



## Kinetics and mechanism of para-chlorophenol photoconversion with the presence of nitrite in ice

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### ABSTRACT

The photochemistry of para-chlorophenol (4-CP) under UV irradiation by using a 125-W high-pressure mercury lamp as light source with the presence of nitrite in a solid water ice matrix had been studied. The experiments were carried out in a photochemical cold chamber reactor at  $-14$  to  $-12$  °C. Each influence factor of the 4-CP photoconversion kinetics in the water ice was inspected. The results show that the 4-CP photoconversion obeys the first-order kinetics model and the initial concentration of 4-CP, the initial concentration of nitrite, pH value, light intensity, inorganic ions and the water quality all have significant influence on the photoconversion rate. In addition, nine intermediate products were characterized by GC–MS, HPLC–ESI–MS and HPLC techniques and the possible photoconversion mechanism was proposed accordingly. It is concluded that the mechanism and photoproducts of 4-CP photolysis in ice are changed due to the presence of  $\text{NO}_2^-$ .

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### 1. Introduction

The photochemistry of organic pollutants in the atmosphere, natural water and soil is extensively studied up to now [1–4]. However, the photochemical properties of the organic pollutants in ice and snow are still poorly understood [5–7]. The ordinary chemical and biological reactions are prohibited in the ice because of the low temperature and the good transparency of ice makes the photochemical reactions possible which is little affected by the temperature. Therefore, the photochemistry plays a very important role in the transformation of the organic pollutants in ice or snow of the cold and warm ecosystem.

The interest in the photochemistry of organic pollutants in ice has increased dramatically since that many organic compounds can have photochemical transformation in the ice phase was reported [2,5–14]. Photochemical transformations in ice were first studied in regard to interstellar ice systems [15]. Berntein et al. [16] investigated the photolysis ( $\lambda < 170$  nm) of polycyclic aromatic hydrocarbons (PAHs) in ice and the results showed that the photolysis resulted in the partial reduction and oxidation of the PAHs. The partial reduction produced partially hydrogenated aromatic hydrocarbons and the partial oxidation yielded ketones, alcohols and bridging ethers when bay regions existed in the parent PAH. Klanova et al. [7,17] had preliminarily researched in the photochemical transformation mechanism of para-chlorophenol (4-CP) in the

ice phase by using a medium-pressure mercury lamp as light source and their results indicated that the transformation mechanism of 4-CP in the ice phase was different from that in the liquid phase and the existence of hydrogen peroxide affected the photoproducts. Similar results were observed by Matykiewiczova et al. [12].

Some studies showed that nitrite plays an important role in ice photochemistry of organic pollutants. The absorption spectrum of nitrite ( $\text{NO}_2^-$ ) ions in aqueous solutions contains weak  $n \rightarrow \pi^*$  bands ( $\lambda_{\text{max}}(\text{NO}_2^-) = 355$  nm) [18]. The photochemistry of nitrite essentially results in the formation of  $\text{HO}^\bullet$  and  $\text{NO}_2^\bullet$  (Eqs. (1)–(4)). It is now well established that nitrite photolysis in natural waters can trigger hydroxylation, nitration and nitrosation reactions of many organic pollutants [19]. Possible formation of highly mutagenic/carcinogenic nitrocompounds unquestionably can be of great environmental interest because the environmental fate and ecological risk of organic pollutants will be changed [20].



However, up to now the reaction between 4-CP and nitrite in ice phase has not been fully studied and all the existing researches are mainly focusing on the photochemical products and the mechanism. The ice photochemical reaction conditions, influence factors and kinetics are almost hardly studied although such work is significant for better understanding the ice photochemistry of organic

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pollutants. In our experiments, we selected a high-pressure mercury lamp as the light source because its spectrum is more similar with that of the sunlight than medium-pressure mercury lamp used by most of other researchers. The experiment temperature is determined by the normal winter temperature in Jilin Province of China. The purpose of this work is to systematically study the ice photochemistry of 4-CP with the presence of nitrite by an indoor simulated experiment. Hence, the effects of different factors on the 4-CP photoconversion kinetics were tested, the intermediate products produced in the photoconversion of 4-CP in ice were identified and the photoconversion mechanism under this experimental condition was proposed. It is very obvious that the results acquired by our experiments are beneficial to the study of ice photochemistry.

