1.84×10^{-24}). The *k* values of $HO^•$-initiated reactions follow the order of TiO_2 $_{VL}$ (6.70×10^{-6}) > A-W_{Ph} (2.69×10^{-6}) > A-W_{VL} (1.73×10^{-7}) > TiO_2 $_{4\text{-}HBA}$ (3.16×10^{-9}) > TiO_2 $_{Ph}$ (3.17×10^{-10}) > A-$W_{4\text{-}HBA}$ (9.49×10^{-11}). (5) Toxicity risk assessment on aquatic species reveal that most of the reaction products are significantly less harmful than the parent compounds. However, products P1, P2, P3, P10, and P11 are more hazardous, and further investigation of their atmospheric fate is recommended.

Ph undergoes transformation to malealdehyde and catechol when exposed to O_3 or $HO^•$ in the troposphere (Xu and Wang, 2013). When

Ph/VL is at the droplet aerosol interface, rapid oxidation to polyhydroxylated compounds occurs (Ma et al., 2021). VL eventually creates tiny molecule aldehydes and acids. This is consistent with experimental observations (Rana and Guzman, 2020). This oxidation process is accelerated when VL is encased in a mineral aerosol represented by TiO_2 clusters. Li et al. found that seasonal average concentrations of total nitrophenol compounds in particulate matter were comparable to those measured in the gas phase (Li et al., 2022) . However, the reactivity order of nitrophenols in the atmospheric compartments is water droplets > gas phase > particles (Vione et al., 2009). The formation of some low molecular weight acids and aldehydes (2,3-dihydroxymalealdehyde, 2,3-dioxpropanoic acid, etc.) confirms their association with the formation of SOA. It is recommended that enterprises producing lignin, such as those in the pulp and paper industry, or factories that employ lignin in the manufacturing of adhesives, rust inhibitors, color dispersants, diluents, or other similar products, be constructed in regions with low relative humidity. It is recommended that treatment facilities that collect lignin pyrolysis products and recycle the byproducts be located in the surrounding area.

Author contributions

Yanru Huo contributed to the manuscript conceptualization, methodology, software, formal analysis, investigation, and writing of the original manuscript. Mingxue Li provided insight into the writing ideas throughout the article. Xueyu Wang offered some guidance on the method section of the manuscript. Jianfei Sun, Yuxin Zhou, and Ma Yuhui reviewed the original manuscript. Maoxia He: Conceptualization, Resources, Writing – review & editing, Supervision, Funding acquisition.

Competing interests

The contact author has declared that none of the authors has any competing interests.

