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Photochemical Transformation of Bisphenol A Promoted by Nitrate Ions

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Bisphenol A [2, 2-bis(4-dihydroxydiphenyl)propane] (BPA) is widely used as a raw material for polycarbonate and epoxy resins. The residue level of BPA in surface water was shown to be at a rather high level, ranging from 4.4×10^{-10} to 5.3×10^{-8} mol L^{-1} by the U.S. Geological Survey (Kolpin et al. 2002) and 5.7×10^{-9} to 5.7×10^{-5} mol L^{-1} in landfill leachates in Japan (Yamamoto et al. 2001). Furthermore, environmental behavior and fate of BPA is of great concern in recent years due to its endocrine-disrupting effect (Bae et al. 2002). Since indirect photolysis of BPA may result in significant change in its environmental fate and ecological risk in natural water, the study on the interaction of BPA with various reactive oxygen species (ROS) such as the hydroxyl radical ($^{\cdot}OH$) is of high interest. Nitrate ions were found to be present at concentrations ranging from 3×10^{-3} to 0.323 mol L^{-1} in natural water and could absorb solar radiation to produce ROS including $^{\cdot}OH$ following two paths (Mack and Bolton 1999; Lam et al. 2003):

$$[NO_3^-]^* \rightarrow NO_2^- + O(^3P) \qquad (1)$$

$$[NO_3^-]^* \rightarrow NO_2^{\cdot} + O^{\cdot-} \xrightarrow{H_2O} NO_2^{\cdot} + {}^{\cdot}OH + OH^- \qquad (2)$$

The $^{\cdot}OH$ is a highly reactive transient that can rapidly oxidize most organic compounds (Brekken and Brezonik 1998). Therefore, a nitrate-induced reaction between $^{\cdot}OH$ and BPA might be a potential degradation pathway to eliminate BPA from natural water and wastewater.

The objectives of the present work are (1) to study the nitrate-induced photodegradation of BPA under simulated solar radiation at different environmental factors (concentration of nitrate and BPA, pH of solution); (2) to characterize the $^{\cdot}OH$ generated from nitrate photolysis; (3) to identify the main intermediate photoproducts and analyze the possibility of the BPA toxicity reduction mechanism in natural water.

MATERIALS AND METHODS

Bisphenol A and sodium nitrate were obtained from Shanghai Chemical Reagent Co. LTD. (China). Methanol, nitrobenzene, dichloromethane, anhydrous sodium sulfate, disodium hydrogen phosphate, sodium phosphate and borax were of

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analytical grade (purity > 99%) and used as received. 5,5-dimethyl-pyroline-N-oxide (DMPO) (purity > 97%) was purchased from Aldrich. HPLC grade acetonitrile was obtained from Tedia Ltd. *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was obtained from Supelco. All experimental solutions were prepared by dissolving the reagent directly in ultra pure water obtained from an ultrafilter from Labconco Corporation (Kansas, USA).

Photochemical experiments were conducted in a NDC-2 photosimulator (Nanjing University, China) equipped with a 500 W medium mercury vapor lamp (Beijing Electric Light Source Institute, China) as the irradiation source. The lamp was immersed inside the cooling jacket through which cold tap water flowed to keep the lamp cool. The light intensity of the lamp at 365 nm was measured as 533 W m^{-2} by UV irradiation photometer (Beijing Normal University, China). The 50 mL reaction solutions were added into quartz tube vertically placed outside the glass well restricting the transmission of wavelengths < 290 nm. One mL of sample was removed at selected time intervals during the photolysis process and analyzed by HPLC. Each photolysis experiment was carried out in triplicate. Control experiment included the BPA photodegradation in pure water at pH 6.8 to investigate the direct photolysis. The pH dependence of BPA photolysis was conducted in buffer solution at pH 7.0 (0.025 mol L^{-1} disodium hydrogen phosphate), 9.0 (0.01 mol L^{-1} borax) and 10.8 (0.1 mol L^{-1} phosphate).

