

Reaction mechanism of 3-chlorophenol with OH, H in aqueous solution

ZHU Jie, CHEN Ye-fei, DONG Wen-bo, PAN Xun-xi, HOU Hui-qi

(Institute of Environmental Science, Fudan University, Shanghai 200433, China. E-mail: jiezero@163.com)

Abstract: The reaction mechanism of 3-chlorophenol with OH, H in aqueous solution was studied by transient technology. The 3-chlorophenol aqueous solutions have been saturated with air or N₂ previously. Under alkaline condition, the reaction of OH radical with 3-chlorophenol produces 3-chlorinated phenoxy radical, with the absorption peaks at 400 nm and 417 nm. Under neutral condition, the reaction of OH radical with 3-chlorophenol produces OH-adduct with the maximal absorption at about 340 nm. And in acid solution, the reaction of H with 3-chlorophenol produces H-adduct with the maximal absorption at about 320 nm. 3-chlorophenol is compared with 4- and 2-chlorophenols from the free radical pathways. The results show that the positions of chlorine on the aromatic ring strongly influence the dehalogenation and degradation process.

Keywords: 3-chlorophenol; OH radical; atomic H; microscopic reactions; transient absorption spectra

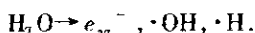
Introduction

Chlorophenols are ranked high among pollutants in the environment owing to their high toxicity, strong stench, and high solubility in water. As far as mono-chlorophenols are concerned, there are three isomers; ortho-, para- and meta-. It was reported that the isomers have similar toxicity, but in contrast to the other two isomers, 3-chlorophenol has a much slower degradation rate and a longer residence time. For example, the minimum time for a 70% decrease of 3-chlorophenol in non-sterile soil is about 80—160 days, and it is much longer than that of 2- and 4-chlorophenols, which are 0.5—1 day and 1—2 days respectively (Krijghsheld, 1986; Beker, 1980). By this conjecture, 3-chlorophenol probably has different physical and chemical properties from 4- and 2-chlorophenols. The isomers' degradation processes are not probably similar due to the different positions of the substituent. The reaction processes of 4- and 2-chlorophenols with OH radical and H in water phase have been intensively studied (Wang, 2001; Dong, submitted), but the mechanism of 3-chlorophenol with these radicals awaits research. In order to study the different properties of chlorophenols, we investigate 3-chlorophenol in water system using pulse radiolysis technique that has been used to study 2- and 4-chlorophenols. This study will help us know the properties of chlorophenols comprehensively, and find out the migrating, transforming, degradation processes in aqueous environment.

1 Materials and methods

3-chlorophenol used was obtained from Fluka and kept at 0—4 °C isopropanol, HClO₄ and NaOH were obtained from Shanghai Feida Co. All samples were prepared in triply distilled water and deaerated by high purity nitrogen (99.99%).

The radiolysis of water may be described by:



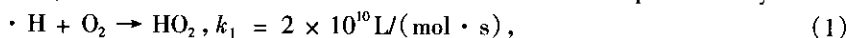
Their *G* values, numbers of particles that are formed or destroyed when the system absorbs every 100 eV energy, are generally 2.7 for e_{aq}^- , 2.7 for OH, and 0.55 for H. In the course of the radiolysis, $\cdot\text{OH}$, $\cdot\text{H}$ and e_{aq}^- react with solute molecular at a high rate and produce transient particles such as free radicals. Pulse radiolysis experiments were conducted by using a linear accelerator providing 10 MeV electron pulse with a duration of 8 ns. The pulse radiation quantity can be adjusted in the range of 10 -

15 Gy. The analytical light source was a 500W xenon lamp powered by a voltage-current stabilizer. The transmitted light entered a monochromator equipped with a photomultiplier (1P28). The signals were collected using HP54510B 500MHz transient recorder, then processed with an IBM/AT personal computer. This system allows transient absorption spectra to be measured in the ultraviolet-visible region (Yao, 1995). The photic leg length of the quartz sample cell is 20 mm. All the experiments were carried out at room temperature.

2 Results and discussion

2.1 Study of 3-chlorophenol in alkaline air-saturated aqueous solution

The concentration of dissolved oxygen in dilute aqueous solution is usually about 0.25 mmol/L. In air-saturated solution, the reaction of OH radicals and chlorophenol molecules is the dominant reaction, because a great deal of the dissolved oxygen reacts as the Reactions (1) and (2) (Andras, 1997). This is the general method used to study the reaction of substances and OH free radical with pulse radiolysis.



The 5 mmol/L 3-chlorophenol aqueous solution was adjusted by NaOH to pH = 11 and saturated by air before radiolysis. The transient absorption spectra of 3-chlorophenol in alkaline aqueous solution are shown as Fig. 1. The three curves in the figure are the spectra detected 1 μs , 8 μs , 40 μs after the electron pulse respectively.

Fig. 1 shows that the strong absorption peaks appear at 376 nm and 393 nm for 1 μs after radiolysis and at 400 nm and 420 nm for 8 μs after radiolysis.

