

Mechanistic study of ozonation of *p*-nitrophenol in aqueous solution

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Abstract: Ozonolysis in the treatment of *p*-nitrophenol solution was studied in this paper. The results indicated that the decomposition of *p*-nitrophenol was accelerated as the gas flow rate or pH value increased. When gaseous ozone concentration was 20.11 mg/L and pH was 3, after 24 min reaction, the removal rate of *p*-nitrophenol reached 73.04%, 86.11%, 91.71% and 95% at the gas flow rate of 32, 40, 48 and 56 ml/min respectively. And when pH was 3, 4, 5, 6, the decomposition rate was 66.38%, 82.09%, 90.46%, 97.50% after a 20 min reaction respectively. It was mainly O₃ molecule that took part in the decomposition when pH was 3. The main intermediates during the decomposition include catechol, *o*-benzoquinone, hydroquinone, *p*-benzoquinone, phenol, fumaric acid, maleic acid, oxalic acid and formic acid. The decomposition mechanism of *p*-nitrophenol was also discussed.

Keywords: ozonation; *p*-nitrophenol; decomposition; mechanism

Introduction

p-Nitrophenol has been widely used in the production of pesticides, herbicides, dyes, and other industrial chemicals. As a result of these widespread applications, wastewaters and water resources, including ground water and surface waters, have become contaminated with this compound. *p*-Nitrophenol, which is listed by the USEPA as a priority pollutant, is toxic and thereby harmful to public health and aquatic life.

Ozone is a powerful oxidizer that can be effective for the decomposition of many pollutants (Wu, 2001; Chu, 2003; Stockinger, 1996). It has been traditionally used in getting rid of color, taste, odor, and pathogen in drinking water (Rice, 1989). Recently, advanced oxidation processes (AOPs) have received much attention for their use in treating waters containing complex, xenobiotic chemicals (Adams, 1994; Guittoneau, 1990; Peyton, 1988; Mokri, 1997; Sierka, 1985; Destailats, 2000). AOPs are, by definition, those processes that utilize the hydroxyl radical for contaminant decomposition and are typically implemented in conjunction with ultraviolet photolysis, hydrogen dioxide, sonolysis, and so on. However, many compounds can be treated with such traditional oxidation techniques as ozonolysis, without the requirement of significant hydroxyl radical formation during treatment. Phenolic compounds, including *p*-nitrophenol, were found by Hoigné and Bader to be relatively reactive with molecular ozone compared with other aromatic compounds (Hoigné, 1983). Although the ozonation-based decomposition kinetics of *p*-nitrophenol have been proposed by others (Beltrán, 1992; Zhang, 1996), little mechanism information concerning the reaction of ozone and *p*-nitrophenol is available in the literature. Therefore, in this paper, *p*-nitrophenol was selected as the model pollutant and its decomposition rate was studied under different conditions. Besides, the decomposition mechanism of *p*-nitrophenol in this process was also studied.

1 Experiments and methods

1.1 Chemicals

Potassium indigotrisulfonate (Dabayer), *p*-nitrophenol

(> 99.5%, AR), hydroquinone (> 98.0%, AR), *p*-benzoquinone (> 98.5%, CP), catechol (> 98.0%, CP), *o*-benzoquinone (> 98.5%, CP), phenol (> 99.9%, AR), fumaric acid (> 99.0%, CP), maleic acid (> 99%—101%, CP), oxalic acid (> 99.5%, AR), Na₂S₂O₃, NaOH, H₃PO₄ and other reagents are analytical grade. These reagents except potassium indigotrisulfonate were purchased from Shanghai Chemical Reagents Company, China.

