

Arsenite Oxidation Initiated by the UV Photolysis of Nitrite and Nitrate

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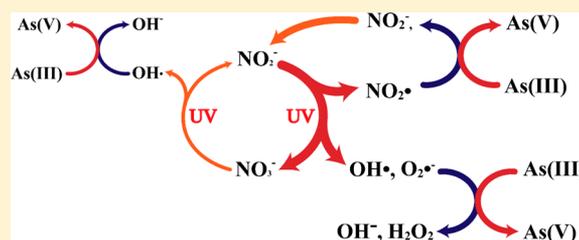
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ABSTRACT: This study demonstrates that the production of reactive oxidizing species (e.g., hydroxyl radical ($\bullet\text{OH}$)) during the photolysis of nitrite (NO_2^-) or nitrate (NO_3^-) leads to the oxidative conversion of arsenite (As(III)) to arsenate (As(V)). While the direct UV photolytic oxidation of As(III) was absent, nitrite (20 or 200 μM) addition markedly accelerated the oxidation of As(III) under UV irradiation ($\lambda > 295 \text{ nm}$), which implies a role of NO_2^- as a photosensitizer for As(III) oxidation. Nitrate-mediated photo-oxidation of As(III) revealed an initial lag phase during which NO_3^- is converted into NO_2^- . UV-Photosensitized oxidation of As(III) was kinetically enhanced under acidic pH condition where nitrous acid (HNO_2) with a high quantum yield for $\bullet\text{OH}$ production is a predominant form of nitrite. On the other hand, alkaline pH that favors the photoinduced transformation of NO_3^- to NO_2^- significantly facilitated the catalytic reduction/oxidation cycling, which enabled the complete oxidation of As(III) at the condition of $[\text{As(III)}]/[\text{NO}_2^-] \gg 1$ and markedly accelerated NO_3^- -sensitized oxidation of As(III) . The presence of O_2 and N_2O as electron scavengers enhanced the photochemical dissociation of NO_2^- via intermolecular electron transfer, initiating the oxidative As(III) conversion route probably involving $\text{NO}_2\bullet$ and superoxide radical anion ($\text{O}_2\bullet^-$) as alternative oxidants. The outdoor experiment demonstrated the capability of NO_2^- for the photosensitized production of oxidizing species and the subsequent oxidation of As(III) into As(V) under solar irradiation.



INTRODUCTION

Oxidative conversion of arsenite (As(III)) to arsenate (As(V)) leads to the reduction in toxicity and mobility of arsenic species in aquatic ecosystems and enhances the arsenic removal efficiency during physical water treatment processes such as coagulation and precipitation.¹ Considering that arsenite is the prevalent arsenic species in the environmental media,^{2,3} the remediation of arsenic-contaminated water matrix requires an oxidative treatment of As(III) as a pretreatment option. Advanced oxidation processes (AOPs) can be employed for rapid oxidative transformation of As(III) because As(III) is highly vulnerable to hydroxyl radical ($\bullet\text{OH}$)-induced oxidation (i.e., $k(\text{AsO}_2^- + \bullet\text{OH}) = 9.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).⁴ Fenton reagent as a precursor of $\bullet\text{OH}$ effectively oxidizes As(III) under acidic pH condition, and also forms high valent iron intermediates (e.g., ferryl ion (Fe(IV))) at circumneutral pH to convert As(III) to As(V) .⁵ Photolytic decomposition of ferric carboxylate complexes leads to high yield generation of $\bullet\text{OH}$ over a relatively broad pH range, resulting in a significant oxidation of As(III) under near UV light irradiation.⁶ Photoinduced oxidation of As(III) in the presence of iron oxyhydroxides has been investigated.^{7,8} Efficient photocatalytic oxidation of As(III) on TiO_2 has been also successfully

demonstrated.^{9–12} The direct photooxidation of As(III) is possible under 254 nm irradiation,¹³ and the oxidation rate is highly enhanced in the presence of iodide, which acts as a photocatalyst under the irradiation of 254 nm.¹⁴

UV photolysis of nitrite (NO_2^-) and nitrate (NO_3^-) efficiently triggers the fission of O–N bonds to produce reactive oxidizing intermediates,¹⁵ which may contribute to (1) photochemical transformation of chemical substances in the aquatic environment^{16,17} and (2) the oxidative treatment of organic/inorganic contaminants and pathogenic microorganisms in water.^{18,19} The main reactions that should be involved in the UV/ $\text{As(III)}/\text{NO}_2^-$ (or NO_3^-) system are listed in Table 1. The photolysis of NO_2^- (or NO_3^-) predominantly produces nitrogen oxide radical ($\text{NO}\bullet$ or $\text{NO}_2\bullet$) and oxide radical anion ($\text{O}\bullet^-$) (reaction A2a or C2a), which undergoes rapid protonation to form $\bullet\text{OH}$ (reaction D1).¹⁵ As a minor reaction pathway, the photodissociation of NO_2^- converts into $\text{NO}_2\bullet$ and hydrated electron (e_{aq}^-) (reaction A2b), which leads to the

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Table 1. Reactions Involved in the Oxidation of As(III) during UV Photolysis of NO_2^- and NO_3^- ^a

