



## Study on the mechanism of photo-degradation of p-nitrophenol exposed to 254 nm UV light

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### ABSTRACT

The degradation mechanism of p-nitrophenol (p-NP) exposed to 254 nm UV light was studied in the presence and the absence of oxygen respectively via both steady-state photolysis and time-resolved laser flash photolysis (LFP) experiments. It has been confirmed that p-NP can be photo-ionized to produce its radical cation (p-NP<sup>•+</sup>) and hydrated electron ( $e_{aq}^-$ ) with a quantum yield of 0.52. In neutral solution p-NP<sup>•+</sup> will be quickly deprotonated to form its phenoxy radical (p-NP<sup>•</sup>) which will react with oxygen to promote the breakage of benzene ring of p-NP. The degradation efficiency of p-NP exposed to 254 nm UV is as low as commonly reported. However, oxygen could improve the photo-degradation efficiency, which is due to the reaction of oxygen with p-NP<sup>•</sup>. The reaction between oxygen and p-NP<sup>•</sup> has been experimentally confirmed both in LFP and in pulse radiolysis.

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### 1. Introduction

With the development of new light sources, photochemical applications in degradation of hazardous compounds in a commercial scale become technically feasible. Low-pressure Hg arcs are commonly used in water disinfection rather than direct removal of organics from water, because UV radiation alone is not effective enough for the total mineralization of organics from water [1], generally due to the low quantum yield and the relatively small molar absorptivity of the target compounds.

Researches and applications of photochemical processes are widely concerned, among which the effect of the primary reactions, e.g., photoexcitation, photo-ionization, initiated by UV light should not be ignored because of the selective absorption of light by substances. On one hand, the target compounds could be decomposed by 254 nm UV directly. On the other hand, they could be transformed into some more reactive or inert intermediates. The reactive intermediates might undergo further reactions and consequently have important effects on the degradation process.

Majority of current researches on UV photolysis have been principally concerned about the degradation kinetics and the intermediates analysis via investigating the effects of pollutant concentration, pH value, temperature and atmosphere [2]. However, radicals generating as primary products after UV excitation and the sequential reactions have barely been focused on yet. As a direct

way to study the primary species generating after the excitation of UV light, LFP has been recommended to be an effective method to study the mechanism of photochemical degradation [3]. In this article, LFP experiments have been employed to essentially elucidate the radical reaction mechanisms.

p-Nitrophenol, as the target compound in this study, is a renowned pollutant with high toxicity and poor biological degradability [4]. It widely exists in industrial discharges of pesticide, herbicide and synthetic dyes [5,6]. Despite that the quantum yields of phototransformation are reportedly very low [7], p-NP exposed to polychromatic light will be suffered from decomposition in aqueous solutions [8].

A facile self-designed photochemical reactor has been applied to study the photo-degradation of organic pollutants exposed to 254 nm UV light. 266 nm LFP experiments have been performed in order to reveal the primary reactions after photolysis. A reasonable mechanism has been proposed on the photolysis of p-NP exposed to 254 nm UV light.

### 2. Materials and methods

#### 2.1. Materials and equipments

All reagents applied, purchased from Shanghai Chemical Reagent Company, were all of analytical grade and used as received. Double distilled water was used throughout the steady-state photolysis experiments, and water purified by Milli-Q plus system was used in LFP experiments. All the experiments were performed under room temperature.