The samples were quantitatively analyzed by HPLC (Agilent 1100, USA) coupled with a Discovery C_{18} reversed-phase column (150 mm × 4.6 mm) at 30 °C with 10 μL injection in duplicate. Detections were performed at the wavelength of 228 nm for BPA and 267 nm for nitrobenzene. Mobile phase composition was acetonitrile-water (60/40, v/v) at a flow rate of 1.0 mL min^{-1}. Electron spin resonance (ESR) experiments were performed at room temperature using an ESR spectrometer (Brucker EMX 10/12, Germany) equipped with a 180 W high pressure mercury lamp. A glass capillary tube containing the prepared solution was vertically placed into a cylindrical quartz ESR tube and irradiated in the cavity of the ESR spectrometer. The ESR measurements were conducted at X band under the conditions: magnetic field, 347.5 ± 2.5 mT; modulation amplitude, 0.1 mT.

For identifying the photoproducts of BPA in nitrate solution, 500 mL mixtures ($[BPA]_0=0.13\times10^{-3}$ mol L^{-1}, $[NO_3^-]_0=4.8\times10^{-3}$ mol L^{-1}) that had been irradiated for 5 hours were extracted using dichloromethane (170 ml × 3). The extracts were dehydrated by anhydrous sodium sulfate, reduced to 2 mL via rotatory evaporation and dried by ultra pure N_2, and then treated with 0.1 mL BSTFA. These silylated mixtures were analyzed by GC/MS (Micromass GCT-TOF, UK) by injecting 0.2 μL at 270 °C into a DB-5 column with helium carrier gas at a flow rate of 1 mL min^{-1}. The MS was operated at the standard electron ionization (EI) of 70 eV. The temperature program was operated with the initial temperature 40 °C for 5 min, then increased by 6 °C min^{-1} to 280 °C with 10 min holding. The NIST/EPA/NIH mass spectral database was used for the analysis of BPA photoproducts.

Pseudo-first-order rate constants for BPA and nitrobenzene were obtained by linear regression of $\ln(C/C_0)$ determined as a function of time. The photolysis ratio was calculated by (1- average level of BPA in tested sample/initial level of BPA) × 100%, i.e. $(1-C/C_0) \times 100\%$. Significant ($P<0.05$) differences between the control and each treatment were examined using one-way ANOVA via SPSS statistical package (Version 10.0 for Windows).

RESULTS AND DISCUSSION

The pK_a of BPA (pK_a=9.5, 10.2) (Staples et al. 1998) lies in the pH range commonly encountered in surface freshwater, implying that photochemical reactions of both molecular and anionic forms of BPA have to be investigated. The direct photolysis of BPA increased with the increasing pH value of water, but was obviously slow compared with the indirect photolysis of BPA in nitrate solution (Table 1). First, in alkaline solution, the absorption spectrum of BPA shifted to above 300 nm which overlaps the terrestrial sunlight spectrum (results not shown here), resulting in the promotion of its direct photolysis. Second, the negatively charged oxygen from deprotonation of the phenolic hydroxyl moiety in alkaline solution enhanced the electron density on the benzene rings of the BPA molecule and thus the reactivity of BPA to the electrophilic $^{\cdot}OH$. It was suggested that the nitrate-induced photochemical reaction could enhance BPA photodegradation and therefore have some depolluting effects on BPA in natural water and wastewater.

BPA photodegradation followed a peusdo-first-order kinetic reaction and was elevated by increasing nitrate concentration (Table 2). Since BPA was found at different level in contamination site, the effect of initial BPA concentration on its degradation in nitrate solution was examined (Figure 1). The photodegradation rate decreased with increasing initial BPA concentration. After irradiation for 7 hours, around 99% of BPA with the initial concentration of 8.8×10^{-6} mol L^{-1} was degraded. The results showed that the nitrate-induced photochemical process was a potential way to effectively eliminate BPA contamination from natural water and wastewater.

Table 1. The photolysis ratio of BPA in solutions at various pH value ($[BPA]_0 = 4.4\times10^{-5}$ mol L^{-1} , $[NO_3^-]_0=1.61\times10^{-3}$ mol L^{-1})

Solution system	pH=6.8 water	pH=7.0 buffer (0.25%)^a	pH=9.0 buffer (21%)^a	pH=10.8 buffer (99%)^a
Photolysis ratio %^{b}	3.00	8.31	32.5	86.8
Photolysis ratio %^{c}	38.3	38.3	73.2	97.0

^{a} anionic form of initial BPA molecules

^{b} direct photolysis in water

^{c} indirectly photolysis in nitrate solution

To determine if the $^{\cdot}OH$ was involved in the nitrate-induced photodegradation of BPA, an excess amount of methanol was added as an efficient and specific $^{\cdot}OH$