	reaction	ref
	UV photolysis of NO_2^- and NO_3^- and production of reactive intermediates	
A1	$\text{NO}_2^- + h\nu \rightarrow \text{NO}_2^{*-}$	15
A2a	$\text{NO}_2^{*-} \rightarrow \text{NO}^\bullet + \text{O}^{*-}$	15
A2b	$\text{NO}_2^{*-} \rightarrow \text{NO}_2^\bullet + e_{\text{aq}}^-$	21
B1	$\text{HNO}_2 + h\nu \rightarrow \text{NO}^\bullet + \bullet\text{OH}$	21
C1	$\text{NO}_3^- + h\nu \rightarrow \text{NO}_3^{*-}$	15
C2a	$\text{NO}_3^{*-} \rightarrow \text{NO}_2^\bullet + \text{O}^{*-}$	15
C2b	$\text{NO}_3^{*-} \rightarrow \text{NO}_2^- + \text{O}(^3\text{P})$	15
D1	$\text{O}^{*-} + \text{H}_2\text{O} \leftrightarrow \bullet\text{OH} + \text{OH}^-$	$pK_a = 11.9$ 15
E1	$e_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^{*-}$	$k_{\text{E1}} = 1.9 \times 10^{10}$ 4
F1	$2\text{NO}^\bullet + \text{O}_2 \rightarrow 2\text{NO}_2^\bullet$	$2k_{\text{F1}} = 4.2 \times 10^6$ 21
F2	$\text{NO}^\bullet + \text{NO}_2^\bullet + \text{H}_2\text{O} \rightarrow 2\text{NO}_2^- + 2\text{H}^+$	$k_{\text{F2}} \approx 1.6 \times 10^8$ 21
F3	$\text{NO}^\bullet + \text{NO}_3^- \rightarrow \text{NO}_2^\bullet + \text{NO}_2^-$	$k_{\text{F3}} \leq 4 \times 10^4$ 21
F4	$\text{NO}_2^\bullet + \text{NO}_2^\bullet + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{NO}_2^- + 2\text{H}^+$	$k_{\text{F4}} \approx 8.0 \times 10^7$ 21
	•OH-mediated reaction	
G1	$\bullet\text{OH} + \text{NO}_2^- \rightarrow \text{OH}^- + \text{NO}_2^\bullet$	$k_{\text{G1}} = 1.0 \times 10^{10}$ 21
G2	$\bullet\text{OH} + \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2^\bullet$	$k_{\text{G2}} \approx 2.6 \times 10^9$ 21
G3	$\bullet\text{OH} + t\text{-BuOH} \rightarrow \text{oxidized products}$	$k_{\text{G3}} = 6.0 \times 10^8$ 23
G4	$\bullet\text{OH} + \text{As(III)} \rightarrow \text{As(IV)}$	$k_{\text{G4}} = 8.5 \times 10^9$ 23
	As(III) oxidation	
H1	$\bullet\text{OH} + \text{As(III)} \rightarrow \text{As(IV)}$	$k_{\text{H1}} = 8.5 \times 10^9$ 23
H2	$\text{O}_2^{*-} + \text{As(III)} + \text{H}^+ \rightarrow \text{As(IV)} + \text{HO}_2^-$	$k_{\text{H2}} = 3.6 \times 10^6$ 11
H3	$\text{NO}_2^\bullet + \text{As(III)} \rightarrow \text{NO}_2^- + \text{As(IV)}$	
H4	$\text{As(IV)} + \text{O}_2 \rightarrow \text{As(V)} + \text{HO}_2^\bullet/\text{O}_2^{*-}$	$k_{\text{H4}} = 1.1 \times 10^9$ 5
H5	$\text{As(IV)} + \text{As(IV)} \rightarrow \text{As(V)} + \text{As(III)}$	23

^aRate constants are given in $\text{M}^{-1} \text{s}^{-1}$ except for reaction F1 ($\text{M}^{-2} \text{s}^{-1}$).

production of superoxide radical anion (O_2^{*-}) with moderate oxidizing power (i.e., $E^0(\text{HO}_2^\bullet/\text{H}_2\text{O}_2) = 1.44 V_{\text{NHE}}$ or $E^0(\text{O}_2^{*-}/\text{HO}_2^-) = 1.03 V_{\text{NHE}}$)²⁰ under air-equilibrated condition (reaction E1).²¹ The one-electron oxidation pathway of NO_2^- is significantly promoted in the presence of ferric ion, iron oxide, and NO_3^- : the accompanying generation of NO_2^\bullet leads to the nitration of phenolic compounds.²² This supports the possible involvement of NO_2^\bullet in the nitrite-mediated photochemical oxidation.

The photosensitizing capability of NO_2^- and NO_3^- to produce reactive oxidizing species can be applied to the oxidative conversion of As(III) to As(V). Although Dutta et al. briefly reported the photolysis of NO_3^- as a mean of generating OH radical for the oxidation of As(III),²³ the mechanism of NO_2^- (or NO_3^-)-mediated photosensitized oxidation of As(III) has not been studied. Nitrogen-containing radicals (i.e., NO^\bullet and NO_2^\bullet) rapidly recombine to regenerate NO_2^- and NO_3^- (reactions F1–4)²¹ in the absence of background organics that are susceptible to nitration. Therefore, a catalytic process based on the cycling of NO_2^- (or NO_3^-) might be utilized to mediate the photochemical oxidation of As(III). Since NO_2^- and NO_3^- are commonly present as background constituents of ground, surface, and wastewater matrixes (e.g., the mean level of NO_2^- and NO_3^- is 2.0, 17.3 mg/L, respectively, in arsenic contaminated groundwater),²⁴ their photolysis under sunlight may contribute to the natural oxidation mechanism of As(III).

This study investigated the photooxidation of As(III) to As(V) in the presence of NO_2^- or NO_3^- under UV irradiation ($\lambda > 295 \text{ nm}$). The oxidation kinetics of As(III) and the accompanying conversion of $\text{NO}_2^-/\text{NO}_3^-$ were investigated by varying the experimental parameters (e.g., pH, $[\text{NO}_2^-]$, dissolved gas). From this study, the roles of NO_2^- (or

NO_3^-) in the photosensitized oxidation of As(III) in aquatic system were successfully demonstrated. The experiments were also performed under sunlight in order to simulate a natural environmental condition.

EXPERIMENTAL SECTION

Chemicals and Materials. Chemicals and reagents used in this work include the followings: NaAsO_2 (As(III), Aldrich), $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (As(V), Kanto), NaNO_2 (Aldrich), NaNO_3 (Aldrich), molybdate reagent solution (Fluka Analytical), *tert*-butyl alcohol (*t*-BuOH) (Samchun Chemicals). Suwannee River humic acid (HA) standard obtained from International Humic Substance Society (IHSS) was used to study the effect of natural organic matter on the As(III) oxidation during NO_2^- photolysis. All chemicals were of analytical grade. Deionized water used was ultrapure (18 $\text{M}\Omega\text{-cm}$) and prepared by a Barnstead purification system. N_2 (99.999% purity) and N_2O (5.02% mol/mol He) were obtained from BOC Gases and Rigas.