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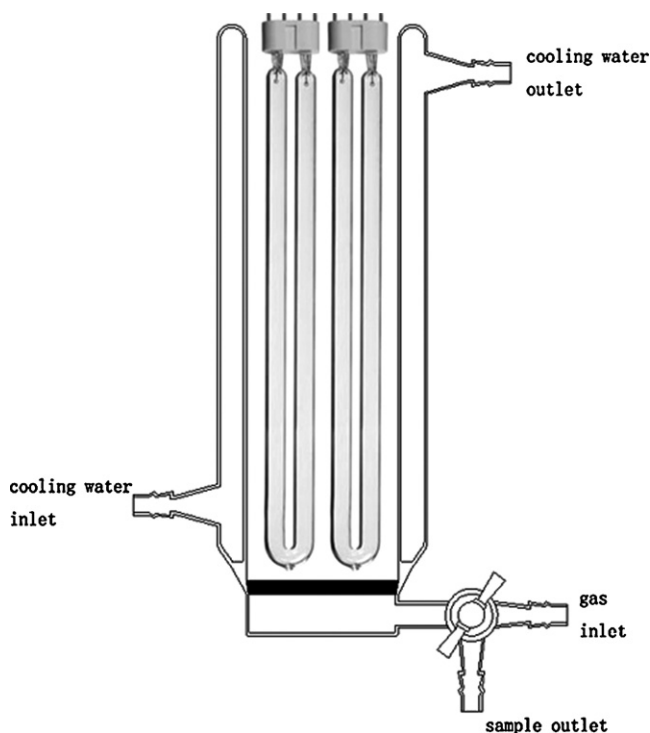


Fig. 1. Ultraviolet irradiation equipment.

The low-pressure mercury vapor lamp (28.5 mm long and a 30 mm external diameter vessel, 40 W electric and 4 W UV output) emitting at 254 nm was purchased from Shanghai Guoda UV Equipment Co., Ltd. (Fig. 1).

A nanosecond LFP apparatus was previously described [9]. An Nd: YAG laser (266 nm, maximum pulse energy of about 40 mJ per pulse and 5 ns duration) was used as an excitation light source. A Xe lamp was used to monitor transient species. A monochromator/photomultiplier combination was used to obtain transient spectra. Signals from the photomultiplier were recorded on a high speed storage oscilloscope (HP 54510B), digitized by a transient digitizer, and transferred to a personal computer. To increase the S/N ratio the analyzing light is folded 100 times during detection time.

The nanosecond pulse radiolysis apparatus was also previously described [10].

The UV–vis absorption spectra were measured using a UV–vis spectrophotometer (Hitachi UV-3010). The total organic carbon (TOC) concentrations of the solutions were measured by using a Shimadzu TOC-5000A TOC analyzer.

## 2.2. Steady-state photolysis

As shown in Fig. 1, the photolysis reactor consists of a 0.5 dm<sup>-3</sup> cylindrical glass vessel with a circulating water jacket, a gas inlet and a sampling port. A u-type UV lamp is located in the center of the water-cooled, double walled glass tubular reactor and totally immersed in the aqueous solution. Water is circulated continuously through the jacket to cool the reaction solution avoiding loss of volatile products. Gas is allowed to flow into the reactor and pass through a porous layer made of glass, dispersing well as small bubbles. Meanwhile, the solution is stirred by bubbling and saturated with the import gas. The whole reactor is covered with an aluminum foil. Prepared sample solutions are transferred into the vessel from the access port on the top of the reactor. After bubbling the solution for 15 min for stirring and gas-saturating, 10 mL of the sample solution is taken as a zero-sample, followed by switching

