

Effects of chlorine content and position of chlorinated phenols on their oxidation kinetics by potassium permanganate

ZHANG Jin¹, LI Gui-bai², MA Jun²

(1. School of Environmental Science and Engineering, Dalian Maritime University, Dalian 116012, China. E-mail: dlhsh-zhj@163.com; 2. School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150008, China)

Abstract: Chlorine content and position of chlorinated phenols have many significant effects on the reactivity of oxido-reduction. The effects of chlorine content and position of chlorinated phenols on their oxidation kinetics by potassium permanganate were evaluated through different kinetics studies. Since chlorine was an electron withdrawing atom, the substitution of chlorine on the aromatic ring decreased the oxidation rate constant by σ -electron withdrawing conductive effect. The substitution of chlorine at ortho or para position on the aromatic ring increased the oxidation rate constant by π -electron donating conjugative effect, and the conjugative effect could counteract the negative impact of the conductive effect to some extent. On the other hand, the substitution of chlorine at ortho position on the aromatic ring decreased the oxidation rate constant by steric hindrance effect. The oxidation rate constants of phenol and chlorinated phenols studied decreased as follow order: 4-chlorophenol > 2,4-dichlorophenol > phenol > 2,6-dichlorophenol.

Keywords: oxidation; kinetics; phenol; 4-chlorophenol; 2,4-dichlorophenol; 2,6-dichlorophenol; potassium permanganate

Introduction

The molecular structures of phenols show characteristic of highly resonance. Since chlorine is a withdrawing electron atom, substitution of chlorine on aromatic ring can cause many significant effects on the reactivity of phenols (Folke, 1986; Barbeni, 1987; Aitken, 1994). For example, Tang *et al.* (Tang, 1996) showed that, for fenton's agent, the rate constants of chlorinated phenols decreased with increasing substitution of chlorine on the aromatic ring. They also reported elsewhere (Tang, 1995a; 1995b) that, for chlorophenols isomers, chlorine position on the aromatic ring would also cause many different effects on the reactivity of chlorinated phenols. For instance, Tang and Huang (Tang, 1995a; 1995b) reported that, for CdS/visible light system, the oxidation rate constants of monochlorophenols decreased according to the order: 3-chlorophenol > 2-chlorophenol > 4-chlorophenol, and the oxidation rate constants of dichlorophenols decreased as the follow order: 2,4-DCP > 2,6-DCP > 3,4-DCP. While Tseng and Huang (Tseng, 1990) reported that, for photo oxidation system, such as TiO₂/UV light system, the oxidation rate constants decreased as the order: 2,6-DCP > 2,5-DCP > 2,4-DCP > 2,3-DCP. From these examples we could see that, for different oxidation systems, chlorine substitution on the aromatic ring can cause many different effects on the reactivity of these chlorinated phenols.

As an oxidation agent, potassium permanganate could remove phenols to some extent by oxidation (Moyers, 1985), but what effects the chlorine substitution on the aromatic ring could cause on the oxidation reaction had not been studied systematically yet. In this study, the author mainly discussed the effects of chlorine content and position of chlorinated phenols on their oxidation kinetics by potassium permanganate through comparison of the pseudo-first order oxidation rate constants under condition of overdose of potassium permanganate.

1 Experimental

The phenol and chlorinated phenols were obtained from a chemical company, with a purity of 98% or greater and used without further treatment. Stock solutions of 1000 $\mu\text{g/L}$ were prepared by dissolving a known amount of chemicals in distilled water, and diluted with distilled water to the known concentration when in use. All the solutions were freshly prepared on the day the experiments were conducted.

The experiments were all conducted in a vase located in an oscillator and the solutions were kept in constant temperature of $16 \pm 1^\circ\text{C}$ with a water bath. The initial concentration of each phenols solution was 100 $\mu\text{g/L}$. Strong acid (H_2SO_4) and strong base (NaOH) were used to adjust the solution pH to 7.20. Then, a known of potassium permanganate solution (initial

concentration was 2000 $\mu\text{g/L}$) was added to the phenols solution, and make them mixed and reacted instantly. For each reacted mixture, samples of 10 ml were withdrawn from the reactor at certain reaction time and quenched with solution of sodium sulfite (concentration was 0.1 mg/L) immediately, and then the concentration of residual phenols was determined by gas chromatography. At last, the diagram of the oxidation kinetics could be made and the rate constants could be calculated.

