Degradation of *p*-Chlorophenol by *γ*-Radiolysis: Radiolytic Intermediates and Theoretical Calculations

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Radiolysis of *p*-chlorophenol (*p*-CP) was investigated through experiments and theoretical calculations. Its radiolytic intermediate products, i.e., phenol, hydroquinone, 4-chlororesorcinol, and 4-chloropyrocatechol, were identified using their mass spectra through a GC/MS system. Three transition states and a prereaction complex of the reaction between hydroxyl radical and *p*-CP were found from the density functional theory (DFT) study. Both the experimental and calculation results demonstrate that the main *p*-CP degradation pathway was the formation of 4-chloropyrocatechol.

Within the last two decades, there has been a growing concern related to serious environmental problems due to the increasing water contamination. Among the top priority pollutants, chlorinated phenols generated as chemical intermediates or by-products in various industries represent an important class of water pollutants. Since chlorophenols are resistant to conventional biological treatments,[1] many efforts have been made in the search for efficient and economical decomposition methods, e.g. Fenton oxidation,[2] photocatalytic,[3,4] and ultrasonic[5] processes.

Radiation-induced degradation is a promising method against organic contaminations.[6,7] Degradation of monochlorophenols by *γ*-irradiation has been investigated.[8,9] Their decomposition and dechlorination efficiencies have been reported. For *p*-CP, phenol under reductive conditions and 4-chlorocatechol and hydroquinone under oxidative conditions were respectively detected in radiolysis. However, the degradation immediate products were just preliminarily determined by their HPLC retention times and UV-spectra, and information about its degradation mechanisms is still sparse. In the present work, *γ*-radiolytic metabolites of *p*-CP were investigated by using GC–MS and FTIR. Furthermore, theoretical calculations about its degradation mechanisms were performed.

Ethyl acetate, *p*-CP and anhydrous magnesium sulfate, all purchased from Shanghai Chemical Reagent Company, were of analytical grade. Ethyl acetate was redistilled prior to use. Double distilled water was used throughout the experiments.

Radiolytic products of *p*-CP were analyzed and identified using an Agilent 6890 GC (Angilent Inc., USA) system coupled to a GCT–MS (Micromass Ltd., UK) through an electron impact interface. Chromatographic measurements were performed with a capillary column DB-5 (30 m × 0.25 mm × 0.25 μm). Irradiated samples were extracted with redistilled ethyl acetate. The extracts were merged and dried with anhydrous magnesium sulfate and were concentrated under reduced pressure. Concentrated extracts of 0.2 μL were subjected to GC–MS determination and FTIR (Magna-IR 750, Nicolet Instrument Co., USA) analysis.

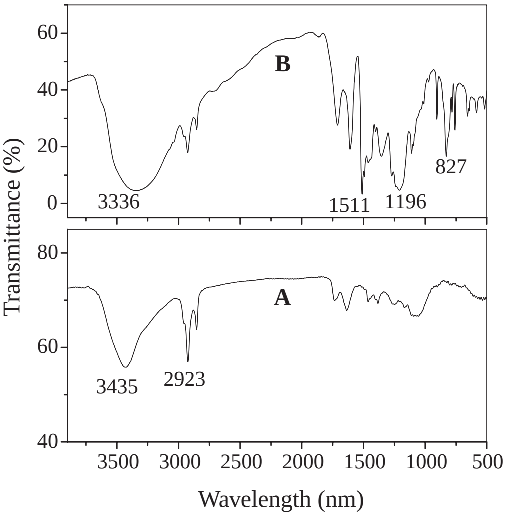


Figure 1. FTIR spectra of *p*-CP (**A**) and the extract of irradiated samples (**B**).

p-Chlorophenol solutions with an initial concentration of 1.0 mmol L^{-1} were saturated with high-pure argon and irradiated in sealed Pyrex glass vessels at a ^{60}Co *γ*-ray dose rate of 49 Gy min^{-1} under ambient temperatures for 2.5 h.

Figure 1 illustrates the evolution of IR spectra during the irradiation. Strong peaks, e.g. at wavenumbers of 1511, 1196, and 827 cm^{-1}, appeared in spectrum **B**, indicating the formation of radiolytic products. The band at a wavenumber of about 3400 cm^{-1} was assigned to the stretching vibration of hydroxyl group. It shifted and broadened significantly after the irradiation, implying that different hydroxyl groups were formed.