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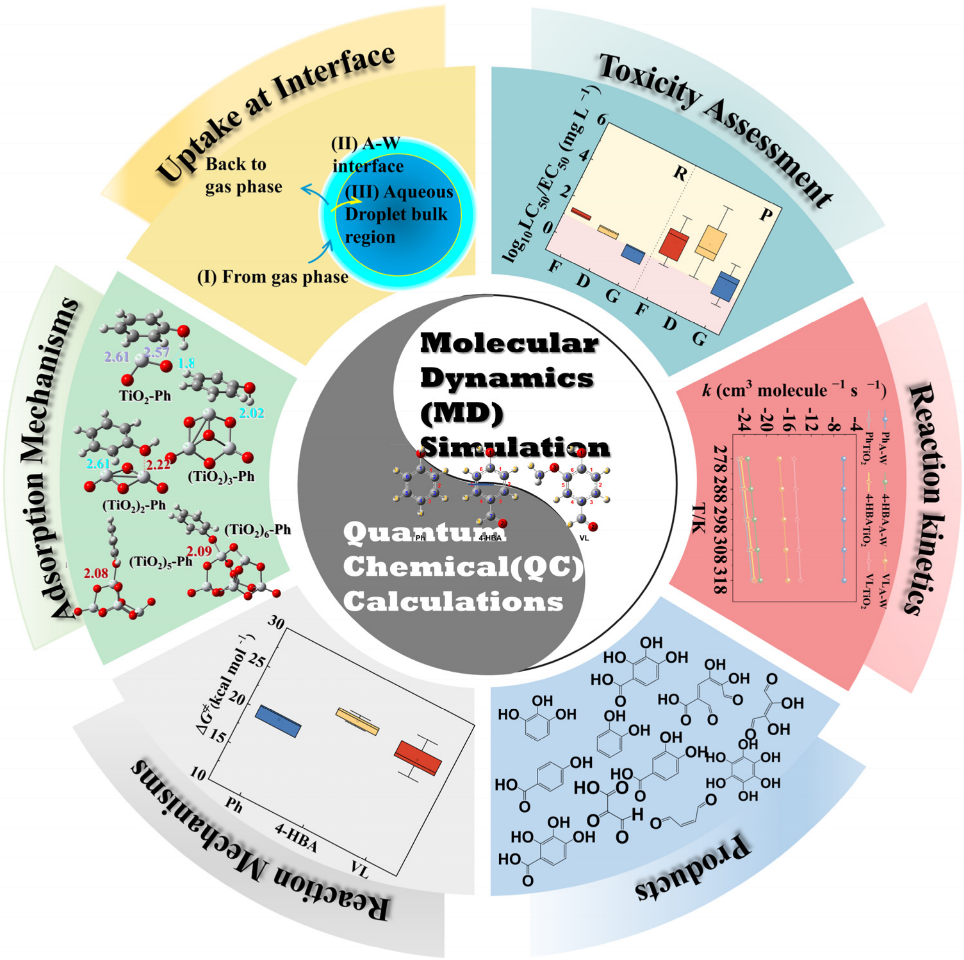

Graphical Abstract

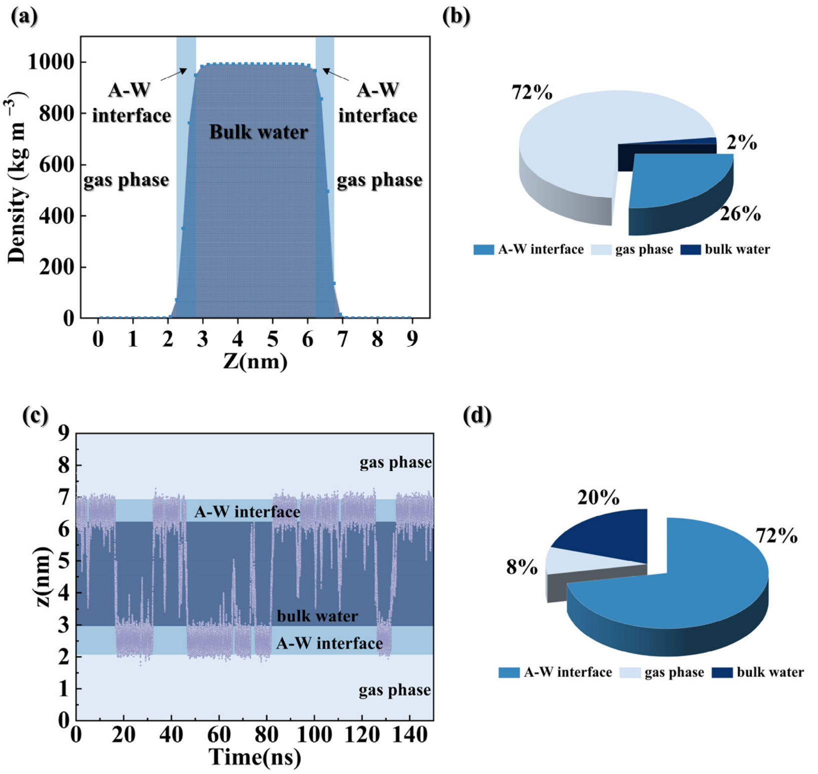

Fig.1 **(a)** Relative concentration distributions in the A-W system along the z-axis; **(b)** probability of O_3 at the A-W interface, in gas phase, and in bulk water; **(c)** MD trajectories of Ph diffusion through the water slab over a 150 ns period; **(d)** probability of Ph at the A-W interface, in gas phase, and in bulk water.