2 Results and discussion

Based on experimental kinetics principle of basic reaction (Fu, 1990), the kinetics equation of this reaction system could be developed as follow:

$$-\frac{dC_t}{dt} = k C_{\text{KMnO}_4}^m C_t^n, \quad (1)$$

where C_t is the concentration of each solution of phenols at any time t ; C_{KMnO_4} is the concentration of solution of potassium permanganate; k is the rate constant; m and n are the reaction order of potassium permanganate and phenols respectively.

Because potassium permanganate was of much overdose and its concentration was far greater than that of phenols, the change of concentration of potassium permanganate could be neglected. Then, Eq.(1) could be simplified as follows:

$$-\frac{dC_t}{dt} = K' C_t^n, \quad (2)$$

where $K' = k C_{\text{KMnO}_4}^m$.

First, we could assume $n = 1$, then the Eq.(2) could be integrated (from 0 to t) and simplified to:

$$\ln \frac{C_0}{C_t} = K' t, \quad (3)$$

where C_0 is the initial concentration of each solution of phenols.

Thus, we could draw a diagram of $\ln \frac{C_0}{C_t}$ Vs t . If $\ln \frac{C_0}{C_t}$ was in direct proportion to t , it proved that the assumption above was correct, which was to say that the reaction was a pseudo-first order reaction to phenols, and the slope of the regression line impressed the total rate constant K' . Otherwise, it showed that the reaction order was not 1 for phenols, and we should continued to deduce the value of n .

Fig. 1, Fig. 2, Fig. 3 and Fig. 4 show the diagrams of $\ln C_0/C_t$ Vs t of phenol, 4-chlorophenol, 2,4-dichlorophenol and 2,6-dichlorophenol respectively.

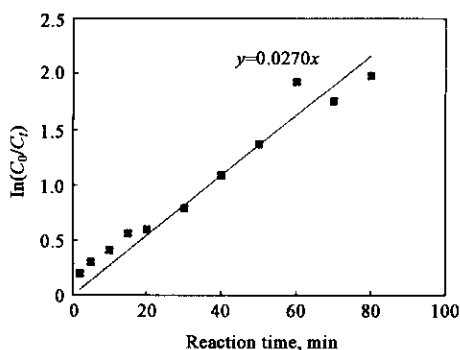


Fig. 1 Curve of $\ln C_0/C_t$ Vs t of phenol

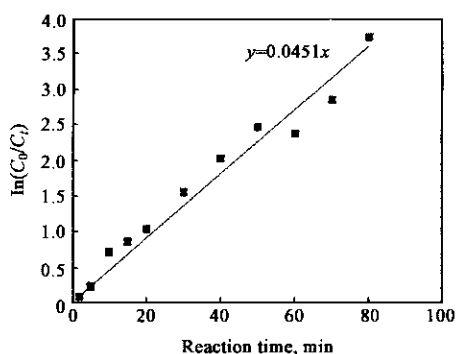
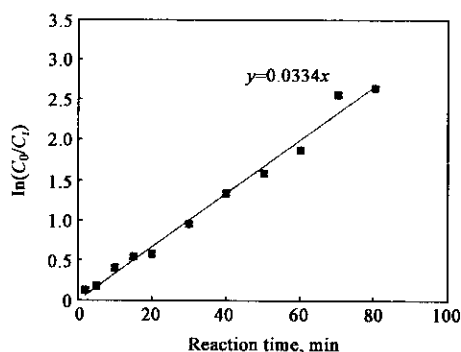
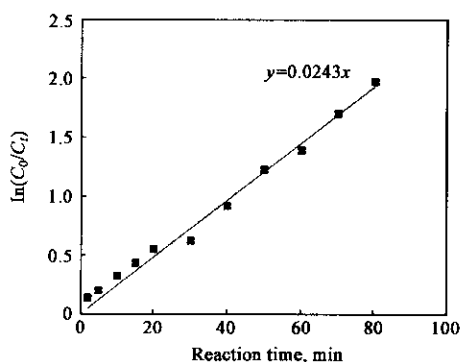