## 2. Experimental

### 2.1. Instrumentation

A GC–MS PRACE-MS equipped with HP-5MS (30 m × 0.25 mm × 0.25 μm) column, and an Agilent 1100 liquid chromatograph equipped with an ABI Q-Trap Mass Spectrometer were used for the identification of the photoproducts. HPLC analyses were performed on a Waters liquid chromatographic system equipped with a Waters 717 plus autosampler, Waters 1525 Binary HPLC pump, Waters 2487 Dual λ absorbance detector and Symmetry 5 C18 column. A Lambda 35 UV/vis spectrometer (PerkinElmer) was used for measuring the spectra of liquid aqueous solutions. Low-temperature photodegradation experiments were accomplished in a cryostat box FRESTECH BC/BD-261. The samples were irradiated using a 125-W high-pressure mercury lamp. The pH values of the solutions were measured by a PHS-3C pH meter. The intensities of the light were measured by a ST-92 luminometer.

### 2.2. Chemicals

4-Chlorophenol (C.R.; Pekin chemical plant), methanol (HPLC grade; Tedia, USA), sodium nitrite, sodium chloride, sodium bicarbonate, ferric chloride, ferrous chloride, acetone and dichloromethane (A.R.; Pekin chemical plant) were used directly without any pretreatment. The water was purified by an UPWS-I-10T ultrapure water system.

### 2.3. Sample preparation and irradiation procedures

4-CP aqueous solutions were prepared by dilution of the stock solution (10 g L<sup>-1</sup>). The aqueous solutions (10 mL) in Ø15 mm × 150 mm quartz tubes, sealed with septa, were solidified in the cryostat box at –20 °C. The homogeneity of frozen samples was tested randomly and was found to be acceptable in all cases. In a cryostat box ( $T = -14$  to  $-12$  °C) the samples were irradiated by a 125-W high-pressure mercury lamp which was set at the center of the samples. Two parallel samples were taken out for analysis every 10 min during the irradiation.

For checking the light transmittance of the ice, the penetrating light intensities were determined before and after the tubes containing the ice samples and it was found that the two light intensities were equal. Hence, the light transmittance of the ice was thought well enough to meet the laboratorial need.

### 2.4. Sample extraction and analysis

After irradiation, the samples thawed at room temperature (about 16 °C) and some solid substances appeared in the thawed samples. The solutions were analyzed on HPLC–ESI-MS directly after percolation with a 0.22 μm colander. The solid substances were separated by centrifugation, dissolved in some acetone after

being rinsed and dried, and then analyzed by GC–MS; the solution after centrifugation was extracted with dichloromethane and analyzed by GC–MS.

For HPLC–ESI-MS analyses, the samples were analyzed on an Agilent 1100 liquid chromatograph (Palo Alto, CA, USA) equipped with a quaternary pump, a heated column compartment and a UV detector. The analytes were separated by a AichromBcnd-AQ-C<sub>18</sub> (250 mm × 4.6 mm i.d., 5 μm) column (Aichrom, USA). The detection wavelength was set from 190 to 400 nm. The binary gradient elution solvent consisted of methanol (70%) and water (30%). The flow rate was kept at 1.0 mL min<sup>-1</sup> and the temperature of column was controlled at 25 °C. An ABI Q-Trap Mass Spectrometer (Applied Biosystems Sciex, Foster City, USA) equipped with an electrospray ionization source was used for ESI-MS analysis. Nitrogen (99.999%) was used for nebulizer gas and curtain gas. The ion polarity was set to negative mode. The voltages, gas pressures, and source temperature were optimized for the detection of 4-CP. The source temperature was set to 500 °C. The curtain gas and nebulizer gas were 40 and 50 psi, respectively. The ion spray voltage was 4500 V. The declustering potential and collision energy were 50 V and 10 eV separately. Sample injection volume was 10 μL.

For GC–MS analyses, the samples were analyzed on a GC–MS instrument equipped with a HP-5MS fused silica column [30 m × 0.25 mm, with a 0.25 μm film of stationary phase (5% phenyl–95% methyl) polysiloxane]. 2 μL of sample was introduced using the splitless technique with the temperature program 80 °C for 1 min, then 20 °C min<sup>-1</sup> to 280 °C, and finally 10 min at 280 °C. Injector and transfer line temperatures were kept at 280 °C. The mass spectra were collected in the scan range  $m/z$  50–550 for identification purpose.