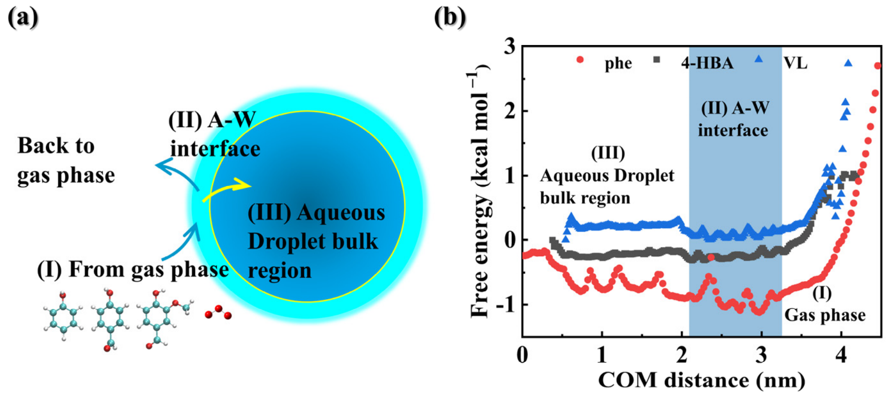

Fig.2 **(a)** Three key processes for the reaction of gaseous PhCs (Ph, 4-HBA, or VL) with the water drops; **(b)** free energy change profile of gaseous PhCs (Ph, 4-HBA, or VL) approaching the bulk water.