Table 2. The effect of nitrate concentration on BPA photodegradation ($[BPA]_0 = 4.4\times10^{-5}$ mol L^{-1}, pH=6.8)

$[NO_3^-]$ / $\times10^{-3}$ mol L^{-1}	k / $\times10^{-2}$ min^{-1}	$t_{1/2}$ /min	n	r
0.161	0.08	866	8	0.981
0.806	0.35	198	8	0.989
1.613	0.64	108	8	0.989
9.677	2.12	33.0	8	0.991

quencher to compete with BPA for $^{\cdot}OH$. Methanol does not absorb solar radiation and was reported to be unreactive towards other ROS (Zhou and Mopper 1990). Figure 2 showed that BPA degradation in a nitrate/methanol system was greatly inhibited and was very close to BPA direct photolysis, which indicated that BPA degradation in nitrate solution was predominantly attributable to the photooxidation of the $^{\cdot}OH$ generated from the excited nitrate ions.

In order to quantify the steady-state concentration of $^{\cdot}OH$ ($[^{\cdot}OH]_{ss}$) produced from the excited nitrate ions, the competitive kinetic experiment was conducted with nitrobenzene as the molecular probe (P) (Brezonik and Brekken 1998; Zepp et al. 1987). In this test, the $^{\cdot}OH$ decayed following two pathways:

$$^{\cdot}OH + BPA \rightarrow \text{products} \qquad (3)$$

$$^{\cdot}OH + P \rightarrow \text{products'} \qquad (4)$$

Since the concentration of $^{\cdot}OH$ reached a steady-state under constant irradiation, the loss of probe (P) can be expressed as:

$$-d[P]/dt = k_{P,OH}\,[^{\cdot}OH]_{ss}[P] = k_{exp}[P] \qquad (5)$$

or

$$\ln([P]/[P]_0) = -\,k_{exp}\,t \qquad (6)$$

where $k_{P,OH}$ is the second-order rate constant for nitrobenzene with $^{\cdot}OH$ (3.0×10^{9} mol^{-1} L s^{-1}) (Zepp et al. 1987); k_{exp} is a measured pseudo-first-order rate constant (s^{-1}), $k_{exp} = k_{P,OH}\,[^{\cdot}OH]_{ss}$; [P] is probe concentration (mol L^{-1}); t is irradiation time. 4.4×10^{-5} mol L^{-1} BPA and 1.61×10^{-3} mol L^{-1} nitrate were irradiated with 7.8×10^{-6} mol L^{-1} nitrobenzene (P) added to maintain a steady-state. A plot of $\ln([P]/[P]_0)$ vs time t yielded a straight line (r=0.992) with the slope $k_{exp}=3.83\times10^{-5}$ s^{-1}, and then the steady-state concentration of $^{\cdot}OH$ was calculated from the ratio: $[^{\cdot}OH]_{ss} = k_{exp}/k_{P,OH} = 1.27\times10^{-14}$ mol L^{-1}. Moreover, the second-order rate constant of BPA with the $^{\cdot}OH$ ($k_{BPA,OH}$) was estimated from the measured pseudo-first-order rate constant of BPA degradation ($k_{exp,BPA}$) in nitrate solution in the same irradiation test and $[^{\cdot}OH]_{ss}$: $k_{BPA,OH} = k_{exp,BPA}/[^{\cdot}OH]_{ss} = 1.01\times10^{10}$ mol^{-1} L s^{-1}, which coincide with the value in literatures (Gozmen et al. 2003; Rosenfeldt and Linden 2004).

For further confirmation of the $^{\cdot}OH$ produced upon the photolysis of nitrate ions, the ESR experiments were carried out with DMPO as the spin trapper. The test results are presented in Figure 3. The ESR signal showed a 1/2/2/1 quartet with hyperfine splitting of $a_N = a_H = 1.505$ mT and g factor 2.0059, which were the typical structure of the DMPO-OH adduct (Brezova et al. 2004). When an excess amount of isopropanol, a known and efficient $^{\cdot}OH$ quencher (Aguer and Richard 1996) was added, the ESR signal of the DMPO-OH adduct was greatly inhibited.