Figure 2 shows the GC chromatogram of the extract from the irradiated sample. Phenol (**1**), hydroquinone (**3**), 4-chlororesorcinol (**4**), 4-chloropyrocatechol (**5**), and remained *p*-CP (**2**) were identified from their mass spectra. In the previous studies, 4-chlororesorcinol was not detected, while phenol was formed by the e_{aq}^- attack.[8,9] The presence of metabolites **3**–**5** indicates that the hydroxyl radicals generated during the irradiation could attack all the positions of the benzene ring. The abundance of 4-chloropyrocatechol was much higher than those of other metabolites. Its formation might be the main radiolysis pathway because the sensitivities on the responses of GC–MS to the species 1, 3, 4, and 5 are of a similar level.

Hydroxyl radical is the most active oxidative species gener-

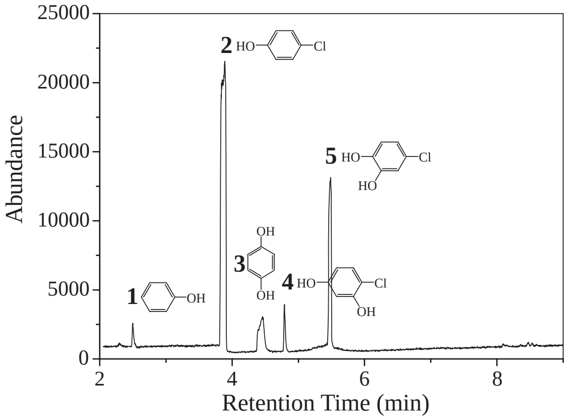


Figure 2. GC chromatogram of the extract from *p*-CP radiolytic products.

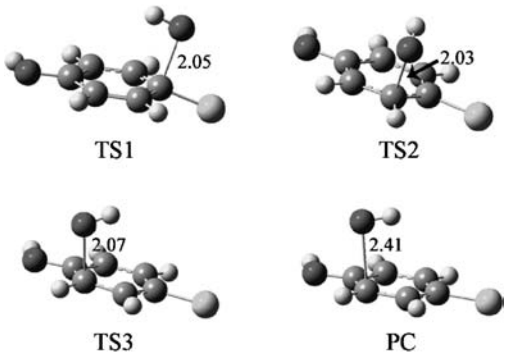
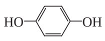
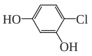
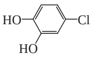
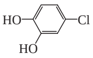


Figure 3. Optimized geometries of the transition states (**TS1-3**) and the prereaction complex (**PC**).

ated in the radiolytic processes. In order to understand the mechanisms of the degradation better, a DFT study of the reaction between hydroxyl radical and *p*-CP molecule was carried out, using Gaussian 98 for the calculation of geometries and energies.[10] Optimizations were performed at the UB3LYP/6-31G (d) level of theory. Ground state and transition state structures were confirmed by frequency analysis at the same level. Transition structures had been characterized by having one imaginary frequency that belonged to the reaction coordinate, corresponding to a first-order saddle point. Zero point vibrational energies (ZPEs) were calculated at the UB3LYP/6-31G(d) level and scaled by the factor of 0.9804. Single point energies (SPEs) were calculated at the UB3LYP/6-311+G (2d,p) level. Solvent effects were modeled using the integral equation formalism polarized continuum model (IEFPCM) within self-consistent reaction field (SCRF) theory, by means of single-point calculations based on the gas-phase geometries.[11]

Three transition states (**TS1-3**), which lead to the respective formation of hydroquinone (**3**), 4-chlororesorcinol (**4**), and 4-chloropyrocatechol (**5**), were found in the calculations (Figure 3). Their corresponding O–C distances ranged from 2.03 to 2.07 Å. Other three transition states, which followed **TS1-3** along the reaction coordinates respectively, were also founded (not shown). A prereaction complex (**PC**) related to **TS3** was observed as the OH radical approached the benzene ring with an –O···C– distance of 2.41 Å. However, no precomplex structure corresponding to **TS1** or **TS2** was found in this work. Relative energies of **TS1-3** and **PC** in the gas phase and water are presented in Table 1. With the benefit of **PC**, **TS3** is lower in energy than the reactants (p-CP + •OH), whereas **TS1** and **TS2** are both higher than them. Furthermore, the relative energies of **TS3** and **PC** decrease notably while those of **TS1** and **TS2** increase in solution, which indicates that solvent has more stabilizing effects on **TS3** and **PC** than the other two transition states. Therefore, it could be concluded that the reaction prefers the 4-chlorocatechol-formation pathway. This is in good agreement with the experimental results.

Table 1. Relative energies of **TS1-3** and **PC** in the gas phase and water

		TS1	TS2	TS3	PC
Relative energy* (kJ mol $^{-1}$)	Gas phase	5.96	0.81	-7.11	-9.98
	water	10.91	0.91	-12.06	-12.70
Corresponding metabolite					

*: Zero points of the relative energies correspond to the sum of the energies of the reactants (p-CP + •OH = −842.852528734 hartree in the gas phase and −842.879536582 hartree in water).

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