Wojnarovit reported that the absorptions at 376 nm and 393 nm were assigned to 2-chlorophenoxy and the absorption at 417 nm were due to 3-chlorophenoxy (Wojnarovit, 1997). Comparing with Wojnarovit's results, we concluded that 2-chlorophenol existed in the 3-chlorophenol systems we studied, and under alkaline condition, OH radical reacted with 3-chlorophenol to form 3-chlorophenoxy as following.

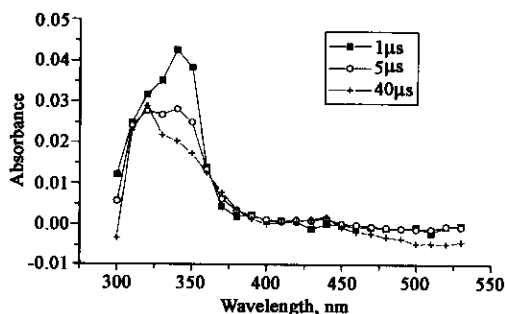
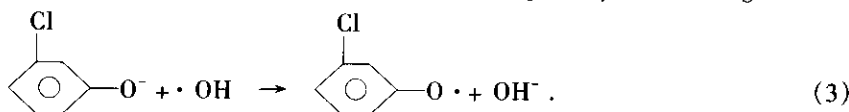


Fig.2 Transient absorption spectra of pulse radiolysis of 3-chlorophenol in neutral air-saturated aqueous solution

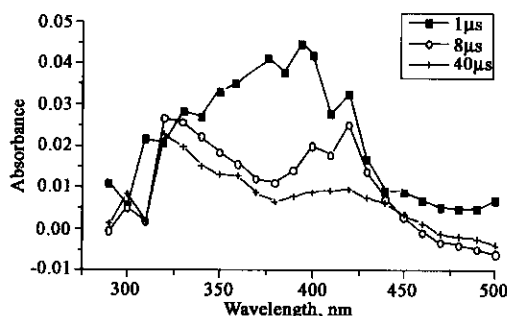


Fig.1 Transient absorption spectra of pulse radiolysis of 3-chlorophenol in alkaline air-saturated aqueous solution

The Reaction (3) shows the charges transform from 3-chlorophenol to OH radical in alkaline system. In comparison with the reaction of the 4-chlorophenol or 2-chlorophenol and OH radical in alkaline solution, the three isomers of chlorophenol all produce chlorophenoxy as intermediate products (Wang, 2001; Dong, submitted). In other words, the primary reactions processes of 3-chlorophenol and OH radical are the same as the other two isomers under alkaline condition.

2.2 Study of 3-chlorophenol in neutral air-saturated aqueous solution

As the environment water bodies are usually under

neutral and weak acid conditions, 3-chlorophenol has the lowest degradation rate and the longest residence time in the environment water bodies. It is suggested that the reaction properties of 3-chlorophenol are different from the other two isomers. So the research of the reaction of OH radical and 3-chlorophenol in the neutral condition is necessary. In this way we can find out the differences and similarities in the properties of 3-chlorophenol, 2-chlorophenol and 4-chlorophenol.

The 5 mmol/L aqueous solution of 3-chlorophenol used in the experiments gives the transient absorption spectra as Fig. 2 after pulse radiolysis in the neutral aerated system without adjust ion of acidity.

In Fig. 2, there are two absorption peaks at about 320 nm and 340 nm respectively. The build-up/decay trends of transient species are also given in Fig. 3.

The absorption peaks at 320 nm and 340 nm are due to 2-chlorophenol OH-adducts and 3-chlorophenol OH-adducts respectively(Wojnarovit, 1997). So, under the neutral condition, 3-chlorophenols react with OH free radicals to produce OH-adducts as (4):

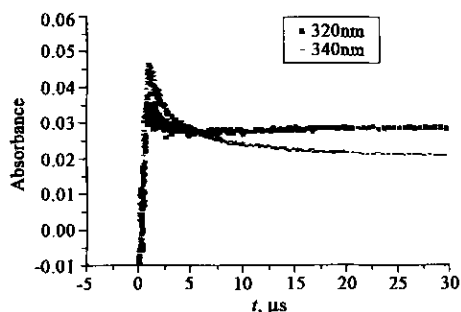
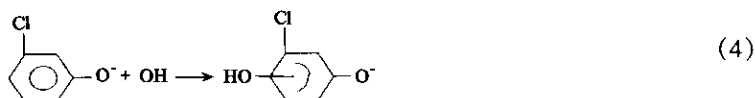
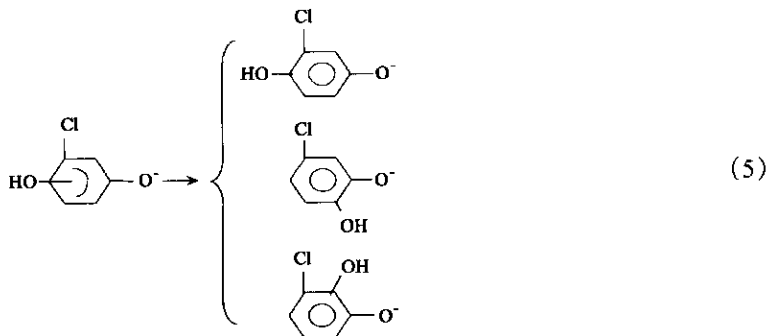


Fig.3 The build-up/decay trends of transient species at 320 nm and 340 nm



Serpone *et al* showed that 3-chlorophenol OH-adducts were transient species and would decay in the way of producing three different structures as Reaction(5)(Serpone, 1994).