Photolysis and Analysis. Typical reaction solutions contained 200 μM NO_2^- (or NO_3^-) and 100 μM As(III). The tested solution was unbuffered and air-equilibrated. The initial pH was adjusted to 9.0 with concentrated solution of NaOH or HClO_4 . A 300-W Xe arc lamp (Oriol) was used as a light source. The light beam was passed through a 10-cm IR water filter and a UV cutoff filter ($\lambda > 295 \text{ nm}$) and then focused onto a cylindrical Pyrex reactor (50 mL) which was mixed on a magnetic stirrer. The incident light intensity in the active wavelength region ($295 < \lambda < 500 \text{ nm}$) was measured to be 1.97×10^{-3} Einstein/min·L by ferrioxalate actinometry.²⁵ For the experiments in the presence of N_2 or N_2O , the reactor was purged with the corresponding gas for 20 min prior to and continuously during photoirradiation. Sample aliquots of 1 mL

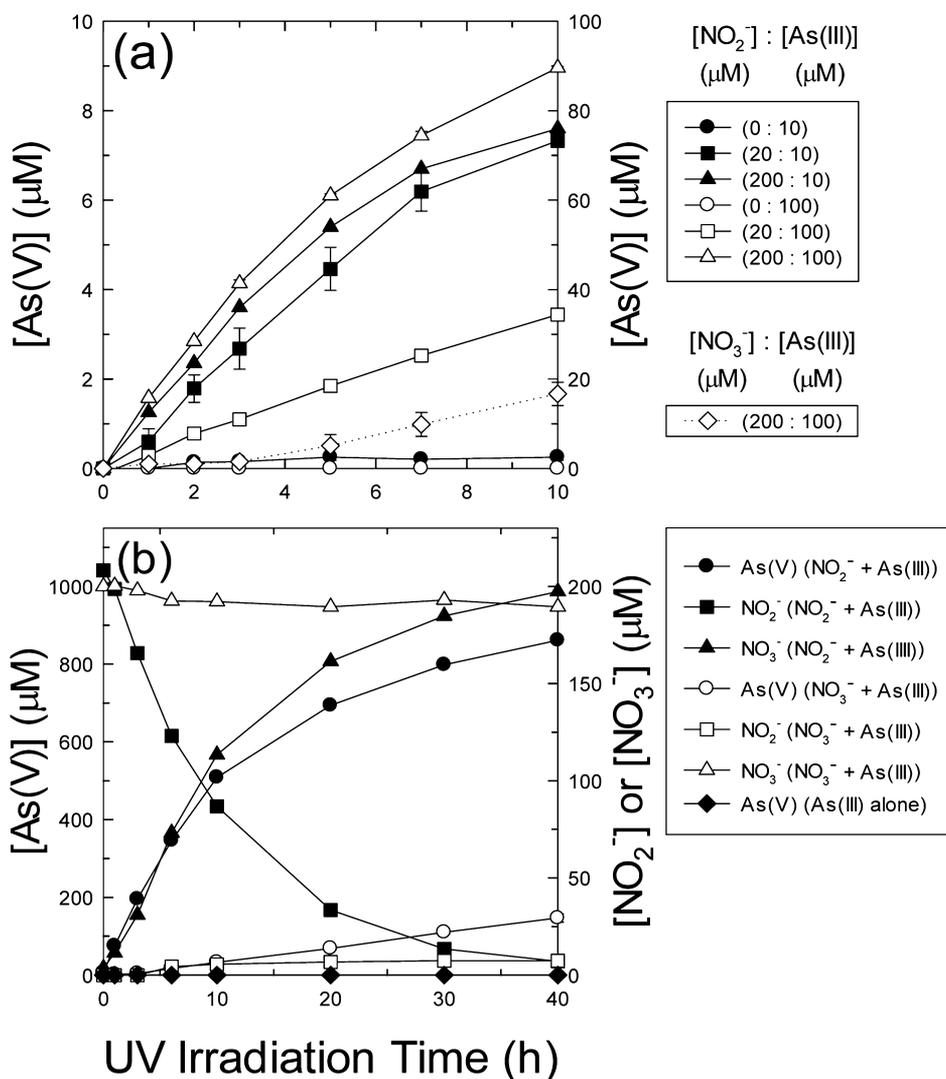
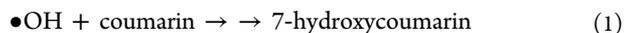


Figure 1. (a) Oxidative conversion of As(III) to As(V) during UV photolysis of NO_2^- (solid line) and NO_3^- (dotted line) at various initial concentrations (air equilibrated; $\text{pH}_i = 9.0$, $[\text{As(III)}]_0 = 10 \mu\text{M}$ (close symbol) or $100 \mu\text{M}$ (open symbol)) and (b) time profiles of NO_2^- decomposition, NO_3^- formation, and As(V) production under UV irradiation (air equilibrated; $\text{pH}_i = 10$; $[\text{As(III)}]_0 = 1000 \mu\text{M}$; $[\text{NO}_2^-]_0 = 200 \mu\text{M}$ or $[\text{NO}_3^-]_0 = 200 \mu\text{M}$).

were withdrawn using a 1-mL syringe from the UV-illuminated reactor at predetermined time intervals and were transferred to a 2-mL amber vial. The concentration of photogenerated As(V) was colorimetrically determined using a molybdenum blue method with a detection limit of $0.8 \mu\text{M}$ in which arsenomolybdate is reduced with ascorbic acid to form an intensively blue complex.²⁶ A solution of 0.1 mL of ascorbic acid and 0.2 mL of molybdate reagent solution was mixed with 4 mL sample solution (diluted 4-fold with deionized water) in a conical tube. After 2 h of color development, the concentration of As(V) was monitored at 870 nm ($\epsilon = 19\,550 \text{ M}^{-1}\text{cm}^{-1}$) using a UV-vis spectrophotometer (Libra S22, Biochrom). Quantitative analyses of NO_2^- and NO_3^- were performed along with that of As(V) using an ion chromatograph (IC, Dionex DX-120). The As(V) concentrations determined by IC matched those measured colorimetrically. The IC was equipped with a Dionex IonPac AS 23 ($4 \times 250 \text{ mm}$) column and a conductivity detector. The eluent was a binary mixture of 3.5 mM Na_2CO_3 and 1 mM NaHCO_3 solutions. In the experiment with $1 \mu\text{M}$ As(III), the quantitative analyses of NO_2^- and NO_3^- , As(V) were performed by using a Dionex ICS-2100 IC

(Dionex IonPac AS18 ($4 \times 250 \text{ mm}$) column and a conductivity detector, 39 mM KOH eluent). Coumarin (1 mM) was employed as a chemical probe of $\bullet\text{OH}$.²⁷



7-Hydroxycoumarin (reaction 1) was measured by monitoring the fluorescence emission at 460 nm under excitation at 332 nm using a spectrofluorometer (Shimadzu RF-5301).