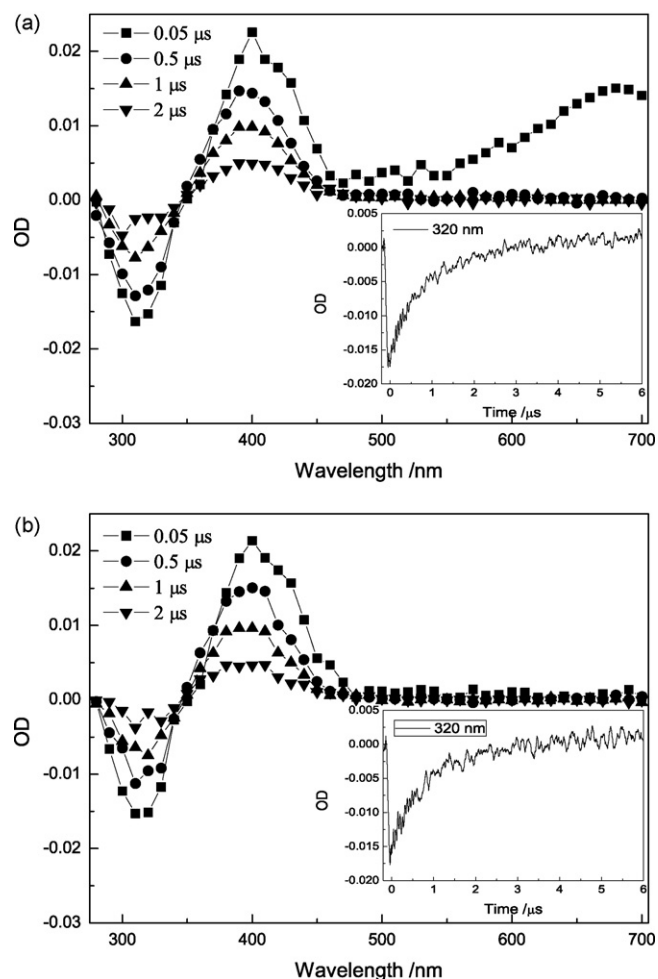


Fig. 2. Transient absorption spectra recorded at different time after 266 nm laser pulse in LFP of 0.1 mM p-NP aqueous solution: (a) oxygen-free, (b) oxygen-saturated. Insets: the time-resolved traces recorded at 320 nm.

on the lamp. During irradiation, bubbling is holding on all the time and 10 mL of irradiated samples are withdrawn at regular intervals. The samples are directly used for UV–vis spectra analysis.

UV detection is conducted in a dark control under an identical experimental condition (sample composition and temperature) except for the absence of UV irradiation, to ensure that no loss of the p-NP occurs via processes other than photolysis (i.e., evaporation).

## 3. Results and discussion

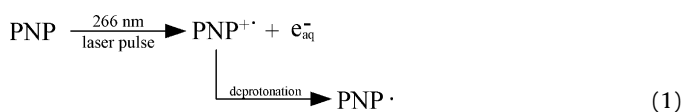
### 3.1. Behavior of p-NP in 266 nm LFP experiments

266 nm LFP experiments were introduced to study the photochemical behavior of p-NP in aqueous solution. As shown in Fig. 2(a) a photo-bleaching with a maximum at 320 nm, strong absorption peak with a maximum at 400 nm and a wide band in 450–700 nm region have been observed in 266 nm LFP of 0.1 mM p-NP oxygen-free aqueous solution. The transient species with absorption in 450–700 nm range could be assigned to  $e_{aq}^-$  as it disappeared when the solution was saturated with  $N_2O$  which is a specific scavenger of  $e_{aq}^-$ . The occurrence of  $e_{aq}^-$  reveals that p-NP has been photo-ionized by 266 nm laser. Thus the transient species with maximum absorption at 400 nm could be assigned to p-NP<sup>•+</sup>. The photo-bleaching with a maximum at 320 nm indicates the consumption of p-NP as it has a characteristic absorption at 320 nm.

Generally, the excited states of p-NP may synchronously generate in 266 nm LFP when photo-ionization occurs as mentioned above. As shown in Fig. 2(a) there is no characteristic transient absorption for excited states of p-NP that could be observed in detectable wavelength region (300–700 nm). In oxygen-saturated system there is no change in the bleaching recorded at 320 nm compared with that in oxygen-free system (see the insets in Fig. 2). In the view of the fact that oxygen is an effective quencher of excited states including singlet and triplet, it can be supposed that in 266 nm LFP of p-NP aqueous solution excited triplet-state of p-NP cannot be detected. However, in our studies the singlet-state p-NP indeed forms because the fluorescence with life-time of 0.3 ns has been observed in oxygen-free solution. So it should be deduced that p-NP could be excited by 266 nm laser in aqueous solution to produce its singlet, but the quantum yield of triplet-state p-NP is too low to be detected probably because the intersystem crossing efficiency from singlet to triplet is very low. To our knowledge, no specific description of the triplet-state p-NP has been reported yet in aqueous solution.

