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Journal of Photochemistry and Photobiology A: Chemistry 157 (2003) 33–38

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Laser photolysis of pyrenesulfonate and pyrenetetrasulfonate via two-photon ionization in aqueous and reverse micellar solutions

Yoshihiro Mori*, Hiroyuki Shinoda, Taku Nakano, Taiji Kitagawa

Department of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, Sugitani, Toyama 9300194, Japan

Received 27 September 2002; received in revised form 18 December 2002; accepted 26 December 2002

Abstract

We investigated the laser photolysis of tetrasodium 1,3,6,8-pyrene-tetrasulfonate (Na_4PS_4) and sodium 1-pyrenesulfonate (NaPS) in aqueous and reverse micellar solutions. The photoproducts as well as their yields were found to strongly depend on the reaction parameters such as pH, dissolved gases and the size of water pool. The primary reaction in aqueous solution was commonly presented by laser-induced formation of the cation radicals followed by hydroxylation of them. In the case of PS_4^{4-}, pyranine was efficiently and highly selectively formed, possibly via desulfonation of the cation radical, $P^{\bullet +}S_4^{4-}$, followed by the hydroxylation. On the other hand, from PS^-, hydroxypyrenesulfonate (PSOH) was initially formed in alkaline solution and desulfonation occurred secondarily, leading to the formation of hydoxypyrene. These photoreactions were markedly suppressed within a small water pool of the reverse micelle. As the size of water pool increased similar photochemical reactions occurred depending on the dissolved gases. The observed micellar effects could be explained based on the pH of water pool and the nature of the cation radicals in it.

Keywords: Laser photolysis; Reverse micelle; Hydroxylation; Desulfonation; Cation radical; Pyrenesulfonates

1. Introduction

Sodium 1-pyrenesulfonate (NaPS) and tetrasodium 1,3,6,8-pyrene-tetrasulfonate (Na_4PS_4) are well known as prominent molecules to probe a micellar microenvironment based on the fluorescence spectroscopy [1,2]. Recently, we investigated the formation and decay processes of transient species other than the fluorescent excited states, involving cation and anion radicals, solvated electrons and triplets, that were produced by laser flash photolysis of PS^- and PS_4^{4-} solubilized in reverse micelles with different sizes and polarities [3]. Their temporal changes were monitored using the transient absorption (TA) spectroscopy. The results provided valuable information on the nature of the water pool and the distribution of the probe molecules within the micelle. These experiments were carried out under a considerably strong laser irradiation because the two-photon process was required to form the valuable transient species such as cation radicals. Such a high laser field induced some destructive photochemical reactions that caused the loss of the starting molecules. To avoid their perturbations in the measurements of TA spectra the sample solution was frequently exchanged for a fresh one [4]. We preliminarily reported that these photochemical reactions might depend on the micellar size as well as the dissolved gases [3,5]. The aim of the present study was to analyze the final products produced in these laser-induced photochemical reactions and elucidate their formation mechanism in aqueous and reverse micellar solutions.

The photochemistry of arenesulfonates under steady-state irradiation conditions was extensively investigated decades ago. Izawa et al. studied the photolysis of sodium arenesulfonates involving anthracene-9- and naphthalene-1-sulfonates in alkaline aqueous solution with a high-pressure Hg lamp [6,7]. They concluded that the photoelimination of SO_3^- group (desulfonation) dominantly occurred in the photolysis of the two sulfonates, yielding anthracene and binaphthyl, respectively. Along with the desulfonation the photoelimination of SO_2 (desulfonylation) was also observed with a smaller branching ratio, leading to the formation of anthraquinone, and naphthol and naphthoquinone, respectively. The photolysis of mesitylenesulfonate in aqueous ethanol solution was found to produce mesitylene as a main product via desulfonation and mesitol as a minor product via desulfonylation [7]. They proved experimentally that the desulfonation and desulfonylation proceeded via T_1 (π–π^*) and S_1 (n–π^*) excited states, respectively

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* Corresponding author. Fax: +81-76-4434-5061.
E-mail address: moriyh@ms.toyama-mpu.ac.jp (Y. Mori).