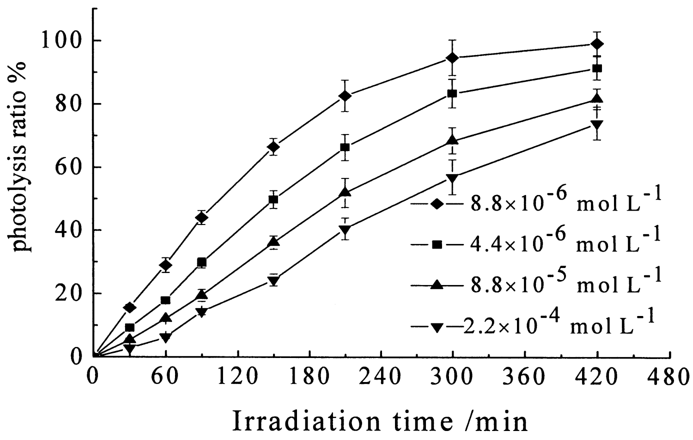

Figure 1. The effects of initial BPA concentration on its photolytic efficiency ($[NO_3^-]_0=1.61\times10^{-3}$ mol L^{-1}, pH=6.8). Data represent means ± standard deviation (n = 6).

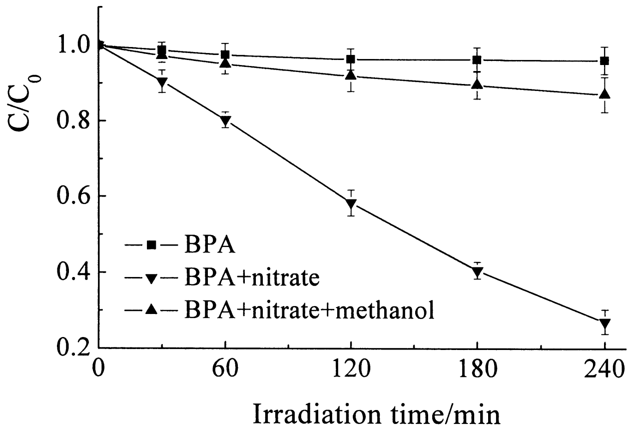

Figure 2. Comparison of BPA photodegradations ($[BPA]_0=4.4\times10^{-5}$ mol L^{-1}, $[NO_3^-]_0=1.61\times10^{-3}$ mol L^{-1}, [methanol] =0.05 mol L^{-1}, pH=6.8). Data represent means ± standard deviation (n = 6).

Since the nitrate photolysis could produce relatively high levels of $^{\cdot}$OH, which rapidly reacts with most organic compounds with the second-order rate constants ranging from 10^{-7} to 10^{-10} mol^{-1} L s^{-1}, it might achieve the mineralization of BPA in water and wastewater in a sufficient length of irradiation time.

Moreover, to make clear that the nitrate-induced photochemical process could have an impact on the toxicity reduction of BPA, the intermediates and

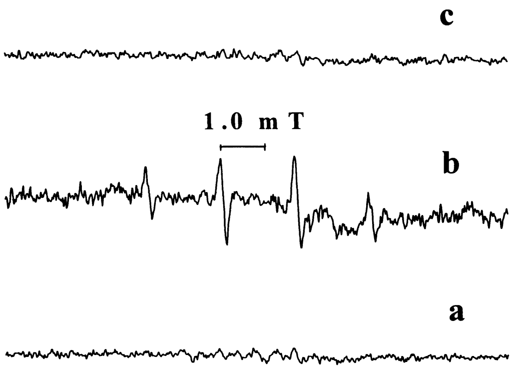

Figure 3. ESR spectra for DMPO-OH adducts in the solutions of 1.61×10^{-3} mol L^{-1} nitrate and 0.044 mol L^{-1} DMPO. Spectrum a: before irradiation; Spectrum b: after 30 minutes irradiation; Spectrum c: after 30 minutes irradiation with the addition of isopropanol (0.1 mol L^{-1})