The outdoor experiments under natural solar light were carried out in a flat circular quartz reactor (diameter 5.5 cm, volume 40 mL, magnetically stirred during reaction) placed on the roof of the Environmental Engineering building at POSTECH (Pohang, Korea: 36°N latitude). The photochemical reactions were performed under clear sky conditions between 8:30 AM and 6:30 PM (on March 11th, 2011) and in a temperature range from 5.5 to 9.4°C . The intensity of sunlight was recorded using a pyranometer (apogee, PYR-P) every minute, and the daily average varied from 63 to $69 \text{ mW}\cdot\text{cm}^{-2}$.

RESULTS AND DISCUSSION

Nitrite-Mediated Photooxidation of As(III). The photochemical experiments with different initial As(III) concentrations of 10, 100, and 1000 μM induced a significant production of As(V) (as a result of As(III) oxidation) when nitrites were copresent (Figure 1). Direct UV photooxidation of As(III) in the absence of nitrites was negligible (Figure 1), which supports the role of NO_2^- as a UV-photosensitizer for the formation of reactive oxidants. Figure 1b shows that a near complete oxidation of As(III) to As(V) is accompanied by a quantitative conversion of NO_2^- to NO_3^- , although the concentration of As(III) is 5-fold higher than that of NO_2^- . This implies that the photolysis of one nitrite leads to the oxidation of multiple arsenites. However, UV photolysis of NO_3^- is much less efficient in inducing the oxidation of As(III) (Figure 1a,b), and there is a lag phase of about 3 h prior to the noticeable production of As(V) (Figure 1a). Since the photolysis of nitrate should be much slower than that of nitrite, the concentration of in situ generated nitrite should be accumulated before it has a noticeable effect on the oxidation of As(III). During the UV photolysis of NO_3^- , the production of NO_2^- was maintained at a minimal level, even after the appearance of As(V). This is probably because NO_2^- is immediately reoxidized to NO_3^- as soon as it is formed. Therefore, a catalytic cycle of NO_2^- and NO_3^- was involved in the mechanism for NO_2^- -mediated photooxidation of As(III), which enables a continual supply of NO_2^- as a precursor of reactive oxidants.

Figure 2 shows the role of As(III) in the photochemical reduction–oxidation (redox) reaction of NO_2^- and NO_3^- . The

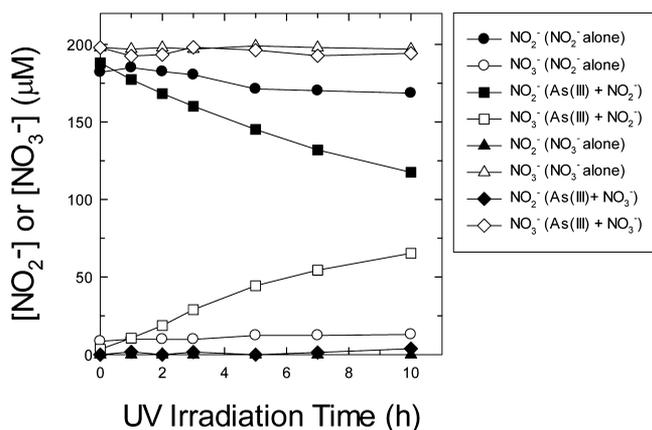


Figure 2. Photochemical conversion of NO_2^- (or NO_3^-) into NO_3^- (or NO_2^-) in the absence and presence of As(III) (air equilibrated; $\text{pH}_i = 9.0$; $[\text{As(III)}]_0 = 100 \mu\text{M}$; $[\text{NO}_2^-]_0 = 200 \mu\text{M}$; $[\text{NO}_3^-]_0 = 200 \mu\text{M}$).

photochemical reduction of NO_3^- to NO_2^- is negligibly slow regardless of the presence of As(III), which confirms the fact that the quantum yield for the photolytic decomposition of NO_3^- is lower than that of NO_2^- decomposition (e.g., $\Phi_{\text{OH},308}$ (quantum yield of $\bullet\text{OH}$ production at 308 nm) = $6.9(\pm 0.9)\%$ for NO_2^- photolysis versus $\Phi_{\text{OH},308} = 1.7(\pm 0.3)\%$ for NO_3^- photolysis).²⁸ However, UV-induced oxidation of NO_2^- to NO_3^- proceeded to a certain degree, which was significantly accelerated when As(III) was copresent. This can be ascribed to the fact that As(III) rapidly scavenges $\text{O}^{\bullet-}/\bullet\text{OH}$ as soon as it is formed (reaction H1), hindering the recombination between NO^{\bullet} and $\text{O}^{\bullet-}$ (in reaction A2a) and facilitating the further oxidation to NO_3^- .²⁹

pH Effect and Nitrite Regeneration. Figure 3a compares the time profiles of As(V) production in the presence of NO_2^-