The 4-CP concentrations in the solutions were analyzed by HPLC directly after percolation with a 0.22 μm colander. The mobile phase was methanol (70%) and water (30%), the flow rate was 1.0 mL min<sup>-1</sup>; the analytical wavelength was 280 nm.

### 2.5. Calculations

The photochemical transformation efficiency ( $\eta$ ) was evaluated by the conversion rate of 4-CP (Eq. (5)).

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (5)$$

where  $\eta$  means the photochemical transformation efficiency;  $C_0$  is the concentration of 4-CP in the sample solution before irradiation;  $C_t$  is the concentration of 4-CP in the thawed sample solution after irradiated  $t$  min.

The first-order kinetic equation was tried to have model fitting to the plot which used  $\ln(C_t/C_0)$  as  $x$  axis and  $t$  (min) as  $y$  axis. Then, the rate constant ( $k$ ) of the apparent reaction was obtained from the plot (Eq. (6)) and the half life ( $t_{1/2}$ ) was calculated (Eq. (7)):

$$k = -\frac{\ln(C_t/C_0)}{t} \quad (6)$$

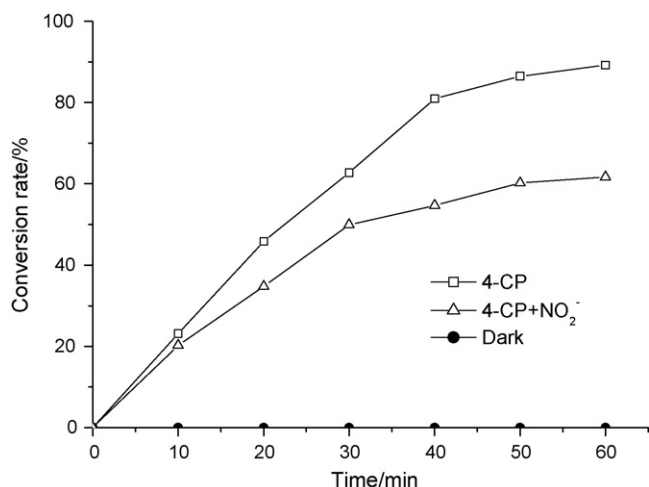
$$t_{1/2} = \frac{0.693}{k} \quad (7)$$

Each plot was obtained on no less than five data.

## 3. Results and discussion

### 3.1. Dark and light comparative experiments

The concentration of 4-CP was unchanged under dark condition. This indicates that 4-CP cannot be degraded without the irradiation and the loss of 4-CP was negligible during the whole icing or thawing process under the experimental condition. 4-CP had direct photolysis under UV light and the conversion rate reached 89%



**Fig. 1.** Conversion of 4-CP under dark and light condition ( $[4\text{-CP}]_0 = 0.69 \text{ mmol L}^{-1}$ ,  $[\text{NO}_2^-]_0 = 0.72 \text{ mmol L}^{-1}$ , pH 6.60, the light intensity is 19,500 lx).

without the presence of nitrite after 60 min irradiation (Fig. 1). But the photoconversion rate of 4-CP reduced to 61% when the nitrite present in ice. This is because  $\text{NO}_2^-$  plays two roles in the photoconversion process in this work: (i) the prohibition effect on the photoconversion by the stronger absorption of irradiation (Fig. 2); (ii) the promotion effect by the production of  $\text{HO}^\bullet$  and  $\text{NO}_2^\bullet$  which brings indirect photolysis of 4-CP. The results show that the net effect of  $\text{NO}_2^-$  is negative, therefore, the prohibition effect of  $\text{NO}_2^-$  plays more important role in the 4-CP photoconversion process.

### 3.2. Effect of different factors on the photoconversion of 4-CP in ice phase

#### 3.2.1. Effect of light intensity on the photoconversion kinetics

The photoconversion kinetics of 4-CP in ice phase with different light intensities was compared in Table 1. The different light intensities came from the different distances between samples and the lamp. The result showed that the rate constant  $k$  increased with the light intensity. This can be explained as the reaction system can obtain more energy under a higher light intensity and produces more active substances such as  $\text{HO}^\bullet$  and  $\text{NO}_2^\bullet$  to accelerate the photoconversion.