1.2 Sonochemical experiments

Experiments were carried out in a self-made glass jacket reactor with a volume of 200 ml, in the bottom of which was a glass gas diffuser. The top of the reactor had four openings providing connections to a thermometer, a pipette for sampling, and two tubes for both feeding and venting the gas. The temperature of reaction solution was controlled through jacket circulation of temperature-fixed water in the outside cistern, while O₃ was produced in 3A ozone producer (made in Hangzhou Rongxin Electronic Equipment Co. Ltd, China). First, a certain amount of *p*-nitrophenol was injected into the reactor and the ozone producer was turned on. Then, to stabilize the gaseous O₃ concentration, we maintained the gross amount of O₃ but diverted some outside and instilled the rest into the reaction solution through the gas diffuser. In addition, pH was adjusted with phosphoric acid and sodium hydroxide and the ionic strength was around 0.1 mol/L. Later, we took 2.0 ml sample at regular intervals. If not for ozone concentration measurement, the remnant O₃ in the sample solution was removed by adding fixed amounts of Na₂S₂O₃.

To analyze the possible stripping of *p*-nitrophenol in the oxidation, a separate experiment of only oxygen was carried out. Measurements made before and after the experiment did not show a significant change in the concentration of *p*-nitrophenol.

1.3 Analytical methods

High-performance liquid chromatograph (HPLC, Shimadzu, Japan) and a gas chromatograph coupled with a mass spectrophotometer (GC-MS, Trace 2000, Thermo Quest, Italy) were employed to analyze *p*-nitrophenol and its

intermediates. 25 μ l aliquots of samples were injected into the HPLC, in which a mobile phase of phosphate buffer solution (pH = 2)/methanol at 70/30 (v/v) was used for the determination of *p*-nitrophenol and its intermediates. The separation was performed using an ODS-18 reversed phase column at a flow rate of 1.0 ml/min and a column temperature of 25 °C. A UV detector was used with the wavelength set at 280 nm. For the GC/MS runs the oven temperatures were as follows: isothermal at 30 °C for 5 min, 30–220 °C at 15 °C/min ramping, and 220 °C for 25 min. Organic acid and NO_3^- produced was determined by ion chromatograph (Metrohm 792 Basic IC, UK). The ozone gas phase concentration was determined by standard methods (EPA, 1989). The concentration of ozone in the solution was determined by the indigo method (Bader, 1981).

2 Results and discussion

2.1 Influence of gas flow rate

Fig. 1 shows the influence of gas flow rate on the decomposition of *p*-nitrophenol under the conditions that gaseous ozone concentration was 20.11 mg/L and pH was 3. It was evident that acceleration of gas flow would speed up the decomposition rate of *p*-nitrophenol. After 24 min reaction, the removal rate of *p*-nitrophenol reached 73.04%, 86.11%, 91.71% and 95.00% when the gas flow rate was 32, 40, 48 and 56 ml/min respectively. When pH value was changed to 6 or 11, similar results were obtained. Ozone transformation from gas phase into liquid phase is a liquid film-controlled process and the liquid phase mass transfer coefficient increases as the gas flow accelerates. In conclusion, under fixed gaseous ozone concentration, the acceleration of its flow increased the amount of liquidized ozone, thus facilitating *p*-nitrophenol decomposition.

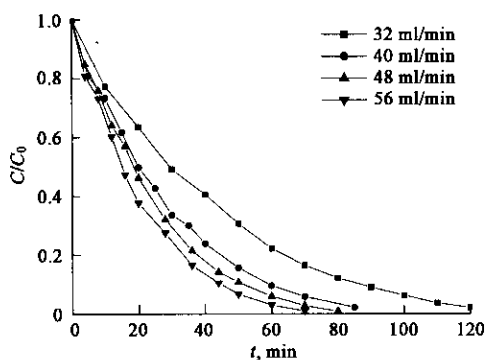


Fig. 1 Influence of gas flow rate
 $C_0 = 50 \text{ mg/L}$; $T = 25^\circ\text{C}$; $\text{pH} = 3.0$; ionic strength 0.1 mol/L ; gaseous ozone concentration 20.11 mg/L

2.2 Influence of pH value

Influence of pH value on the *p*-nitrophenol decomposition is shown in Fig. 2. When $\text{pH} \leq 6$, it was obvious that the increase of pH value accelerates the decomposition, after 20 min reaction, the removal rate was determined to be 66.38%, 82.09%, 90.46%, 97.50% when pH was 3, 4, 5, 6 respectively. When $\text{pH} > 6$, however, the effect was not remarkable.