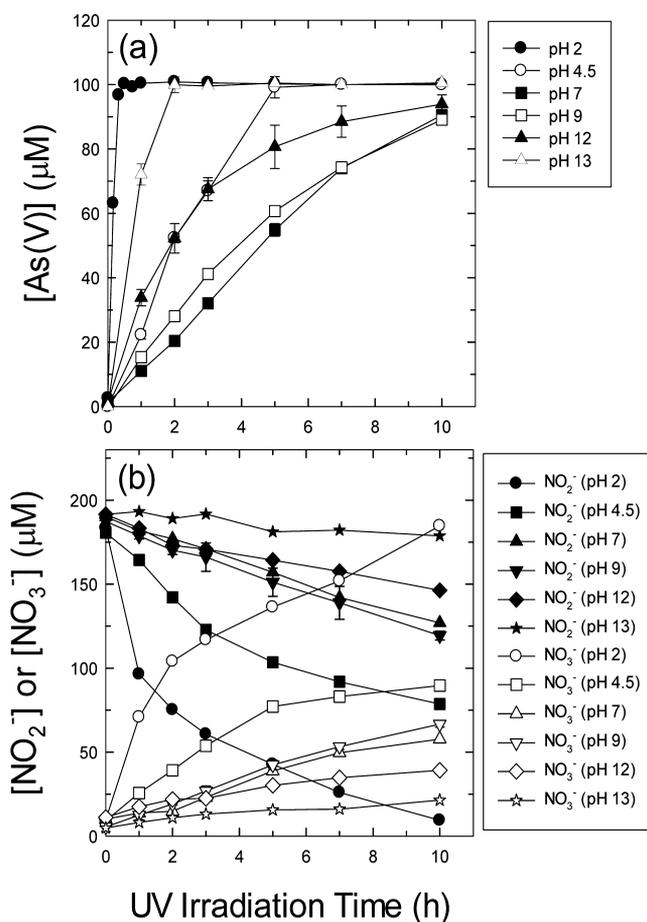


Figure 3. (a) Photosensitized oxidation of As(III) (i.e., stoichiometric production of As(V)) and (b) the concurrent conversion of NO_2^- into NO_3^- at various pH conditions (air equilibrated; $[\text{As(III)}]_0 = 100 \mu\text{M}$; $[\text{NO}_2^-]_0 = 200 \mu\text{M}$). The pH was changed during the reaction (2 \rightarrow 2.07, 4.5 \rightarrow 4.15, 7 \rightarrow 6.31, 9 \rightarrow 6.65, 12 \rightarrow 10.67, 13 \rightarrow 12.82).

under varying pH conditions. Either acidic or alkaline pH favored the photochemical oxidation of As(III), whereas NO_2^- photolysis at neutral pH led to relatively slow production of As(V). The rapid As(III) oxidation at acidic pH is ascribed to the increased concentration of nitrous acid (HNO_2 , $\text{p}K_a = 3.2$), which is more effectively photolyzed to produce $\bullet\text{OH}$ than its deprotonated counterpart, NO_2^- (e.g., $\Phi_{\text{OH},300} = 36.2(\pm 4.7)\%$ for HNO_2 photolysis versus $\Phi_{\text{OH},300} = 6.7(\pm 0.9)\%$ for NO_2^- photolysis).²¹ The simultaneous monitoring of the photolytic removal of NO_2^- and the accompanying generation of NO_3^- shows that the efficiency of the oxidative conversion of NO_2^- to NO_3^- gradually decreases with increasing pH (Figure 3b). Under acidic and neutral ($\text{pH} \leq 7$) condition, both photochemical conversions of ($\text{NO}_2^- \rightarrow \text{NO}_3^-$) and (As(III) \rightarrow As(V)) increase with lowering pH, which indicates that the photochemical dissociation of HNO_2 (or NO_2^-) is accompanied by the concurrent production of $\bullet\text{OH}$ and NO_3^- (reaction B1). However, at alkaline pH (≥ 9), the conversion of NO_2^- to NO_3^- was significantly retarded whereas the oxidation of As(III) was accelerated with increasing pH. In addition, it should be noted that the oxidative conversions of (As(III) \rightarrow As(V)) and ($\text{NO}_2^- \rightarrow \text{NO}_3^-$) were not

stoichiometrically balanced: the ratio of the As(V) production to NO_2^- removal ($R = \Delta[\text{As(V)}]/-\Delta[\text{NO}_2^-]$) increased from 0.57 at pH_i 2 to 7.82 at pH_i 13 (0.57, 0.98, 1.34, 2.07, and 7.82 at pH_i 2, 4.5, 7, 12, and 13, respectively). The fact that $R > 1$ at alkaline pH condition implies that NO_2^- has some catalytic role in the photooxidation of As(III) and that the photochemical regeneration of NO_2^- from NO_3^- should be highly enhanced at alkaline pH. Note that the literature rate data for the photolytic conversion of NO_3^- to NO_2^- is indeed higher at higher pH (e.g., r_{300} (the rate of NO_2^- formation during the photolysis of 1 M NO_3^- with the light above 300 nm) = $26.5 \mu\text{M min}^{-1}$ at pH 13 vs $r_{300} = 5 \mu\text{M min}^{-1}$ at pH 5).³⁰

In order to further assess the pH dependence of the photolysis of NO_3^- to NO_2^- , Figure 4 compares the efficiency

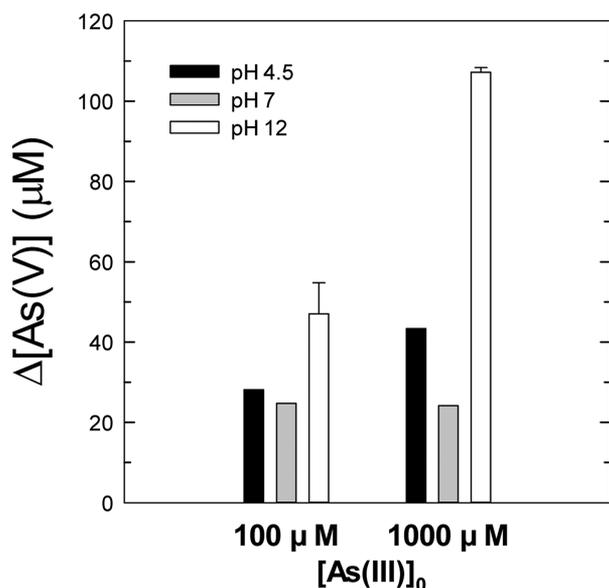


Figure 4. Effect of initial pH on the efficiency of NO_3^- -mediated photooxidation of As(III) (air equilibrated; $[\text{NO}_3^-]_0 = 200 \mu\text{M}$). $\Delta[\text{As(V)}]$ was measured after 10 h irradiation. With $100 \mu\text{M}$ As(III), the pH changed from 4.5, 7, 12 to 4.3, 7.0, 10.9; with $1000 \mu\text{M}$ As(III), from 4.5, 7, 12 to 4.53, 7.8, and 11.1, respectively.