Fig. 2 Curve of $\ln C_0/C_t$ Vs t of 4-MCP

From these figures we can see that for phenol and each chlorinated phenols, the relationship between $\ln C_0/C_t$ and t was nearly in fit. This indicated that the reaction orders were approximate to 1 for these phenols. So, the slopes of the four lines could be considered to be the total rate constants (K') for phenol and each chlorinated phenols respectively. Compared the regression equations of the four lines we could see that the values of K' differed with each other, and decreased as follow order: 4-chlorophenol > 2,4-dichlorophenol > phenol > 2,6-dichlorophenol. These results also indicated that substitution of chlorine on the aromatic ring has significant effects on the oxidation kinetics of phenols by potassium permanganate.

Fig.3 Curve of $\ln C_0/C_t$ Vs t of 2,4-DCPFig.4 Curve of $\ln C_0/C_t$ Vs t of 2,6-DCP

From the results we could analyze the effects of chlorine substitution on the aromatic ring on the oxidation kinetics by potassium permanganate. First, let us see the situation of the three chlorinated phenols. From Fig.2, Fig.3 and Fig.4, we can see that the rate constants of 2,4-DCP and 2,6-DCP were both less than that of 4-MCP. From this result we could conclude that the rate constant decreased with increasing chlorine substitution. While at the same time, the rate constant of 2,4-DCP was greater than that of 2,6-DCP. This indicated that the rate constant decreased with increasing of chlorine substitution at ortho position on the aromatic ring (2,6-DCP has two ortho positions substituted by chlorine, while 2,4-DCP has one ortho position substituted by chlorine). We assumed that these results were caused by the characteristics of chlorine substitution and the oxidation mechanisms of phenols.

In the oxidation process of phenols by potassium permanganate, potassium permanganate first attacked on phenolate anion (ArO^-) and produced phenoxy radicals ($\text{ArO}\cdot$) and polymers (Fu, 1990). So, the substitution that make phenoxy radicals more steady would accelerate the oxidation (because the structure of the intermediate is similar to that of the product). Chlorine was a σ -withdrawing electron group (Sedlak, 1991), so chlorine substitution would make the phenoxy radicals less stable through electron withdrawing conductive effect. At the same time, with increasing of chlorine contents on the aromatic ring, the $\text{p}K_{\text{a}}$ values of the chlorinated phenols decreased, and the hydrophobicity increased (Yun, 1990), and then the attack chances between molecules decrease, thus the oxidation reaction became more difficult. So, the oxidation rate constants decreased with increasing of chlorine on the aromatic ring. So the rate constants of 2,4-DCP and 2,6-DCP were less than that of 4-MCP.

While, for isomers with the same chlorine content, chlorine position has many significant effects on the reactivity of chlorinated phenols. This can be explained from the mechanisms of oxidation reaction. We have stated above that potassium permanganate first attacks on phenolate anion to form phenoxy radicals and then polymers, then the electron transfer occurred. Because chlorine was bigger in volume than that of hydrogen, the chlorine substitution at ortho position expressed strong steric hindrance effect. So, in chlorinated phenols with the same chlorine contents, the more chlorine atoms substituted at ortho positions, the more difficult the formation of inner polymers and the transfer of electron later became, and then the more difficult the oxidation of phenols were. So, the rate constant of 2,4-DCP was greater than that of 2,6-DCP.

So, under the same experimental conditions, the total oxidation rate constants of the three chlorinated phenols studied in this research decreased as follow order: 4-CP > 2,4-DCP > 2,6-DCP.

The experimental results showed that the rate constants of 4-CP and 2,4-DCP were greater than that of phenol, which was greater than that of 2,6-DCP. We thought that this result was also caused by the effect of chlorine substitution on the aromatic ring.