For *p*-nitrophenol, $\text{p}K_a = 7.14$, as pH value increases, on the one hand, more and more O_3 in the solution was decomposed into $\cdot\text{OH}$ which has higher oxidation

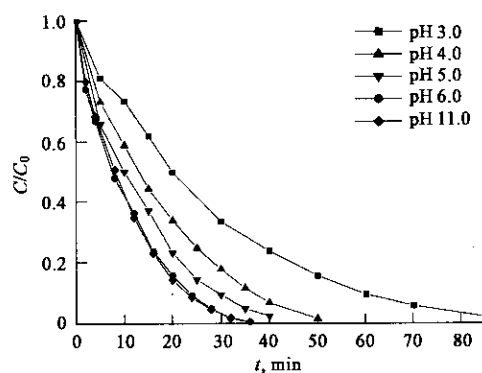


Fig. 2 Influence of pH value
 $C_0 = 50 \text{ mg/L}$; $T = 25^\circ\text{C}$; ionic strength 0.1 mol/L ; O_3/O_2 flow rate 40 ml/min ; gaseous ozone concentration 20.11 mg/L

potential; on the other hand, more and more dissociated form of *p*-nitrophenol in the solution was found whose *ortho* and *para* positions have higher electron density and favors the electrophilic reaction to take place with O_3 and $\cdot\text{OH}$. Therefore, it accelerates the *p*-nitrophenol decomposition. When $\text{pH} > 6$, however, although the increase of pH value brought to accelerated the removal rate, less ozone can be dissolved in the aqueous solution, resulting in the decrease of mass transfer urge. In the meantime, under alkali conditions, the intermediate CO_2 turned into CO_3^{2-} and HCO_3^- , which have considerably high reaction constant with $\cdot\text{OH}$, that is, $4.2 \times 10^8 \text{ L}/(\text{mol}\cdot\text{s})$ and $1.5 \times 10^7 \text{ L}/(\text{mol}\cdot\text{s})$ (Langlais, 1991). Thus the amount of $\cdot\text{OH}$ was reduced and the decomposition rate was slowed. When $\text{pH} > 6$, the different effects are similarly powerful, thus similar decomposing rates.

2.3 Radical scavenger effects

Generally, radical scavenger include mainly CO_3^{2-} , HCO_3^- , tertiary butanol, which react with $\cdot\text{OH}$ at the speed of $4.2 \times 10^8 \text{ L}/(\text{mol}\cdot\text{s})$, $1.5 \times 10^7 \text{ L}/(\text{mol}\cdot\text{s})$ and $5.0 \times 10^8 \text{ L}/(\text{mol}\cdot\text{s})$ (Langlais, 1991) respectively. Among them, tertiary butanol (tBuOH) is the most active, and it is also indifferent to pH value changes. To testify whether $\cdot\text{OH}$ or ozone molecule took part in the reaction, at $\text{pH} = 3$, 50 mg/L tertiary butanol was put into the solution and Fig. 3 indicates the results. According to the figure, 40 minutes later, the removal rate decreased from 76.06% to 69.46%, which was attributed to the relatively trivial influence of tertiary butanol. Thus it can be concluded that $\cdot\text{OH}$ does took part in the reaction, but the main part of it remains direct oxidization of ozone molecule.

2.4 Decomposition mechanism

Ozone may react with an organic via two different mechanisms: direct O_3 molecule oxidization and indirect oxidization through $\cdot\text{OH}$.

There are cycloaddition reaction, nucleophilic addition reaction and electrophilic addition reaction during direct O_3 molecule oxidization and the primary mode of oxidization is electrophilic addition reaction. For some aromatic compounds, electrophilic addition reaction generally takes place at positions which have higher electron density. The electron-donating substituent compounds (including $-\text{OH}$, $-\text{NH}_2$ etc.) react faster with O_3 when O_3 attacks the *ortho*