The  $e_{aq}^-$  with absorption band in 450–700 nm region produced in photo-ionization of p-NP should be captured by p-NP itself to form its radical anion, p-NP $^{\bullet-}$ . However, as shown in Fig. 2(b) the transient absorption spectra recorded in oxygen-saturated system show no change compared with that in oxygen-free system despite that  $e_{aq}^-$  is scavenged by oxygen completely. It should be noted that the life-time of  $e_{aq}^-$  (0.4  $\mu$ s) is significantly shorter than that expected [11], and it is probably due to the reaction of  $e_{aq}^-$  with p-NP to generate p-NP $^{\bullet-}$ . Therefore, it should be supposed that p-NP $^{\bullet-}$  has no absorption in detectable wavelength range or its molar extinction coefficient is too low to be detected in our experiment. Pulse radiolysis experiments have also been performed and no signal of p-NP $^{\bullet-}$  produced from the reaction of p-NP with  $e_{aq}^-$  has been observed in the range of 300–700 nm.

Thus, the mechanism of 266 nm LFP of p-NP can be illustrated as follows (Eq. (1)): p-NP could be photo-ionized directly by 266 nm UV light in aqueous solution generating  $e_{aq}^-$  and its cation radical, which will be transferred into its phenoxyl radical by deprotonation as discussed later.



In order to identify if the 266 nm laser photo-ionization of p-NP in aqueous solution is a single-photon or double-photon process, the variation of intensity per pulse of 266 nm laser has been performed from 5 to 40 mJ. It has been observed that there is a lineal relationship between laser intensity and concentration of  $e_{aq}^-$  calculated from transient absorbance measured at 650 nm in series of laser intensities and taking the molar extinction coefficient of  $e_{aq}^-$  as 17,000  $\text{M}^{-1} \text{cm}^{-1}$  [12]. Therefore, the photo-ionization of p-NP is a single-photon process in our experimental condition. Taking 266 nm laser photo-ionization of KI aqueous solution as reference [13], the quantum yield for photo-ionization of p-NP in aqueous solution is determined to be 0.52. By ignoring the contributions of excited triplet-state and radical anion of p-NP at 400 nm, which have already been discussed earlier in this section, the amount of phenoxyl radical of p-NP produced from photo-ionization must be equal to both of  $e_{aq}^-$  and consumption of ground-state p-NP. And the absorbance recorded at zero time after laser pulse recorded at 320, 400 and 640 nm ( $\text{OD}_{0,\lambda}$ ) should be directly related to its molar extinction coefficient. Thus the molar extinction coefficient of phenoxyl radical of p-NP, p-NP $^{\bullet}$  at 400 nm, can be determined to be 33,400  $\text{M}^{-1} \text{cm}^{-1}$  by taking both of ground-state p-NP and  $e_{aq}^-$  as references.