#### 3.2.2. Effect of the initial concentration of $\text{NO}_2^-$ on the photoconversion kinetics

The prohibition effect of  $\text{NO}_2^-$  plays more important role in the photoconversion process when the concentration of  $\text{NO}_2^-$  increases, the prohibition effect of  $\text{NO}_2^-$  becomes stronger, the photons obtained by per-molecule of 4-CP decreases and the direct photolysis of 4-CP is weakened. Hence the rate constant  $k$  decreased with the increase of the initial concentration of  $\text{NO}_2^-$  (Table 1).

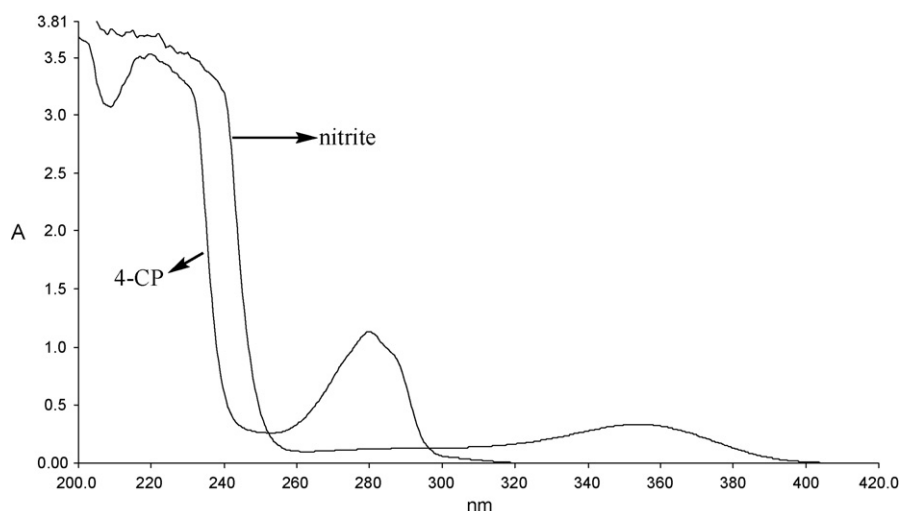
#### 3.2.3. Effect of the initial concentration of 4-CP on the photoconversion kinetics

Features of the photoconversion kinetics of 4-CP in ice phase with different initial concentrations of 4-CP are compared in Table 1.  $\text{NO}_2^-$  mainly takes prohibition effect on the photoconversion in this work as pointed in Section 3.1 and in addition, the quantity of photons produced by the light source during the photochemical reaction is constant under the definite irradiation condition. Therefore, when the initial concentrations of 4-CP is very low such as in the range of  $0.07\text{--}0.19 \text{ mmol L}^{-1}$ , the quantity of photons is large enough both for 4-CP and  $\text{NO}_2^-$ , the direct photolysis of 4-CP can proceed very fast and the negative influence of  $\text{NO}_2^-$  is not obvious. When the concentration of 4-CP is very high such as in the range of  $1.48\text{--}2.14 \text{ mmol L}^{-1}$ , almost all the photons are absorbed by the 4-CP and the negative effect of nitrite is negligible also. Under these two circumstances, the photons obtained by each molecule of 4-CP decreases with the increasing of the concentration of 4-CP and the rate constant  $k$  decreases.

However, in this study when the concentration of 4-CP is in the range of  $0.19\text{--}1.48 \text{ mmol L}^{-1}$ , the rate constant  $k$  increased with the increasing of the initial concentration of 4-CP. This is because 4-CP competes with  $\text{NO}_2^-$  for photons under this concentration conditions. When the concentration of 4-CP increases, more photons are absorbed by 4-CP and the prohibition effect of  $\text{NO}_2^-$  is weakened. This conclusion still needs further research due to the complex process of the reactions.

#### 3.2.4. Effect of the pH value on the photoconversion kinetics

In this work, solutions of hydrochloric acid and sodium hydroxide were used to adjust the initial pH of the 4-CP solution varying from 2 to 12. The result (Table 1) suggests that the pH value has a great effect on the rate constant  $k$ . When pH 6.60 (the initial pH of the 4-CP solution), the rate constant  $k$  was the minimum and it obviously increased when the pH changed. Hydrated electron will be produced in the solution containing organic compounds under



**Fig. 2.** Absorption spectra of sodium nitrite ( $0.8 \text{ mmol L}^{-1}$ ) and 4-CP ( $0.8 \text{ mmol L}^{-1}$ ) in aqueous solution ( $20^\circ\text{C}$ , 200–420 nm).