of photooxidation of As(III) in aqueous solution of NO_3^- at initial pH of 4.5, 7, and 12. Whereas As(III) photooxidation with NO_2^- was slightly faster at pH 4.5 than at pH 12 (see Figure 3a), the efficiency of photooxidation of As(III) with NO_3^- was significantly higher at pH 12 than at pH 4.5. This implies that the UV-induced conversion of NO_3^- to NO_2^- is more preferred at higher pH, subsequently leading to the enhanced photooxidation of As(III). The kinetic enhancement at alkaline pH was more pronounced with a higher concentration of As(III) under the same concentration of nitrate (Figure 4). This is likely attributed to the role of As(III) as an effective scavenger of the solvent-caged radical pair (i.e., NO_2^\bullet and $\text{O}^{\bullet-}$ in reaction C2a in Table 1) through reaction H3, which subsequently increases the quantum yields for the production of NO_2^- and $\bullet\text{OH}$.³¹ At neutral pH condition, both, the fraction of the photoactive form of nitrite (e.g., HNO_2) and the photoefficiency for NO_3^- to NO_2^- conversion, is low. As a result, the As(III) photooxidation in the presence of NO_3^- or NO_2^- is the lowest at pH 7 (see Figure 3a and Figure 4).

Nature of Involved Photooxidants. The efficiency of photogeneration of $\bullet\text{OH}$ from the photolysis of NO_2^- was

measured by using coumarin as a chemical trap of $\bullet\text{OH}$. The production of 7-hydroxycoumarin (through reaction 1) was monitored in the UV-irradiated solution of NO_2^- in the presence of various dissolved gases including air, O_2 , N_2 , and N_2O (Figure 5a). The significant formation of 7-hydroxycou-

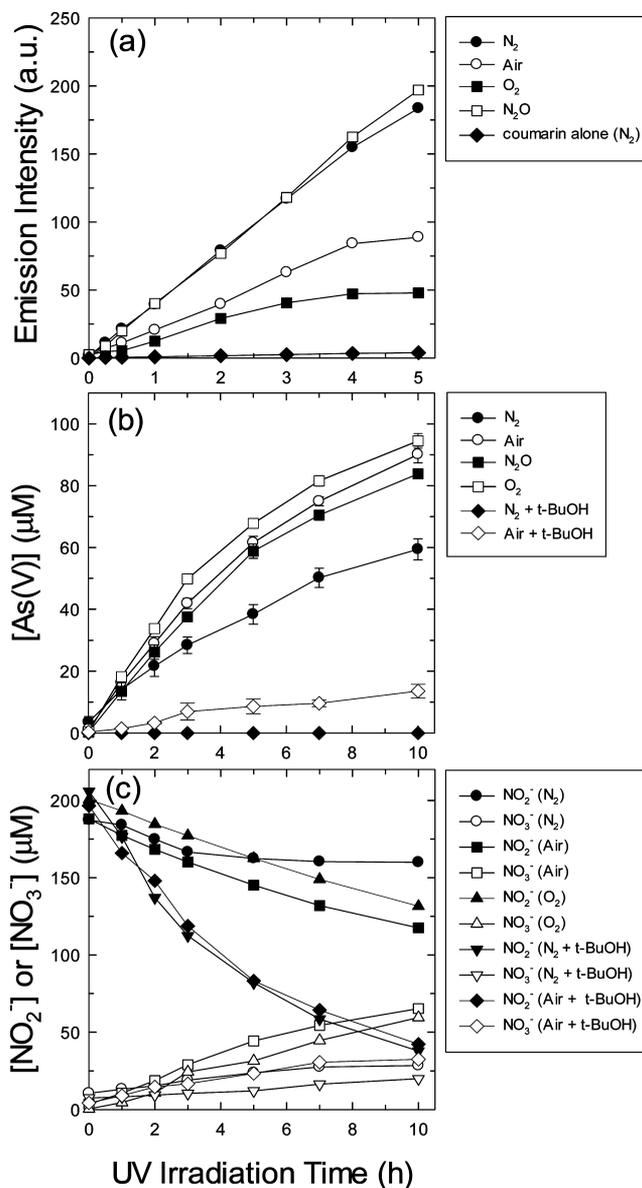
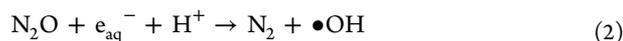


Figure 5. (a) Production of 7-hydroxycoumarin (coumarin- $\bullet\text{OH}$ adduct) (pH_i = 9; $[\text{NO}_2^-]_0 = 200 \mu\text{M}$; [coumarin] = 1 mM), (b) oxidative conversion of As(III) into As(V) during NO_2^- photolysis, (c) photochemical conversion of NO_2^- into NO_3^- in the presence of various gases (N_2 , air, O_2 , and N_2O) and/or *t*-BuOH as a scavenger of $\bullet\text{OH}$ (pH_i = 9; $[\text{As(III)}]_0 = 100 \mu\text{M}$; $[\text{NO}_2^-]_0 = 200 \mu\text{M}$; [*t*-BuOH] = 0.5 M).

marin under irradiation indicates the UV-photosensitizing activity of NO_2^- for $\bullet\text{OH}$ generation and the efficiency decreases in order of $\text{N}_2\text{O} \approx \text{N}_2 > \text{air} > \text{O}_2$ (Figure 5a). The oxic condition where O_2 acts as an electron scavenger inhibits the recombination of the solvent-cage pair of $\text{NO}_2^\bullet/e_{\text{aq}}^-$ (reaction A2b in Table 1) with facilitating the formation of NO_2^\bullet and hydrated electron (e_{aq}^-) (rather than NO^\bullet and $\text{O}^{\bullet-}/\bullet\text{OH}$ via reaction A2a) as the primary photolysis products of