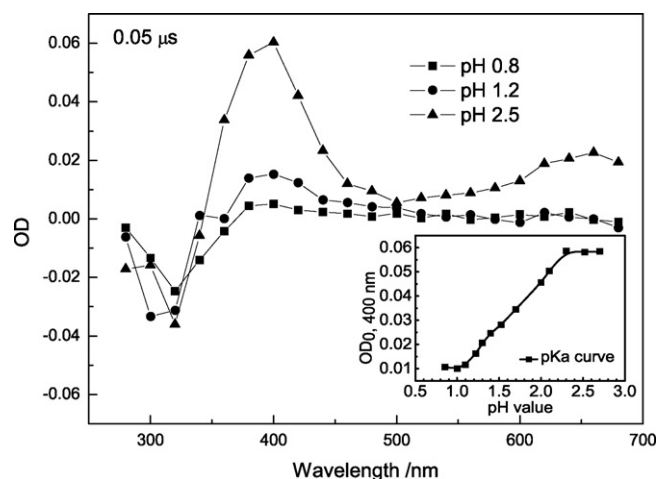


Fig. 3. (a) Transient absorption spectra of 0.1 mM p-NP in nitrogen-saturated aqueous solution recorded at 0.05  $\mu$ s after laser excitation at different pH. (b) pK<sub>a</sub> curve of p-NP cation radical obtained via measuring the OD<sub>0</sub> at 400 nm at different pH.

The p-NP $^{+\bullet}$  formed in LFP is instable in aqueous solution as it will be deprotonated rapidly to yield p-NP $^{\bullet}$  [14]. As shown in Fig. 3(a), the transient absorption peak at 400 nm disappears completely in acidic condition, synchronously accompanied with a new absorption region around 320 nm showing up, which makes an overlap with the bleaching of ground-state p-NP. This phenomenon is attributed to the emergence of p-NP $^{+\bullet}$ . A series of OD<sub>0</sub> at 400 nm have been measured with variation of pH of aqueous solution and the pK<sub>a</sub> value for deprotonation of p-NP $^{+\bullet}$  has been obtained to be around 1.6 (Fig. 3(b)). It is exactly demonstrated that the transient species observed in LFP of 0.1 mM p-NP aqueous solution around pH 7 (Fig. 2) at 400 nm is p-NP $^{\bullet}$  rather than p-NP $^{+\bullet}$ .

### 3.2. 254 nm UV photolysis

The efficiency of 254 nm light in the degradation of p-NP was investigated. 0.1 mM p-NP aqueous solution (pH 7) was prepared and then poured into a specially designed vessel and exposed to 254 nm UV light under nitrogen bubbling and air bubbling, respectively. The typical evolution of UV-vis absorption spectra of the p-NP aqueous solution along with the exposure time in the oxygen-free system is shown in Fig. 4.

The ultraviolet characteristic absorption peak of p-NP is located at 316 nm [15], which represents significantly red-shifted absorp-

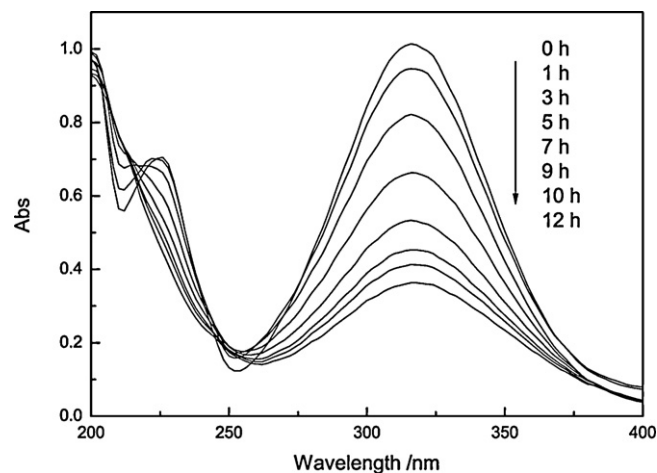


Fig. 4. Absorption spectra evolution of 0.1 mM p-NP in aqueous solution (pH 7) exposed to UV ( $\lambda = 254 \text{ nm}$ ) with nitrogen bubbling continuously.

tion of  $\rho$  band of the ring from the contribution of both the electron donating group  $-\text{OH}$  and the electron withdrawing group  $-\text{NO}_2$ . The UV absorption at 316 nm is commonly used to detect the concentration evolution of p-NP. In acidic and neutral conditions ( $\text{pK}_a = 7.15$ ), p-NP exists as its molecular form (Eq. (2)):



As seen in Fig. 4, the absorbance of p-NP decreases along with exposure time. It means that the aromatic ring structure of p-NP may be demolished. TOC of the solution has been measured to be 70 and 26 mg/L before and after 12 h treatment, respectively, which reveals that organic carbon is mineralized in a considerable amount. These results have a good agreement with previous works [16].