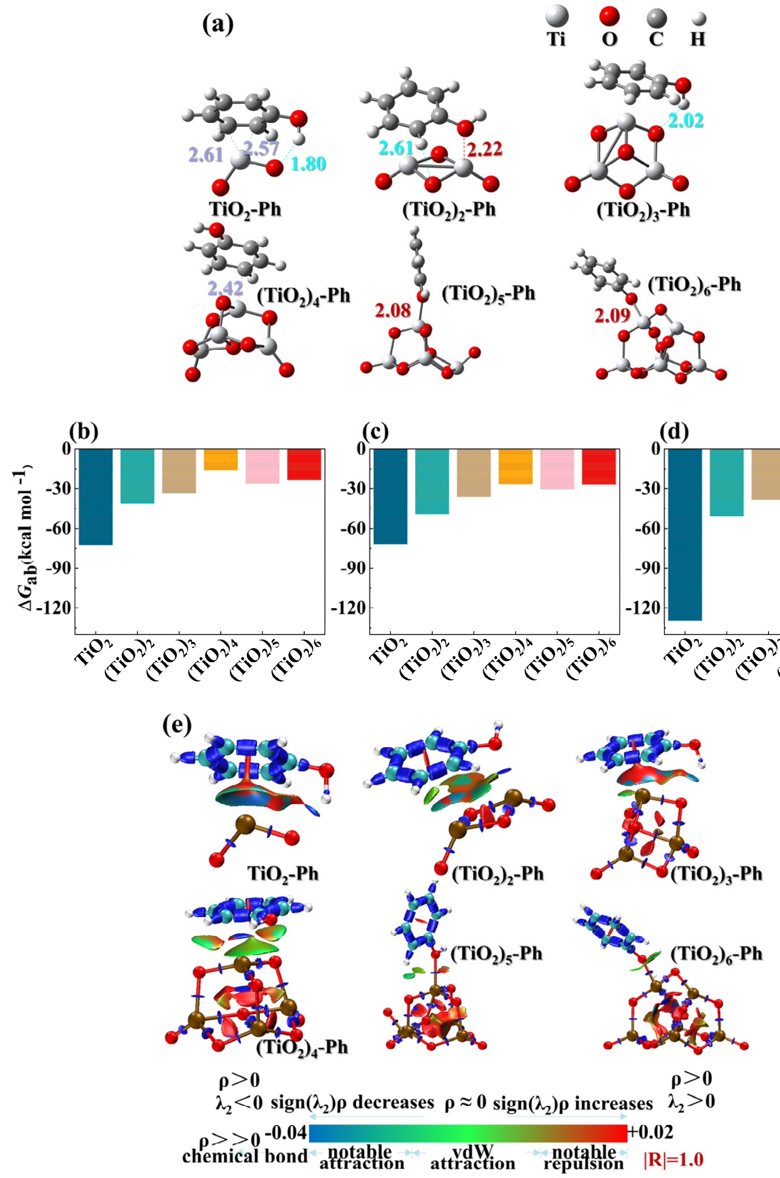

Fig. 3 Adsorption details of PhCs on $(TiO_2)_n$ (n = 1–6) clusters; **(a)** structure of Ph adsorption on $(TiO_2)_n$ (n = 1–6) surface; adsorption energy of **(b)** Ph, **(c)** 4-HBA, and (d) VL on $(TiO_2)_n$ (n = 1–6, unit: kcal mol^{-1}); **(e)** Interaction region indicator (IRI) analyses of Ph on $(TiO_2)_n$ (n = 1–6) surface.