NO_2^- . As a result, the efficiency of $\bullet\text{OH}$ production was significantly retarded in the presence of dissolved O_2 under air-equilibrated or O_2 -saturated conditions. However, the use of N_2O as an alternative electron acceptor, which might behave similarly as O_2 in promoting the photodissociation of NO_2^- into NO_2^\bullet and e_{aq}^- , was as effective as the N_2 -saturated case for the production of $\bullet\text{OH}$. This might be ascribed to that N_2O reacts with e_{aq}^- to form $\bullet\text{OH}$ via an alternative pathway (reaction 2).³²



In contrast to the inhibitory effect of O_2 on the production of $\bullet\text{OH}$ (Figure 5a), the photooxidation of As(III) in the presence of NO_2^- was higher in the air-equilibrated or O_2 -saturated solution than that in the N_2 -saturated solution (Figure 5b). This implies the involvement of alternative oxidants (other than $\bullet\text{OH}$) of As(III), which likely includes $\text{O}_2^{\bullet-}$ and NO_2^\bullet with moderate oxidizing power (i.e., $E^0(\text{O}_2^{\bullet-}/\text{HO}_2^-) = 0.50 \text{ V}_{\text{NHE}}$ ²⁰ at pH 9; $E^0(\text{NO}_2^\bullet/\text{NO}_2^-) = 1.03 \text{ V}_{\text{NHE}}$ ³³ versus $E^0(\text{As(V)}/\text{As(III)}) = -0.13 \text{ V}_{\text{NHE}}$ ²⁰ at pH 9). The presence of O_2 causes the rapid oxidation of NO^\bullet to NO_2^\bullet (reaction F1 in Table 1) and the production of $\text{O}_2^{\bullet-}$ from the reaction with e_{aq}^- (reaction E1). The comparison of the effect of *t*-BuOH (an $\bullet\text{OH}$ scavenger via reaction G3) addition on the As(III) photooxidation reveals the nature of photooxidants (Figure 5b). Under N_2 -saturated conditions, the photooxidation of As(III) was completely inhibited, which indicates that $\bullet\text{OH}$ is the sole oxidant in this case. However, in the air-equilibrated condition, the addition of *t*-BuOH did not completely inhibit the photooxidation, which implies the possible contribution of $\text{O}_2^{\bullet-}$ to As(III) oxidation.^{9,10}

In agreement of the above discussion, the photolysis of NO_2^- is sensitively affected by the presence of interfering components. Figure 5c shows that the photolysis of NO_2^- and the concurrent production of NO_3^- is clearly faster in the air-equilibrated condition than in the N_2 -saturated condition. The explanation is similar to the effect of O_2 on the production of $\bullet\text{OH}$ (Figure 5a): O_2 acting as an electron scavenger inhibits the recombination of the solvent-cage pair of $\text{NO}_2^\bullet/e_{\text{aq}}^-$ (reaction A2b in Table 1) with facilitating the decomposition of NO_2^- . In the presence of *t*-BuOH, the photolysis of NO_2^- was markedly accelerated in both air-equilibrated and N_2 -saturated conditions probably because an alternative pathway is facilitated: *t*-BuOH as a scavenger of $\bullet\text{OH}/\text{O}^{\bullet-}$ inhibits the recombination of the solvent-cage pair of $\text{NO}^\bullet/\text{O}^{\bullet-}$ (reaction A2a in Table 1) with facilitating the decomposition of NO_2^- . However, the presence of *t*-BuOH greatly inhibited the production of NO_3^- (Figure 5c) along with a drastic inhibition of As(III) photooxidation (Figure 5b). This implies that the photogenerated NO^\bullet might react with *t*-BuOH or *t*-BuOH-derived intermediates to form nitrogenous compounds.

Under the N_2O -saturated condition, both efficiency of $\bullet\text{OH}$ production and As(III) oxidation were highly enhanced. As for the production of $\bullet\text{OH}$, the N_2O -saturated condition was as effective as the N_2 -saturated condition. However, the former was more efficient than the latter for the As(III) photooxidation, which implies the presence of additional oxidants in the N_2O -saturated solution. Since the presence of N_2O as an electron acceptor preferentially photodecomposes NO_2^- into NO_2^\bullet and e_{aq}^- (as mentioned above), NO_2^\bullet may act as an additional oxidant of As(III) (reaction H3).

Environmental Implications. Sunlight driven oxidation in the As(III)/ NO_2^- solution was performed to assess the implication of the studied photochemical process for the fate of a natural water matrix contaminated with As(III). The nitrite has a significant spectral overlap with the sunlight (see the UV-vis absorption spectrum of NO_2^- in Figure 6a). Figure 6b