In Fig. 4 the absorption in 200–220 nm region exhibits an increment followed by a decrement along with the exposure time. The increment may be due to the ring opening to generate low-molecular-weight acids, e.g. maleic acid, which is known to have characteristic absorption right in this region [17]. It is reported that maleic acid is one of the detectable products in the 254 nm direct photolysis of p-NP [16]. Other acids, e.g. acrylic acid and methyl acrylic acid, also have absorption in this region.

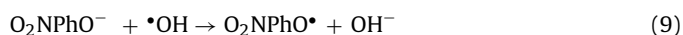
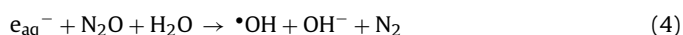
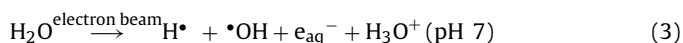
The degradation efficiency of p-NP, as shown in Fig. 5, is very slow. About 75% p-NP is removed from 0.1 mM p-NP aqueous solution for as long as 12 h. The presence of oxygen has been found to be able to accelerate the degradation rate of p-NP in 0.1 mM aqueous solution, which is consistent with the result reported before by Chun et al. [18]. However, there was no detailed discussion on the mechanism in their manuscript.

It has been reported that the ring opening reaction of phenol follows a double-photon mechanism via the generation of 6-oxo-1,3,5-hexatrienyl-1 radical [19]. However, the photo-degradation of p-NP exposed to 254 nm is not a double-photon process but a single-photon ionization as confirmed in 266 nm LFP (Section 3.1). It is difficult to explore how the p-NP $^{\bullet}$  induce the ring breakage to form maleic acid in subsequent photolysis while the solution system is saturated with nitrogen. In air bubbling condition, according to absorptivity at 254 nm and respective concentrations both of p-NP and oxygen in aqueous solution, above 99% of the incident UV light is absorbed by p-NP in this case. Thus, the effect of dis-

solved oxygen on the degradation of p-NP might be explained by the generation of  $\text{O}_2^{\bullet-}$  radicals rather than singlet oxygen. However, to our knowledge, the removal of organics induced by  $\text{O}_2^{\bullet-}$  has not been reported yet. The triplet-state p-NP can be ignored according to the result obtained in LFP. Therefore, the possible presence of singlet oxygen formed from triplet-state p-NP to oxygen via excited energy transfer can be eliminated. Therefore, molecular oxygen may be directly involved in the oxidation of p-NP to improve the efficiency of ring opening of p-NP exposed to UV light. It is suggested that molecular oxygen may react with p-NP $^{\bullet}$  and promote its ring breakage. In 266 nm LFP of 0.1 mM p-NP the decay of p-NP $^{\bullet}$  in oxygen-saturated aqueous solution observed at 400 nm was accelerated slightly compared to that in oxygen-free solution, which is also in agreement with the suggestion.

### 3.3. Reaction between phenoxyl radical and $\text{O}_2$

An experimental condition was designed to study the reaction between phenoxyl radical with oxygen using pulse radiolysis as follows:



Water is decomposed to form hydrogen atom,  $\text{OH}^{\bullet}$ ,  $\text{H}_3\text{O}^+$  and  $\text{e}_{\text{aq}}^-$  as main products in the pulse radiolysis of pH 7.2 aqueous solution containing 0.1 mM p-NP (Eq. (3)). The solution is saturated by  $\text{N}_2\text{O}$  to transform  $\text{e}_{\text{aq}}^-$  into  $\text{OH}^{\bullet}$  (Eq. (4)). The  $\text{OH}^{\bullet}$  is able to abstract hydrogen atom from p-NP to generate p-NP $^{\bullet}$  (Eq. (5)) or adduct to phenyl ring to form biphenolic radical (Eq. (7)). However, at pH 7.2 a majority of p-NP are dissociated into its phenoxyl anion (Eq. (8)) and  $\text{OH}^{\bullet}$  will mainly capture an electron from phenoxyl anion to form p-NP $^{\bullet}$  (Eq. (9)) with a maximum absorption at 400 nm. The transient absorption spectra recorded in the reaction of p-NP with  $\text{OH}^{\bullet}$  is shown in Fig. 6(a). Obviously, p-NP attacked by  $\text{OH}^{\bullet}$  has been transferred into p-NP $^{\bullet}$  and a bleaching occurs at 320 nm, which is in good agreement with what observed in LFP.

As shown in Fig. 6(b), in the pulse radiolysis of the system saturated with both  $\text{N}_2\text{O}$  and  $\text{O}_2$ , the transient absorption spectra have some changes compared with Fig. 6(a). There is a new transient absorption with maximum around 375 nm recorded at 8  $\mu\text{s}$ , which can be supposed to be new transient species when oxygen is present in aqueous solution.

By subtracting the transient absorption in the attack by  $\text{OH}^{\bullet}$  as shown in Fig. 6(a) from that in the attack by  $\text{OH}^{\bullet}$  in the presence of  $\text{O}_2$  as shown in Fig. 6(b), Fig. 6(c) is obtained with the forming of a long-living intermediate with a strong absorption ranged from 330 to 420 nm. The transient species could be assigned to the peroxide radical of p-NP from reaction of p-NP $^{\bullet}$  with molecular oxygen, which has been reported in gas phase [20]. It is also briefly reported by Feitelson et al., etc, that oxygen could accelerate the degradation of p-NP in UV photolysis [21].

Nevertheless, the degradation products generated from reaction of p-NP $^{\bullet}$  and biphenolic radical with molecular oxygen must be different. The identification studies of these photo-degradation products of p-NP are being carried out in our group and new results will be published in next paper.