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doi:10.1016/S1010-6030(03)00075-3

[6,8]. Ogata et al. found that benzenesulfonic acid produced benzene and biphenyl via photochemical desulfonation [9]. Different photolytic processes were observed in the photolysis of sodium 1,4-naphthoquinone-2-sulfonate in water [10]. One of them was the photoreduction process to form 1,4-naphthalenediol-2-sulfonate. The other was the nucleophilic attack of OH^- to the C–H bond in the n–π^* excited state where sodium 3-hydroxy- and 5-hydroxy-1,4-naphthoquinone-2-sulfonates were formed. Similar reactions were found to occur in the photolysis of anthraquinone sulfonates [11,12]. The latter (hydroxylation) process was reported in the photochemical reaction of 1-nitropyrene, known as one of the potent mutagens [13,14]. The reaction products were identified as 2-hydroxy- and 9-hydroxy-1-nitropyrenes under different reaction conditions. The latter product was found to show much lower mutagenic potency than 1-nitoropyrene [14].

2. Experimental

2.1. Materials and sample preparation

Bis(2-ethylhexyl) sodium sulfosuccinate (AOT (Tokyo Kasei)) was purified following the method reported by Politi et al. [15]. Pyrene derivatives (Na_4PS_4 and NaPS) were purchased from Molecular Probe and used as received. The other reagents and solvents commercially available were used without further purification. AOT reverse micellar solutions were prepared by mixing a constant volume of water containing $2–3 \times 10^{-5}$ M of pyrene derivatives with 0.1 M AOT/isooctane solution. Two micellar solutions with different molar ratios of $[H_2O]/[AOT]$ ($=W$) equal to 10 or 50 were used in the experiments. The sample solution was deaerated via several freeze-pump-thaw cycles and then displaced by Ar, O_2 or N_2O gas. The aqueous solution displaced by an appropriate gas with similar procedures was weakly acidic (pH 5.5–6.0) because CO_2 gas remained dissolved. When the dissolved air was removed by bubbling nitrogen gas the aqueous solution was neutral.

2.2. Photochemistry

The photochemical reaction was carried out by irradiating a constant volume (ca. 3.5 cm^3) of sample solution with the third harmonics of Nd: YAG laser at 355 nm. A quartz cell (1 cm × 1 cm) was used for the reaction cell. Laser irradiation conditions were as follows: energy; about 5 mJ/pulse, repetition frequency; 0.2–0.4 Hz, effective area of laser irradiation; ca. 0.3 cm^2. Under these conditions the effective irradiation volume was estimated to be less than 5% of the whole sample solution. This situation was similar in the measurements of transient absorption spectra. The solution was sufficiently stirred and thereby a fresh volume was available for each pulse of irradiation. Photoproducts were monitored with UV-Vis absorption spectroscopy as a function of the number of laser shots. The observed spectra were considered to reflect the final products (not intermediates) because the interval required for measurement of UV-Vis spectra was in the order of minutes. The method for measurements of the absorption spectra and the decay behaviors of laser-induced transient species was described previously [5], in which the transient photoproducts that formed in the temporal range from 0.1 to 100 μs were detected.

3. Results and discussion

3.1. Na_4PS_4

Fig. 1 shows the spectral change as a function of the number of laser shots (N_s), where the neutral aqueous solution containing 2×10^{-5} M Na_4PS_4 was irradiated as gently bubbling nitrogen gas at pH 7. Two new peaks appeared at 405 and 455 nm by laser irradiation. Their intensities increased with N_s and then the original spectra due to Na_4PS_4 smeared after 900 shots. This reaction was greatly dependent on pH. As shown in Fig. 2, only the 455 nm peak was detected in an alkaline solution (0.1 M NaOH) while the 405 nm peak dominantly grew in a weakly acidic solution (pH 5.5). The reaction occurred more efficiently in alkaline solution than in neutral and acidic solutions. When the alkaline solution after irradiation with 720 laser shots was acidified, the spectrum was immediately changed: the 455 nm peak disappeared and instead, the 405 nm peak appeared. The pH-dependent spectral changes agreed well with those in pyranine demonstrated in the inset of Fig. 2. In addition to these results, the existence of definite isobestic points, shown in Fig. 1, suggests that pyranine was the only photoproduct detectable in the spectral range investigated during the laser photolysis of $PS_4{}^{4-}$.