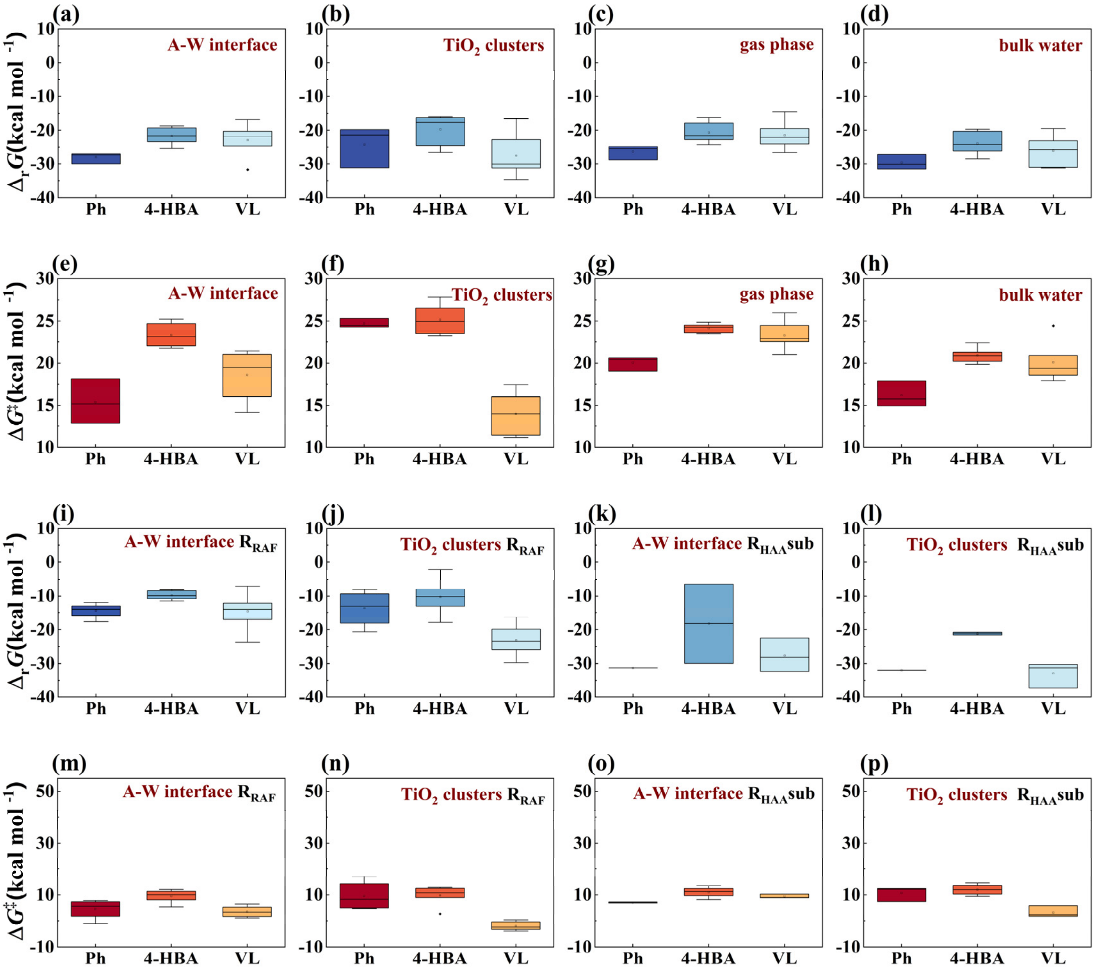

Fig. 4 Statistical charts of calculated **(a)–(d)** Δ_rG and **(e)–(h)** $\Delta G^{\ddagger}$ values for O_3-initiated reactions; **(i)–(l)** Δ_rG and **(m)–(p)** $\Delta G^{\ddagger}$ values for HO$^{\bullet}$-initiated reactions.

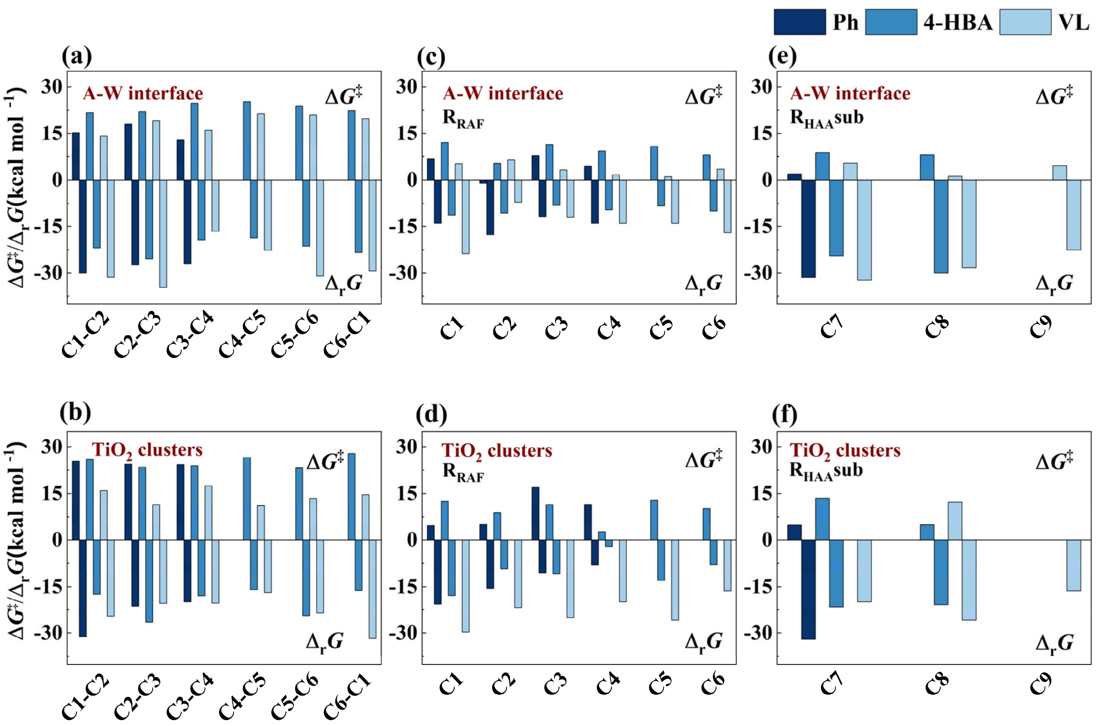

Fig.5 Δ_rG and $\Delta G^\ddagger$ values of **(a)**–**(b)** O_3-initiated reactions and **(c)**–**(f)** $HO^\bullet$-initiated reactions at different reaction positions.