**Table 1**  
Effects of different factors on the photoconversion of 4-CP in ice phase<sup>a</sup>.

	Rate constant of apparent reaction, $k$ ( $\text{min}^{-1}$ )	Half life $t_{1/2}$ (min)	Correlation coefficient, $r$
Initial concentration of 4-CP ( $\text{mmol L}^{-1}$ ) (irradiated for 60 min; $[\text{NO}_2^-]_0 = 0.72 \text{ mmol L}^{-1}$ ; pH 6.60; the light intensity is 19,500 lx)			
0.07	0.0239	29.00	0.9903
0.14	0.0116	59.74	0.9889
0.19	0.0105	66.00	0.9954
0.26	0.0115	60.26	0.9845
0.54	0.0148	46.82	0.9830
0.69	0.0162	42.78	0.9768
1.48	0.0222	31.22	0.9739
2.14	0.0187	37.06	0.9965
Initial concentration of nitrite ( $\text{mmol L}^{-1}$ ) (irradiated for 60 min; $[\text{4-CP}]_0 = 0.69 \text{ mmol L}^{-1}$ ; pH 6.60, the light intensity is 19,500 lx)			
0	0.0440	15.75	0.9904
0.07	0.0422	16.42	0.9739
0.27	0.0264	26.25	0.9978
0.54	0.0176	39.38	0.9787
0.72	0.0162	42.78	0.9768
1.44	0.0150	46.20	0.9948
2.16	0.0117	59.23	0.9831
pH value (irradiated for 60 min; $[\text{4-CP}]_0 = 0.69 \text{ mmol L}^{-1}$ ; $[\text{NO}_2^-]_0 = 0.72 \text{ mmol L}^{-1}$ ; the light intensity is 19,500 lx)			
2.06	0.0816	8.493	0.9559
3.94	0.0275	25.20	0.9874
6.02	0.0190	36.47	0.9656
6.60	0.0162	42.78	0.9768
7.93	0.0282	24.57	0.9883
9.94	0.0303	22.87	0.9730
11.73	0.0705	9.830	0.9832
Light intensity (lx) (irradiated for 60 min; $[\text{4-CP}]_0 = 0.69 \text{ mmol L}^{-1}$ ; $[\text{NO}_2^-]_0 = 0.72 \text{ mmol L}^{-1}$ ; pH 6.60)			
9230 lx	0.0066	105.0	0.9961
11,200 lx	0.0093	74.52	0.9985
15,200 lx	0.0119	58.24	0.9986
18,000 lx	0.0148	46.82	0.9758
19,300 lx	0.0162	42.78	0.9768
Ion (irradiated for 60 min; $[\text{4-CP}]_0 = 0.69 \text{ mmol L}^{-1}$ ; $[\text{NO}_2^-]_0 = 0.72 \text{ mmol L}^{-1}$ , pH 6.60; the light intensity is 19,500 lx)			
Blank	0.0162	42.78	0.9768
$\text{Fe}^{2+}$	0.0041	169.0	0.9880
$\text{Fe}^{3+}$	0.0236	29.36	0.9541
$\text{HCO}_3^-$	0.0225	30.80	0.9868
$\text{Cl}^-$	0.0199	34.82	0.9911

<sup>a</sup>  $r_{(0.01)} = 0.874$ .

irradiation, then it will react with oxygen rapidly to be  $\text{O}_2^{\bullet-}$  (Eq. (8)). Under acidic condition, the  $\text{O}_2^{\bullet-}$  can be protonated to form  $\text{H}_2\text{O}_2$  (Eq. (9)). After that,  $\text{HO}^\bullet$  will be produced by the photolysis of  $\text{H}_2\text{O}_2$  (Eq. (10)). Simultaneously, the photochemistry of nitrite results in the formation of  $\text{O}^{\bullet-}$  (Eq. (1)) and the  $\text{O}^{\bullet-}$  can be protonated to form  $\text{HO}^\bullet$  when  $\text{H}^+$  exists (Eq. (2)) [18]. Hence, when the pH decreases, the increase of  $\text{H}^+$  will accelerate reactions (2) and (9) and lead to the formation of much more  $\text{HO}^\bullet$ , then the photoconversion rate will be improved.

The faster 4-CP degradation occurring at the higher pH can be attributed to two reasons: firstly, more hydroxyl radicals are formed in alkaline solution as Eq. (11); secondly, the functional group of phenol is dissociated to the phenate ion at high pH and the phenate ion is easier to absorb UV light energy than phenol [21,22].