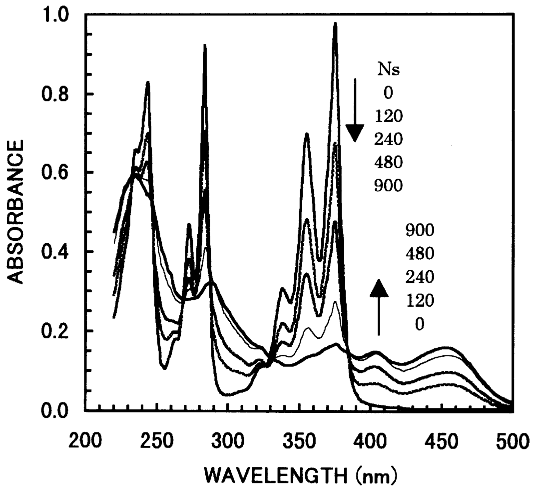

Fig. 1. Spectral change in the laser photolysis of $PS_4{}^{4-}$ as a function of the number of laser shots (N_s). The photoreaction was carried out in neutral aqueous solution under N_2.

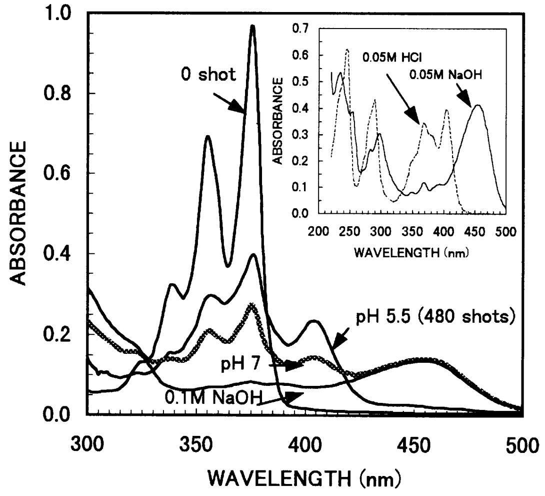

Fig. 2. Spectra of photoproducts produced in the photolysis of PS_4^{4-} under N_2 in aqueous solutions at different pH. The spectra were observed after irradiation with 480 laser shots. The inset shows the pH dependence of UV-Vis spectra of pyranine in aqueous solution.

Several quenching experiments were performed in this photochemical reaction to elucidate the formation mechanism of pyranine. Similar spectral changes with an increase in N_s were observed under O_2 and N_2O although the reaction proceeded most efficiently under N_2O. On the other hand, the added iodide anion (I^-) markedly quenched the formation of pyranine. For example, in neutral solution containing 7×10^{-4} M of KI, neither the 405 nor 455 nm peak was detected and the peak intensity at 375 nm due to PS_4^{4-} decreased only slightly (a few percent) even after irradiation with 600 laser shots. These results suggest that pyranine is formed via the cation radical of PS_4^{4-} ($(PS_4^{4-})^{\bullet +}$) because the cation radical, which can be transiently produced by the two-photon ionization of PS_4^{4-}, is efficiently quenched by I^- but is little affected by O_2 and N_2O [5]. One-photon process via triplet or singlet excited states did not significantly participate in the formation of pyranine because the quenching effect by O_2 molecules was negligibly small. Furthermore, the formation of pyranine was greatly inhibited in the presence of SO_3^{2-} anion. This effect was also consistent with the formation mechanism of pyranine via the cation radical considering the unusual quenching behaviors of this anion on the cation radical of PS_4^{4-} [5]. The strong inhibition by SO_3^{2-} anion suggests that the hydroxylation may proceed via desulfonation from the cation radical. In fact, the recombination between SO_3^{2-} anion and the reaction intermediate formed via desulfonation from the cation radical allows the formation of an inactive molecule, maybe the starting one (PS_4^{4-}).