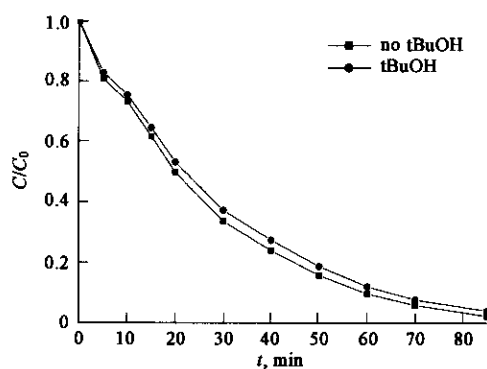
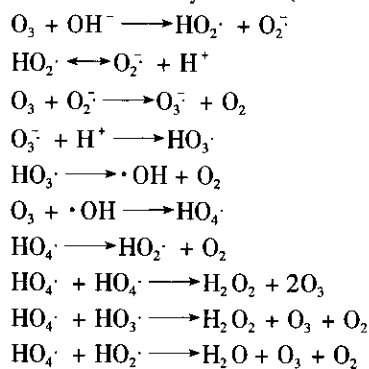


Fig. 3 Radical scavenger effect

$C_0 = 50$ mg/L; $T = 25$ °C; ionic strength 0.1 mol/L; O_3/O_2 flow rate 40 ml/min; gaseous ozone concentration 20.11 mg/L

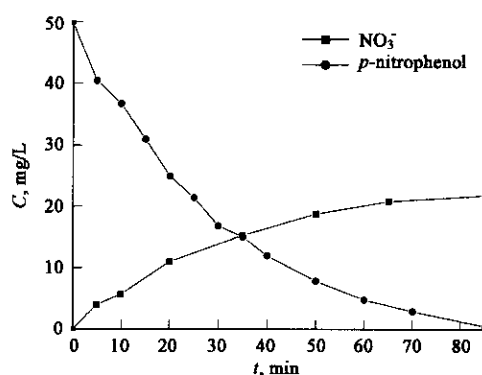
and *para* positions primarily. In contrast, the electron-withdrawing substituent compounds (including $-\text{COOH}$, $-\text{NO}_2$ etc.) react relatively slower with O_3 when O_3 attacks the *meta* position mostly. It is convenient for O_3 to electrophilic reaction with electron donor-contained phenol compounds, resulting in *ortho* and *para* positions hydroxylic oxides which can be further oxidized, thus quinonoid compounds and later aliphatic compounds concluding hydroxide radical and carboxy.

In aqueous solution, O_3 can be decomposed into $\cdot\text{OH}$, which oxidizes soluble inorganics and organics through electrons transfer, dehydro reaction and electrophilic addition reaction. The followings indicate how radicals like $\cdot\text{OH}$ was produced and how they worked (Staelin, 1982):



In conclusion, when $\text{pH} = 3$, OH^- concentration in the solution was low, and the reaction rate of O_3 and OH^- can only be as high as 70 L/(mol·s), thus *p*-nitrophenol decomposition mainly relies on direct O_3 molecule oxidization.

Theoretically, in the 50 mg/L *p*-nitrophenol solution, 16.55 mg/L is $-\text{NO}_2$, that means NO_3^- is 22.30 mg/L. In order to explore the decomposition mechanism of *p*-nitrophenol using O_3 approach, the change of NO_3^- mass concentration was measured (Fig. 4). In fact, the mass concentration kept increasing until it reached a point of theoretical delivery amount. After 10 min, the removal rate of *p*-nitrophenol was 26.6%, that is, NO_3^- mass concentration should be 5.93 mg/L in theory, but it was measured as 5.71 mg/L in practice, 96.29% of the theoretical delivery amount. After 85 min, the removal rate reached 99.02%, which means that compared with a theoretical 22.08 mg/L, NO_3^- mass concentration was 21.75

Fig. 4 Mass concentration change of NO_3^- in accordance with *p*-nitrophenol changes

$C_0 = 50$ mg/L; $T = 25$ °C; ionic strength 0.1 mol/L; O_3/O_2 flow rate 40 ml/min; gaseous ozone concentration 20.11 mg/L

mg/L, 98.50% of the former. Provided unavoidable experimental errors, it could be inferred that in the decomposition process of *p*-nitrophenol, $-\text{NO}_2$ was first oxidized and shifted into NO_3^- .