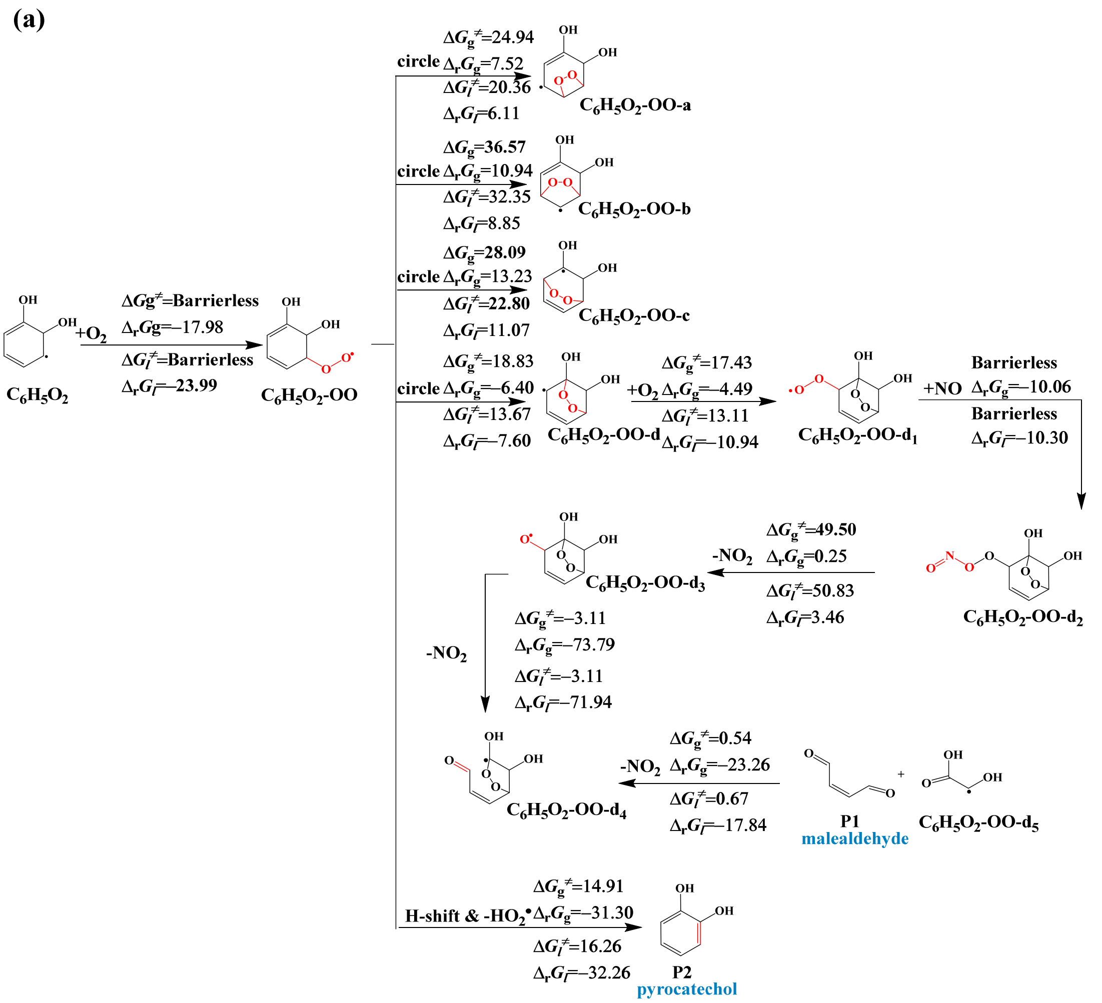

Fig.6 Subsequent reaction mechanisms of important intermediates (IMs) (unit: kcal mol $^{-1}$) in **(a)** gas phase (g) / bulk water (l) and at **(b)** A-W interface (Continue on the next page).