photoproducts of BPA were analyzed by GC-MS. A possible degradation pathway of BPA in nitrate solution was proposed in Figure 4. On the one hand, products 9, 11 and 12 indicated the addition of $^{\cdot}OH$ and $NO_2^{\cdot}$ to substrate BPA, possibly forming the *ortho-* derivatives to the phenolic hydroxyl moiety due to the steric inhibition of the isopropyl group. On the other hand, photocleavage of the two phenyl groups in BPA by attack of $^{\cdot}OH$ may cause the production of isopropylphenol radical ($^{\cdot}C(CH_3)_2C_6H_4OH$) and phenol radical ($^{\cdot}C_6H_4OH$), further forming product 1, 3 and 4 respectively. The latter underwent further oxidation to product 6 and also converted to dehydroxylated product 2. Furthermore, $^{\cdot}OH$ and $NO_2^{\cdot}$ also attacked an intermediate phenol radical or product 1 to form *ortho-* or *para-* hydroxy and nitro derivatives 5, 7 respectively. Product 10 was also detected due to the radical reaction of products 3 and 7. Products 1 to 7 have been confirmed by comparing with mass spectra of standard chemicals with the library data and retention times on GC-MS. Among the main intermediate products detected, product 6 and 9 transiently accumulated at relatively high levels. It has been reported that the estrogen activity of 2-(3,4-dihydroxyphenyl)-2-(4-hydroxyphenyl)propane (product 9 here) and 4-hydroxyacetophenone (product 6 here) were approximately 10 and 100 times less than that of BPA respectively, while both showed lower acute toxicity compared with BPA (Suzuki et al. 2004; Ike et al. 2002; Nakagawa and Suzuki 2001). As for the other main intermediate products such as hydroxy and nitro derivatives (product 11 and 12 etc.), the toxicity and the estrogen activity have not been evaluated and therefore would be brought to further study.

The results of this study showed that the nitrate-induced photochemical process is effective for eliminating BPA contamination from natural water and wastewater.

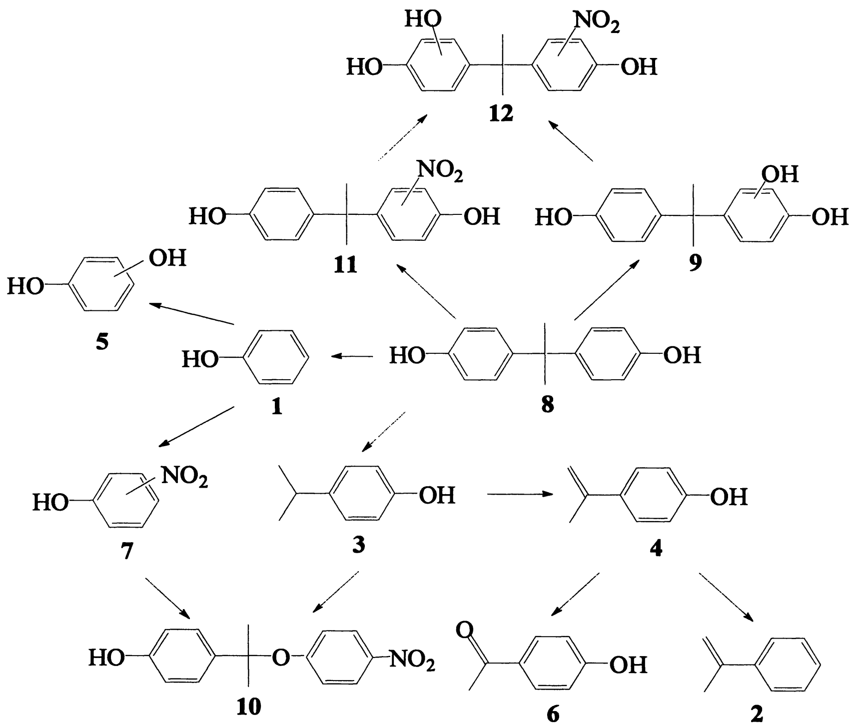

Figure 4. Proposed photodegradation pathway of BPA in nitrate solution

BPA underwent a slightly direct photolysis in neutral and acidic water, but a significant indirect photolysis in the presence of nitrate ions, following a pseudo-first-order kinetic reaction. The BPA photodegradation rate increased with the increasing nitrate concentration and decreasing initial BPA concentration as well. The $^{\cdot}$OH generated from nitrate photolysis was determined by molecular probe and an ESR experiment as well. Moreover, its steady-state concentration was measured as 1.27×10^{-14} mol L^{-1}. Some of the main intermediate and degradation products of BPA in nitrate solution showed lower toxicity and weaker estrogen activity than BPA, while others remained uncertain. Further work should be focused on ascertaining the toxicity and estrogen activity of the other main degradation products including nitro derivatives and controlling the reaction conditions for the efficient mineralization of BPA.

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