This photoreaction was investigated in AOT reverse micellar solutions with $W = 50$ and 10. Under any gaseous environments the reaction hardly occurred in a small water pool of the $W = 10$ micelle as shown in Fig. 3A. In a large water pool of the $W = 50$ micelle, however, a significant amount of PS_4^{4-} molecules were photochemically transformed into pyranine. The efficiency under N_2O was found to be much larger than the efficiencies under Ar (N_2) and O_2. These trends were consistent with the dependence of the formation yield of $(PS_4^{4-})^{\bullet +}$ on W and gaseous quenchers reported previously [3]. Fig. 4 demonstrated its dependence in an explicit way, where the contribution from the triplet–triplet (T–T) absorption was eliminated based on the established spectra of T–T absorption in PS_4^{4-} [3,5]. Therefore, the present curves exhibited decay behaviors purely attributable to the cation radicals. In a previous study [3], we interpreted these decay behaviors in terms of the existence of two types of the cation radical species: the intramolecular charge-separated cation radical ($P^{\bullet +}S_3^{3-} \rightarrow S^{2-}$) and the charge-separated one ($P^{\bullet +}S_4^{4-}$). Both contain the cation radical from the pyrenyl frame ($P^{\bullet +}$), resulting in similar TA spectra having an absorption peak at 505 nm. The decay behaviors, however, were quite different. The former was detected only within a larger water pool with a moderate ionic strength. The lifetime of this cation radical steeply decreased with the decrease in W, i.e. the size of water pool. The latter slowly decayed and its contribution markedly

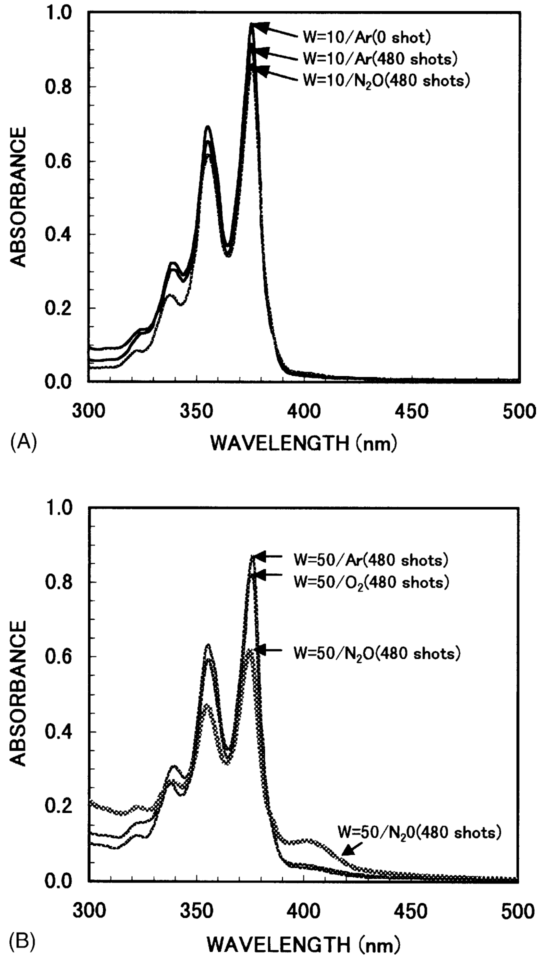

Fig. 3. Photolysis of PS_4^{4-} in reverse micellar solutions with $W = 10$ under Ar and N_2O (top; A) and $W = 50$ under Ar, O_2 and N_2O (bottom; B). All the spectra were observed after irradiation with 480 laser shots.

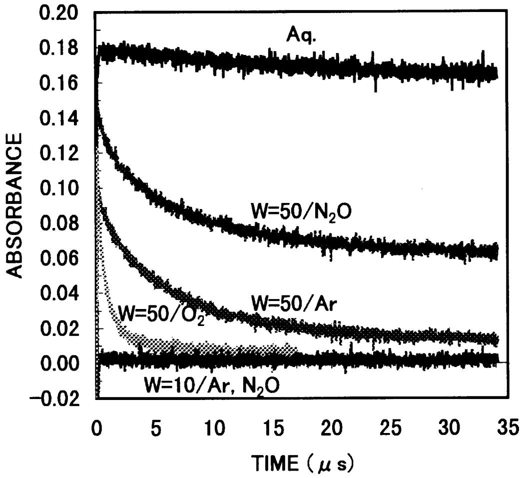

Fig. 4. Decay curves of the cation radical from PS_4^{4-} observed at 505 nm. The cation radicals were produced by laser irradiation at 355 nm in aqueous and reverse micellar solutions with $W = 10$ and 50 under Ar, O_2 and N_2O. The observed decay curves at 505 nm were corrected by subtracting the contribution from the T–T absorption.