For 4-MCP, though the σ -electron withdrawing conductive effect of chlorine substitution on the aromatic ring made the formation of phenolate anion difficult, but on the other hand, chlorine that substituted at para position was a π -electron donating group which increased the electron density of phenoxy radicals and made it more steady through electron donating conjugative effect (Stone, 1991). The π -electron donating conjugative effect counteracted the negative impact of σ -electron

withdrawing conductive effect to some extent. So, compared with phenol, the oxidation of 4-CP by potassium permanganate was easier, and its rate constant was greater too. The situation of 2,4-DCP was as the same as that of 4-CP. For 2,4-DCP, chlorines substituted at ortho and para positions took on strong π -electron donating conjugative effects, which in a certain extent counteracted the negative impacts of steric hindrance effect (at ortho position) and the σ -electron withdrawing conductive effect and so on. So, the rate constant of 2,4-DCP was also greater than that of phenol. While for 2,6-DCP, because two chlorines were both substituted at ortho positions, the impact of steric hindrance effect became significant, which was disadvantage to oxidation by potassium permanganate. So the rate constant of 2,6-DCP was smaller than that of phenol.

3 Conclusions

The effect of chlorine content and position of chlorinated phenols on their oxidation kinetics by potassium permanganate had been evaluated. Results showed that chlorine substituted on the aromatic ring have many significant effects on the oxidation rate constants by potassium permanganate. In the chlorinated phenols, the oxidation rate constants decreased with increasing of chlorine contents. While in the isomers with the same chlorines, the more chlorine substituted at ortho position, the smaller the rate constant became. The effect of chlorine substitution on the aromatic ring on the reactivity of phenols was mainly caused by σ -electron withdrawing conductive effect, π -electron donating conjugative effect and steric hindrance effect of chlorine. Among these effects, the impact of π -electron donating conjugative effect was more greater than that of σ -electron withdrawing conductive effect. Compared with that of both π -electron donating conjugative effect and σ -electron withdrawing conductive effect, the impact of steric hindrance effect of chlorine at ortho position was more significant. The rate constants of phenol and chlorinated phenols studied in this research decreased as follow order: 4-CP > 2,4-DCP > phenol > 2,6-DCP.

Acknowledgement: The authors thank for Mr. Chen Z. L. for his help and discussions concerning this work.

References:

- Aitken M D, Massey I J, Chen T *et al.*, 1994. Characterization of reaction products from the enzyme catalyzed oxidation of phenolic pollutants [J]. *Wat Res*, 28(9): 1879—1889.
- Barbeni M, Minero C, Pehzzetti E *et al.*, 1987. Chemical degradation of chlorophenols with fenton's reagent[J]. *Chemosphere*, 16(11): 2225—2237.
- Folke J, Berklund J, 1986. Danish coastal water levels of 2,3,4-tetrachlorophenol, pentachlorophenol and total organohalogens in blue mussels (*Mytilus edulis*)[J]. *Chemosphere*, 15: 896—900.
- Fu X C, Shen W X, Yao T Y, 1990. Physical chemistry[M]. Beijing: Higher Education Publisher. Fourth edition.
- Moyers B, Wu J Y S, 1985. Removal of organic precursors by permanganate oxidation and alum coagulation[J]. *Wat Res*, 19(3):309—314.
- Sedlak D L, Andren A W, 1991. Oxidation of chlorobenzene with fenton's reagent[J]. *Environ Sci Technol*, 25:777—782.
- Stone A T, 1991. Reductive dissolution of manganese(III/IV) oxides by substituted phenols[J]. *Environ Sci Technol*, 21: 979—988.
- Tang W Z, Huang C P, 1995a. Oxidation pathways in photocatalytic degradation of 2,4-DCP by CdS in acidic and basic aqueous solutions[J]. *Wat Res*, 29:745—756.
- Tang W Z, Huang C P, 1995b. The effect of chlorine position of chlorinated phenols on their dechlorination kinetics by fenton's reagent[J]. *Waste Manage.*, 15(8): 615—622.
- Tang W Z, Huang C P, 1996. Effect of chlorine content of chlorinated phenols on their oxidation kinetics by fenton's reagent [J]. *Chemosphere*, 33(8): 1621—1635.
- Tsang J, Huang C P, 1990. Mechanistic aspects of the photocatalytic oxidation of phenol in aqueous solutions[M]. *Emerging technologies in hazardous waste management*. Washington, DC: American Chemical Society. 12—39.
- Yun K H, 1990. Organic chemistry[M]. Beijing: Higher Education Publisher.

(Received for review March 6, 2002. Accepted May 27, 2002)