With the attenuation of the absorption of 3-chlorophenol OH-adducts in Fig. 2, there is no new absorption peak appearing at 400 nm and 417 nm. It means that the OH-adducts of 3-chlorophenol are not easy to produce chlorophenoxy radical as Reaction(6). This has not been reported in previous researches.



The reactions we studied were the primary steps of the chlorophenols degradation. From this result, we found 3-chlorophenol OH-adduct was hard to form 3-chlorophenoxy, not similar to 2- and 4-chlorophenols. We suggested that 3-chlorophenol is more stable than the other two isomers especially in neutral air-saturated solutions. As we know, most water in the environment is approximately neutral and air-saturated. This result is useful to the explanation of the fact that 3-chlorophenol has the longest

residence time in the environment of the three isomers. By utilizing UV/H₂O₂ method in the degradation process of chlorophenols, H₂O₂ gives OH radical, and OH reacts with 3-chlorophenol to form OH-adducts (Huang, 1995). As far as our results are concerned, the chlorine on the benzene ring will not be off immediately in the process, dechlorination using this method will not be efficient.

2.3 Reaction of H atom and 3-chlorophenol

Isopropanol can react with OH radical to form H₂O as shown as Reaction(7)(Buxton, 1988) and it is an effective OH radicals scavenger. In order to study the reaction of H atom and 3-chlorophenol by pulse radiolysis, isopropanol was added to the deoxygenated aqueous solutions of 3-chlorophenol. H atoms in acid aqueous solution come from two sources; by hydrated electrons and H₃O⁺, and through the primary electronic radiolysis. A number of H⁺ ions were acted by e_{aq}⁻ to produce H atoms through Reaction (8) (Anbar, 1967). Therefore the reaction of H atom with 3-chlorophenol in the acid solution with isopropanol became the dominant reaction.

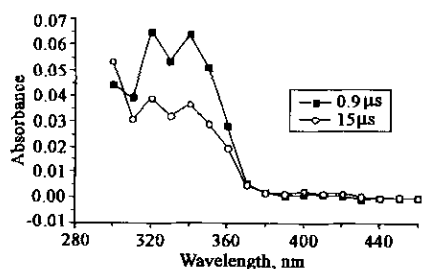
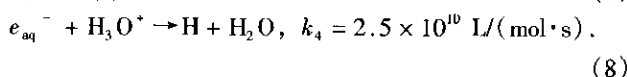
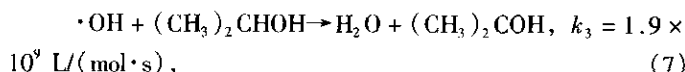
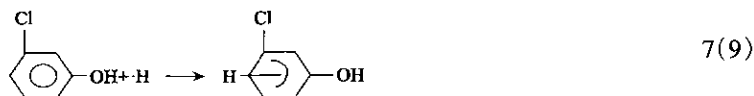


Fig. 4 Transient absorption spectra of pulse radiolysis of 3-chlorophenol in acid N₂-saturated aqueous solution with isopropanol



According to the above principle, the pH of 5 mmol/L 3-chlorophenol aqueous solution with 0.05 mmol/L isopropanol was adjusted to about 2 by HClO₄, and then aerated with N₂ for about 20 min to remove dissolved oxygen. Under the acid condition, the transient absorption spectra by pulse radiolysis are shown in Fig. 4.

The reference(Getoff, 1986) reported that 2-chlorophenol H-adducts have the absorption peak at about 340 nm and 3-chlorophenol H-adducts have the absorption peak at about 320 nm. They are similar to the results shown in Fig. 4. Therefore we suggest that the reaction of H atoms and 3-chlorophenol is as follows.



H-adducts are produced when H atoms react with chlorophenols. This is the common property of chlorophenols as we showed in the previous research(Wang, 2001; Dong, submitted). The Reaction(9) occurs when using hydrolysis technology in the degradation process of 3-chlorophenols.

3 Conclusions

Our study showed that 3-chlorophenol had some common properties and different properties with 2- and 4-chlorophenols. Under alkaline conditions, the reaction of OH radicals with chlorophenols produces chlorophenoxy radicals. Chlorophenols can all react with H atoms to produce H⁻ adducts. But under neutral conditions, the reaction of OH radical with 3-chlorophenol produces OH-adducts and chlorophenoxy radical is not easy to produce, which is not similar to 2- and 4-chlorophenols. We suggested that 3-chlorophenol is not as active as 2- and 4-chlorophenols. This result is corresponding to the fact that 3-chlorophenol has longer residence time in the environment than the other two isomers.

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