increased under N_2O. The latter cation radical could be easily annihilated through the recombination with the (hydrated) electron since the two transient species (cation radical and hydrated electron) were forced to coexist within the same water pool. N_2O molecules can prevent this recombination process because they are very effective quenchers of electrons [16]. Nevertheless, the water pool in a micelle with $W = 10$ was so small that the recombination dominantly occurred and then no cation radicals were detected even under N_2O. In a large water pool of the $W = 50$ micelle, however, the (hydrated) electron could be efficiently captured by solubilized N_2O molecules prior to the recombination with the parent $P^{\bullet +}S_4^{4-}$, resulting in a marked enhancement of the slowly decaying component ($P^{\bullet +}S_4^{4-}$) under N_2O in Fig. 4. It is shown in Fig. 3B that the yield of pyranine under N_2O, measured from the absorbance at 405 nm, is about one order of magnitude larger than the yields obtained under Ar and O_2. Such a large difference could not be explained by the observed small difference in the initial yields of the cation radical, i.e. the absorbance difference at $t = 0$. The large increment in the yield of $P^{\bullet +}S_4^{4-}$ (slowly decaying component) under N_2O was consistent with these photochemical results. Therefore, it is very likely that pyranine is formed from the charge-separated cation radical, $P^{\bullet +}S_4^{4-}$.

From these results the following reaction scheme is suggested:

$$PS_4^{4-} + 2h\nu \rightarrow P^{\bullet +}S_4^{4-} + (e^-)_{hyd} \quad \text{and}$$
$$P^{\bullet +}S_3^{3-} \rightarrow S^{2-} \tag{1}$$

$$P^{\bullet +}S_4^{4-} \rightarrow (P^{\bullet +}S_3^{3-})^{\bullet} + SO_3^{\bullet -} \tag{2}$$

$$(P^{\bullet +}S_3^{3-})^{\bullet} + OH^- \rightarrow PS_3^{3-}OH \tag{3}$$

$$PS_3^{3-}OH \leftrightarrow PS_3^{3-}O^- + H^+ \tag{4}$$

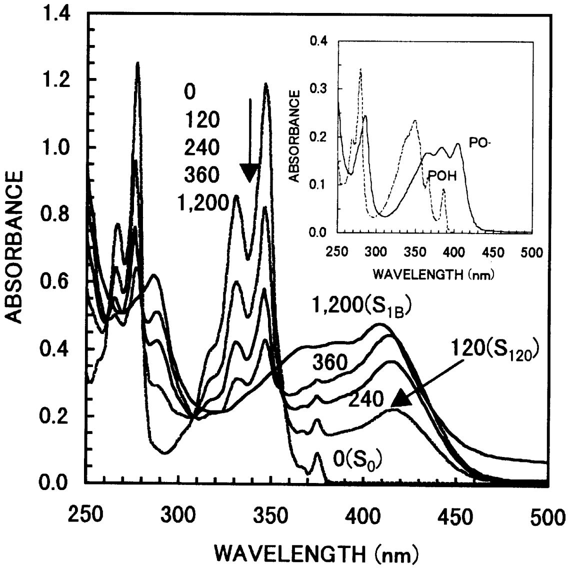

Fig. 5. Spectral change in laser photolysis of PS^- in 0.1 M NaOH under N_2 as a function of N_s ($N_s = 0$–1200, [NaPS] $= 3 \times 10^{-5}$ M). The inserted spectra show the spectra of hydroxypyrene and its anionic form.