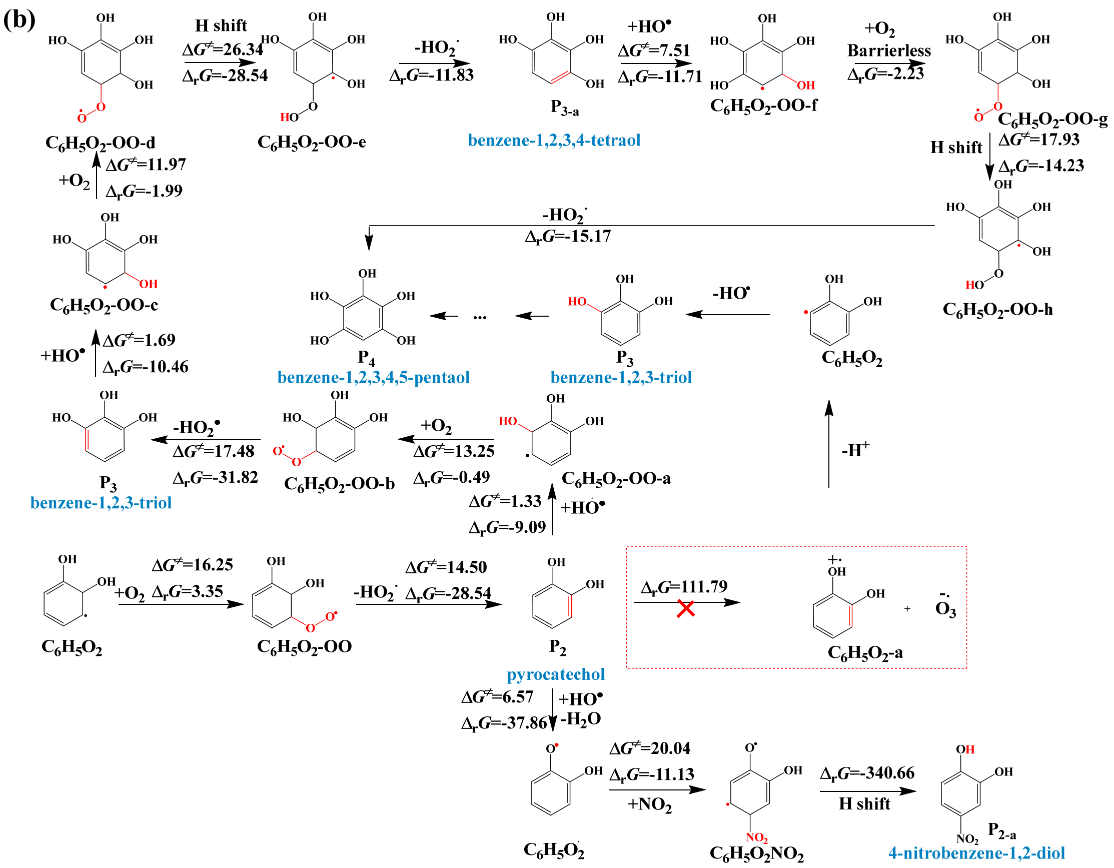

Fig.6 (Continue) Subsequent reaction mechanisms of important intermediates (IMs) (unit: kcal mol $^{-1}$) in **(a)** gas phase (g) / bulk water (l) and at **(b)** A-W interface.