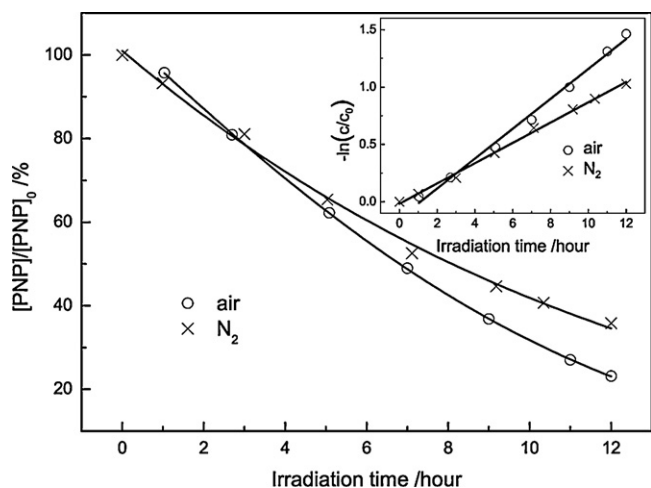
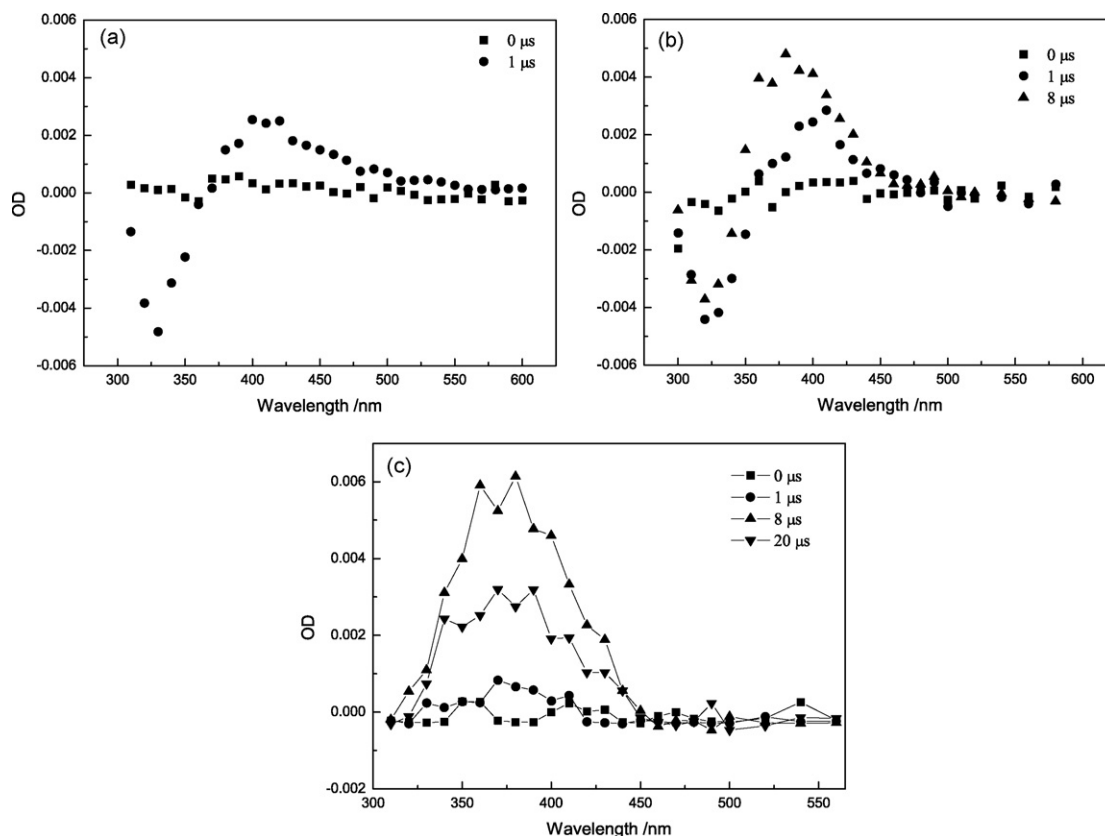


Fig. 5. The degradation of 0.1 mM p-NP in aqueous solution exposed to UV ( $\lambda = 254 \text{ nm}$ ) in the presence and the absence of oxygen. Inset:  $-\ln(c/c_0)$  versus exposure time.



**Fig. 6.** The transient absorption spectra obtained in pulse radiolysis of 0.1 mM p-NP aqueous solution saturated with different gases at pH 7. (a)  $N_2O$  saturated, (b)  $N_2O$  and  $O_2$  saturated, (c) subtracting (a) from (b).

#### 4. Conclusion

Correlating the results obtained in 266 nm LFP and 254 nm steady-state photolysis, the photo-degradation of p-NP could be summarized as follows. In the 266 nm laser flash photolysis p-NP can be photo-ionized to produce its radical cation and  $e_{aq}^-$  with a quantum yield of 0.52. p-NP radical cation will be quickly deprotonated to form its phenoxyl radical at neutral pH. The  $pK_a$  value of its radical cation, molar extinction coefficient of phenoxyl radical of p-NP has been determined to be 1.6 and  $33,400 M^{-1} cm^{-1}$ , respectively. However the excited triplet has not been observed in laser flash photolysis of p-NP aqueous solution. The 254 nm UV light can break the ring of p-NP to make it degrade despite the low efficiency. Meanwhile oxygen can improve the degradation efficiency as oxygen will react with phenoxyl radical, which has been confirmed both in laser flash photolysis and in pulse radiolysis.

#### Acknowledgement

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