### 3.2.5. Effect of ions on the photoconversion kinetics

The existence of inorganic anions and cations such as chloride, bicarbonate, ferric iron and ferrous iron are considerably common in natural water. In order to study the effects of anions and cations on the photoconversion kinetics of 4-CP in ice phase,  $\text{NaHCO}_3$ ,  $\text{NaCl}$ ,  $\text{FeCl}_2$  and  $\text{FeCl}_3$  were added into 4-CP solutions, respectively, and

the concentration of the ions was the same as 4-CP. Generally speaking,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  are considered as scavengers of radicals which prohibit the photoreaction. But in this experiment (Table 1),  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{Fe}^{3+}$  advanced the rate constant  $k$  from 0.0162 to 0.0199, 0.0225 and 0.0236  $\text{min}^{-1}$ , respectively. The reason is that although chloride ions can act as scavengers of hydroxyl radical through reaction (12), the dichloride radical anion  $\text{Cl}_2^{\bullet-}$  from the further reaction of  $\text{Cl}^-$  with  $\text{Cl}^\bullet$  (Eq. (13)) is reactive with organic substances [23]. When  $\text{NaHCO}_3$  is added into the solution,  $\text{OH}^-$  ions will be produced and it will also accelerate the photoconversion of 4-CP. When  $\text{Fe}^{3+}$  is added into the system, hydroxyl radical will increase through reaction (14), then the photoconversion of 4-CP will be accelerated [24]. But  $\text{Fe}^{2+}$  held back the rate constant  $k$  from 0.0162 to 0.0041  $\text{min}^{-1}$ . This is because  $\text{Fe}^{2+}$  has quite strong absorption abilities for ultraviolet irradiation and prohibits 4-CP from absorbing the irradiation.



### 3.3. Photoproducts identification

During the photoconversion process of 4-CP with the presence of  $\text{NO}_2^-$ , both the color change of the samples after irradiation and solid substances appearance in the thawed samples predicts the

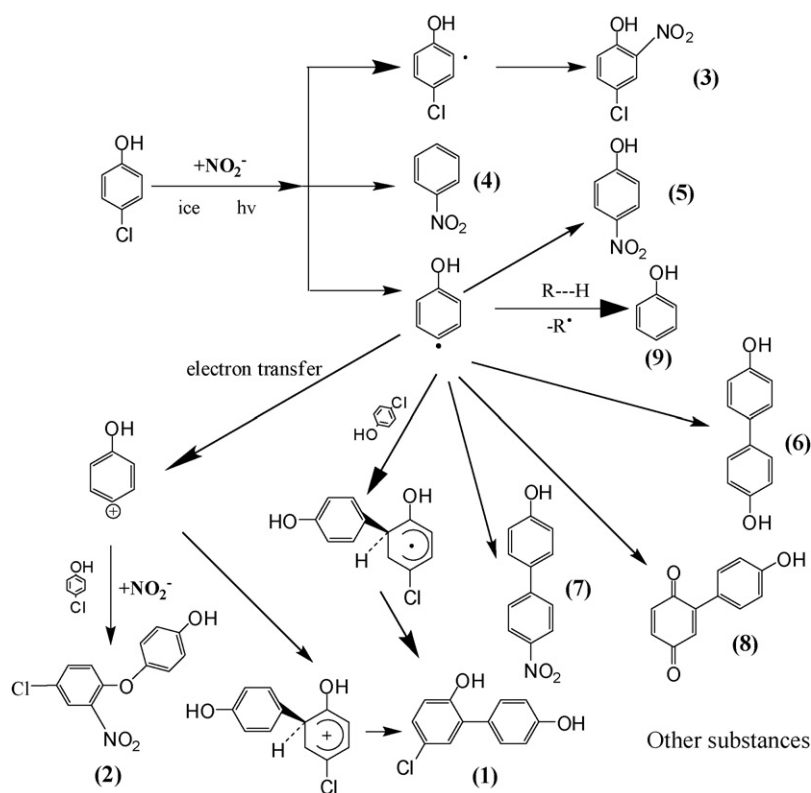


Fig. 3. Proposed mechanism of the photoconversion of 4-CP in ice phase.

presence of intermediate products. The structures of nine characterized photoproducts are shown in Fig. 3, numbered (1)–(9).