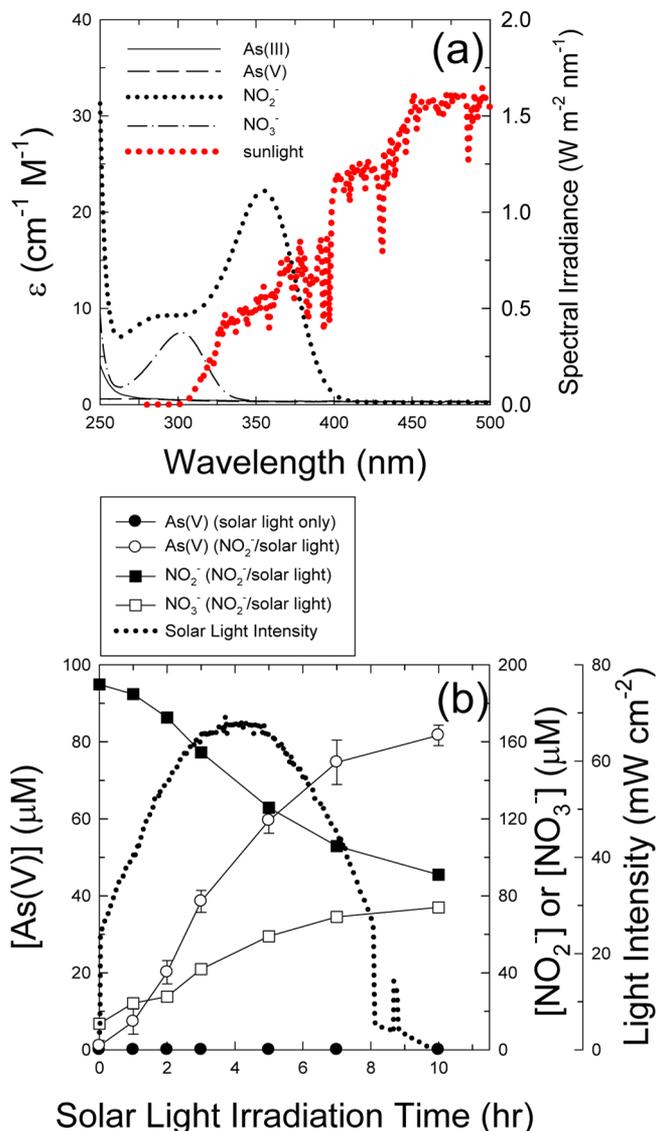


Figure 6. (a) UV-vis absorption spectra of As(III), As(V), NO_2^- , and NO_3^- in aqueous solution (pH not adjusted, all species at 50 mM) and AM 1.5 solar spectrum (ASTM G173-03, Air Mass 1.5 Global Tilt Standard) and (b) Photosensitized oxidation of As(III) during photolysis of NO_2^- into NO_3^- under solar light irradiation (air equilibrated; $\text{pH}_i = 4.5$; $[\text{As(III)}]_0 = 100 \mu\text{M}$; $[\text{NO}_2^-]_0 = 200 \mu\text{M}$).

demonstrates that significant oxidative conversion of As(III) to As(V) occurred, along with the production of NO_3^- during the solar photolysis of NO_2^- , while no detectable production of As(V) was observed in the absence of NO_2^- . The solar photolysis of nitrite alone and the accompanying production of nitrate were the same as those in the (As(III) + NO_2^-) system (data not shown), which indicates that the photolysis characteristic of nitrite is not influenced by the presence of As(III). The effects of natural organic matter on this photochemical transformation were also investigated. Humic

acid (HA) was added as a proxy of natural organic matters at a concentration of 3 mg/L (typically, 2–10 mg/L in groundwater³⁴), and the results are shown in Figure 7. The addition of

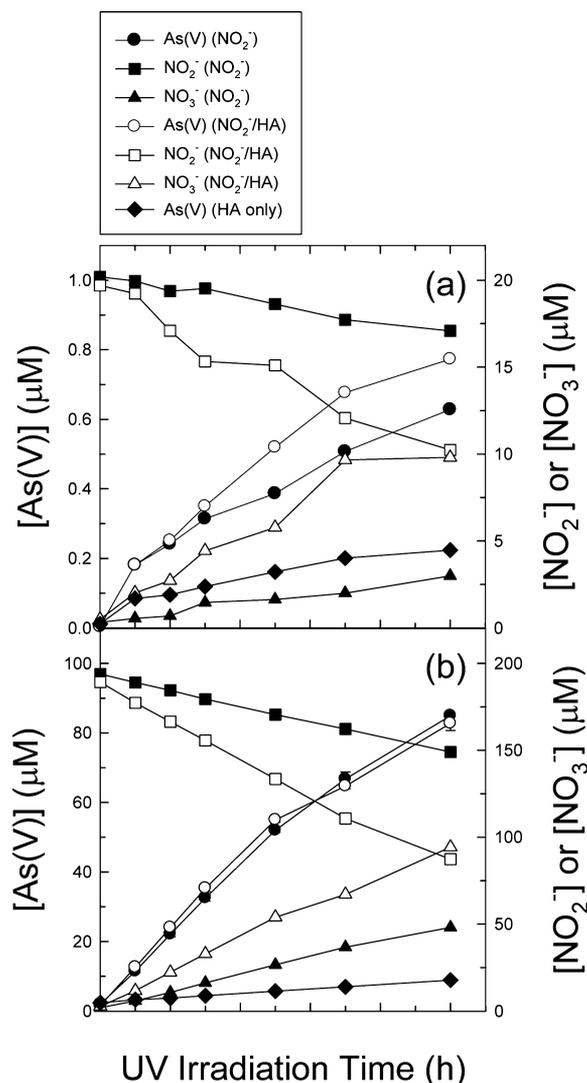


Figure 7. Photosensitized production of As(V) from As(III) and the concurrent conversion of NO_2^- into NO_3^- in the air-equilibrated solution in the absence or presence of humic acid (HA). (a) $[\text{HA}] = 3 \text{ mg/L}$, $[\text{As(III)}]_0 = 1 \text{ } \mu\text{M}$, $[\text{NO}_2^-]_0 = 20 \text{ } \mu\text{M}$; $\text{pH}_i = 7.0$ and (b) $[\text{HA}] = 3 \text{ mg/L}$, $[\text{As(III)}]_0 = 100 \text{ } \mu\text{M}$, $[\text{NO}_2^-]_0 = 200 \text{ } \mu\text{M}$; $\text{pH}_i = 7.0$.

HA little changed or even moderately enhanced the conversion rates of As(III) and NO_2^- . This seems to be caused by the HA-sensitized production of superoxide.³⁵ The control photolysis experiments of (As(III) + HA) mixture in the absence of NO_2^- showed a small (but not negligible) production of As(V), which supports the sensitizing role of HA. The fact that the presence of HA did not retard the photooxidation rate at all implies that As(III) is highly susceptible to oxidation by photooxidants (e.g., $\bullet\text{OH}$) derived from the photolysis NO_2^- even in the presence of natural organic matters that may react with $\bullet\text{OH}$. In addition, the observation that the stoichiometric conversion of NO_2^- to NO_3^- was achieved even in the presence of humic acid (Figure 7) indicates that the production of nitrated organic byproducts should be negligible in the UV/As(III)/ NO_2^- process. The levels of NO_2^- and NO_3^- are typically in the range of 10–163 and 23–779 μM , respectively, in arsenic

contaminated ground and surface water matrixes.²⁴ The photochemical reactions of NO_3^- are accompanied with the production of reactive oxidizing species (e.g., $\bullet\text{OH}$) and NO_2^- even in the absence of NO_2^- . Therefore, the typical surface and ground waters contaminated with As(III) and $\text{NO}_2^-/\text{NO}_3^-$ can be phototransformed with converting As(III) to As(V) under sunlight irradiation.

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Notes

The authors declare no competing financial interest.

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