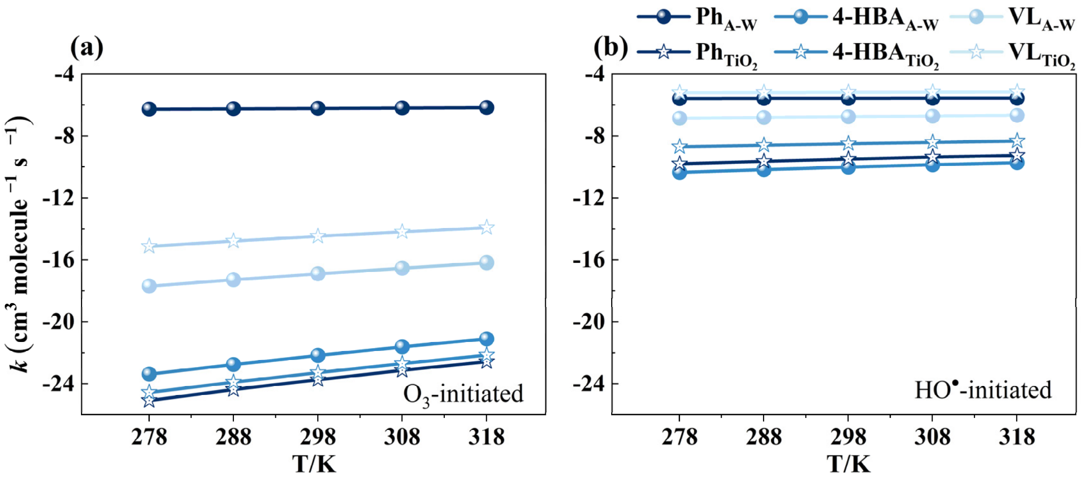

Fig. 7 Calculated rate constants for the initial reactions of Ph, 4-HBA, and VL with O_3 and HO$^\bullet$ at different temperatures (278–318 K) and 1 atm.

Table 1 The available experimental and calculated reaction rate constants (k) values of O_3- and HO$^\bullet$-initiated reactions at 298 K. Unit: cm^3 molecule $^{-1}$ s $^{-1}$.

Compounds	$k_{tot\text{-}A\text{-}W,\text{cal}}{}^{a}$	$k_{tot\text{-}TiO_2,\text{cal}}{}^{b}$	$k_{tot\text{-}gas,\text{cal}}{}^{c}$	$k_{tot\text{-}wat,\text{cal}}{}^{d}$	$k_{,\text{exp}}$	Ref.
Ph	5.98×10^{-7}	1.84×10^{-24}	5.27×10^{-20}	4.02×10^{12}	$(13.5 \pm 1.1) \times 10^{-18,\ e}$	Zein et al. (2015)
	2.69×10^{-6}	3.17×10^{-10}	2.34×10^{-9}	4.46×10^{13}	—	
4-HBA	6.79×10^{-23}	5.32×10^{-24}	4.93×10^{-24}	1.97×10^{12}	—	
	9.49×10^{-11}	3.16×10^{-9}	7.90×10^{-11}	2.52×10^{13}	—	Rana et al. (2020)
VL	1.27×10^{-17}	3.30×10^{-15}	1.35×10^{-22}	2.20×10^{12}	$(0.40 \pm 0.31) \times 10^{-18,\ f}$	Zein et al. (2015)
	1.73×10^{-7}	6.70×10^{-6}	1.14×10^{-10}	3.15×10^{13}	$6.00 \times 10^{-11,\ g}$	Rana et al. (2020)

[a]: calculated values of phenolic compounds at A-W interface;

[b]: calculated values of phenolic compounds on TiO_2 clusters;

[c]: calculated values of phenolic compounds in the gas phase;

[d]: calculated values of phenolic compounds in the bulk water.

[e]: experimental values of catechol in the gas phase;

[f]: experimental values of guaiacol in the gas phase;

[g]: experimental average $k_{HO^\bullet}$ values of methoxyphenols in the gas phase.