The identification from GC–MS shows that the components of the solid substances are 5-chlorobiphenyl-2,4'-diol (1), 4-(4-chloro-2-nitrophenoxy)phenol (2), 4-chloro-2-nitrophenol (3) and some other large molecular weight substances whose structures still need further study. The result from HPLC–ESI–MS shows that the components of the solutions are 5-chlorobiphenyl-2,4'-diol (1), 4-chloro-2-nitrophenol (3), nitrobenzene (4), 4-nitrophenol (5), biphenyl-4,4'-diol (6), 4'-nitrobiphenyl-4-ol (7), 2-(4-hydroxyphenyl)cyclohexa-2,5-diene-1,4-dione (8) and some other substances whose structures also need further study. The qualitative analysis by HPLC suggests that phenol (9) is also the photoproduct during the reaction.

Without the presence of  $\text{NO}_2^-$ , the photoproducts are 5-chlorobiphenyl-2,4'-diol, phenol, 4-(4-chlorophenoxy)phenol, biphenyl-4,4'-diol, 2-(4-hydroxyphenyl)cyclohexa-2,5-diene-1,4-dione, 2,6-bis(4-hydroxyphenyl)cyclohexa-2,5-diene-1,4-dione and some other substances whose structures still need further study, too.

Thus it is seen that the photoproducts and photoconversion ways of 4-CP in ice is changed by  $\text{NO}_2^-$ .

#### 3.4. Mechanism of the photoconversion of 4-CP in ice phase

On the basis of the identification of 4-CP photoproducts as well as the chemical properties of 4-CP and  $\text{NO}_2^-$ , it can be inferred that during the process of photoconversion 4-CP is excited by ultraviolet light to phenolic free radical which tends to have electrophilic substitution; the phenolic free radical forms ion pairs and aryl cations by electron transfer; simultaneously,  $\text{HO}^\bullet$  and  $\text{NO}_2^\bullet$  are created by the photolysis of  $\text{NO}_2^-$ , and then they have further reactions. With the help of the report from Klanova et al. [7], the scheme of 4-CP photoconversion in ice phase is shown in Fig. 3.

#### 3.5. The photoconversion kinetics of 4-CP in natural water ice

Natural water of the Second Songhua River of Jilin, China was used as the solvent to get 4-CP ice samples and the result shows that the 4-CP photoconversion obeys the first-order kinetics model, too. The first-order kinetics process could be described by the equation:  $\ln(C_t/C_0) = -0.0377t + 0.0315$  ( $r = 0.9801$ ). The rate constant  $k$  was  $0.0377 \text{ min}^{-1}$ , half life  $t_{1/2}$  was 18.38 min. The photoconversion rate of 4-CP in the natural water ice was faster than that in the distilled water ice (the rate constant  $k$  was  $0.0162 \text{ min}^{-1}$ , half life  $t_{1/2}$  was 42.78 min). The reason would be that there are more active substances in natural water and their oxidation abilities are strong enough to increase the 4-CP transformation.

## 4. Conclusion

The results of our experiments show that the photoconversion kinetics of 4-CP in ice can be described by the first-order kinetics equation. The rate constant  $k$  of the equation is in direct proportion to the light intensity and in inverse proportion to the initial concentration of  $\text{NO}_2^-$ . The effect of the initial concentration of 4-CP is complex and not a single influence trend. The changing of the initial pH value, no matter increasing or decreasing, accelerates the kinetics reaction.  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{Fe}^{3+}$  advances the photoconversion rate of 4-CP, while  $\text{Fe}^{2+}$  hold back the photoconversion rate; the photoconversion rate of 4-CP in the natural water ice is faster than that in the distilled water ice.

The main photoproducts of 4-CP photoconversion in ice are 5-chlorobiphenyl-2,4'-diol, 4-(4-chloro-2-nitrophenoxy)phenol, 4-chloro-2-nitrophenol, nitrobenzene, 4-nitrophenol, biphenyl-4,4'-diol, 4'-nitrobiphenyl-4-ol, 2-(4-hydroxyphenyl)cyclohexa-2,5-diene-1,4-dione, phenol and some other substances whose molecular structures need further analysis. The mechanism is proposed as 4-CP is first excited by ultraviolet light to phenolic free

radical which tends to have electrophilic substitution; then the phenolic free radical forms ion pairs and aryl cations by electron transfer; simultaneously,  $\text{NO}_2^\bullet$  is created by the photolysis of  $\text{NO}_2^-$ , and finally they have further reactions.

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