Through HPLC, GC-MS and IC, catechol, *o*-benzoquinone, hydroquinone, *p*-benzoquinone, phenol, fumaric acid, maleic acid, oxalic acid and formic acid were detected as the main intermediates of *p*-nitrophenol decomposition. Fig. 5 indicates the mass concentration changes of some intermediates. According to it, *p*-benzoquinone and catechol were the most concentrated, which were followed by hydroquinone and *o*-benzoquinone, and then phenol the least concentrated. Through measurement of NO_3^- , $-\text{NO}_2$ was first lost and shifted into phenol. Since $-\text{OH}$ is an electron-donating group whose inductive effect and conjugative effect result in the *ortho* and/or *para* positions have higher electron density to the hydroxyl group and the electrophilic reaction favors a high electron density position, phenol turned into hydroquinone and catechol quickly by the attack of O_3 and $\cdot\text{OH}$ at the *ortho* and/or *para* positions to the hydroxyl group. Then hydroquinone and catechol turned into *p*-benzoquinone and *o*-benzoquinone quickly by dehydro reaction. It could also be seen from Fig. 5 that hydroquinone and *p*-benzoquinone concentration were higher than that of catechol and *o*-benzoquinone, which was attributed to the steric effect of $-\text{OH}$ in phenol that make O_3 and $\cdot\text{OH}$ more convenient to attack at the *para* position to the hydroxyl group and produced hydroquinone. As the

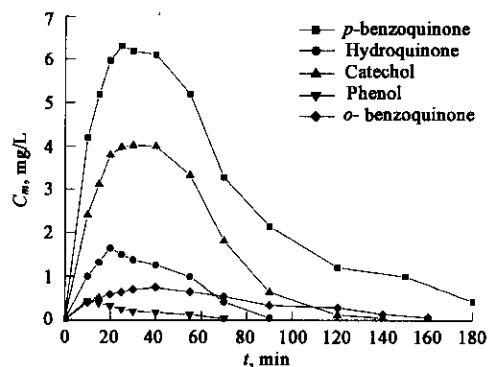


Fig. 5 Intermediates mass concentration changes

$C_0 = 50$ mg/L; $T = 25$ °C; ionic strength 0.1 mol/L; O_3/O_2 flow rate 40 ml/min; gaseous ozone concentration 20.11 mg/L

reaction continues, the intermediates were further oxidized and then fumaric acid, maleic acid, oxalic acid and formic acid etc. were formed, which were finally oxidized into CO₂ and H₂O.

Based on the above analysis, the decomposition of *p*-nitrophenol under O₃ could be described in Fig.6.

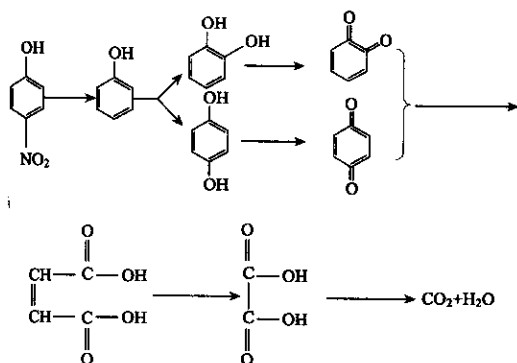


Fig.6 Decomposition pathway of *p*-nitrophenol

$C_0 = 50 \text{ mg/L}$; $T = 25^\circ\text{C}$; ionic strength 0.1 mol/L ; O₃/O₂ flow rate 40 ml/min ; gaseous ozone concentration 20.11 mg/L

3 Conclusions

Under certain gaseous O₃ concentration, the acceleration of gas flow increased the decomposition rate of *p*-nitrophenol. When $\text{pH} \leq 6$, as its value rises, the removal rate was increased, while when $\text{pH} > 6$, it hardly exert any influence. When $\text{pH} = 3$, the decomposition mainly depend on the O₃ molecule oxidization. Under O₃ system, —NO₂ was first lost and *p*-nitrophenol turned into phenol, which was further oxidized into hydroquinone, *p*-benzoquinone, catechol, *o*-benzoquinone etc. As the reaction proceeded, these intermediates were further being oxidized and several ring openings occurred, resulting in the formation of fumaric acid, maleic acid, oxalic acid and formic acid, which finally led to the production of CO₂ and H₂O.

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