3.2. NaPS

Photolysis of NaPS in 0.1 M NaOH solution was investigated under N_2 gas. Fig. 5 shows the change in the UV-Vis spectra as a function of N_s. In the initial photoreaction ($N_s < 300$; decomposition ratio < 0.5) the photoproduct having the absorption maximum at 416 nm was detected. With an increase in N_s this peak shifted to a shorter wavelength. Finally, after irradiation with 1200 laser shots the solution was changed to a yellowish color and showed a thoroughly new spectrum (S_{1B}), while residual PS^- molecules were undetectable in the UV-Vis spectra. When this solution was acidified by adding a few droplets of concentrated HCl solution the spectral shape was changed from S_{1B} to S_{1A} as shown in Fig. 6. The acidified solution was extracted with $CHCl_3$ solvent. The spectra of aqueous (acidic) and organic phases were given as S_{2A} and S_{2O}, respectively. A significant amount of the products (about 1/4) were transferred from the aqueous phase into the organic one. When the acid extract was re-alkalinized the spectrum S_{2A} was markedly changed into S_{2B}. S_{2B} was clearly different from S_{1B}. The absorption maximum in S_{2B} was found to be 416 nm in agreement with the absorption spectra observed at the initial stage. In fact, the spectrum after irradiation with 120 laser shots (S_{120} in Fig. 5) was reproducible as a sum of S_0 and S_{2B} with a decomposition ratio of 0.39, i.e. $0.61S_0 + S_{2B}$, where S_{2B} was normalized at 416 nm. Therefore, it is very likely that S_{2B} and S_{2A} present the spectra of the initial photoproduct in alkaline and acidic solutions, respectively. This molecule was easily soluble in neutral and acidic water and exhibited strongly pH-dependent spectra. The latter was typical of the hydroxy-substituted pyrene derivatives. In addition to these properties, the spectral similarity of S_{2A}

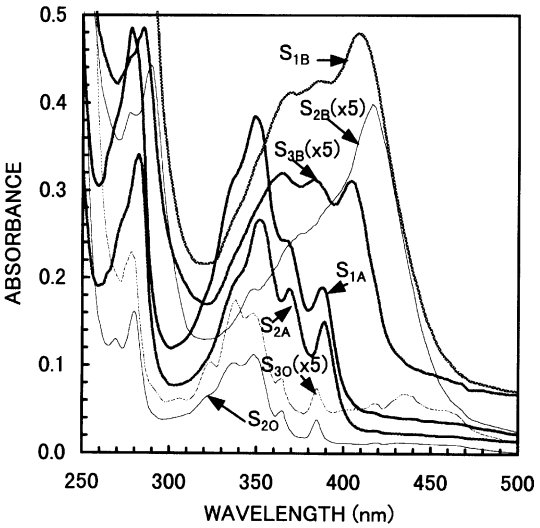

Fig. 6. Photoproduct analysis of PS$^-$ using UV-Vis spectroscopy in combination with solvent extraction after 1200 shots of laser pulses were irradiated in 0.1 M NaOH. The procedure in the solvent extraction, discriminated by subscripts, 1–3, was described in the text. Subscripts, A, B and O, mean the spectra observed in acidic (A) and basic (B) aqueous solutions and organic solution (O).

to that of 6-hydroxy-1-pyrenesulfate [17] suggested that the initial photoproduct is hydroxypyrenesulfonate (PSOH), although the position of the hydroxy substituent was not identified. The residual and minor photoproducts solubilized in the organic phase, represented by spectrum S_{2O}, were further separated by extraction with 0.1 M NaOH solution. The resulting spectra were shown as S_{3B} and S_{3O}. A large amount of the products contained in the organic phase were transferred into 0.1 M NaOH solution. Its spectrum (S_{3B}) was similar to that of PO$^-$ (see the inserted spectra in Fig. 5) but quite different from S_{2B}. This suggests that desulfonation (–SO_3^-) secondarily occurs from the primary product of PSO$^-$. Similar photoreactions involving hydroxylation followed by desulfonation were also observed in alkaline solution under N_2O. The efficiency was found to be slightly higher than that under N_2.

It is well known that the two reactions, desulfonation ($-SO_3^-$) and desulfonylation ($-SO_2$), dominantly occur in the steady-state photolysis of arenesulfonates [6–9]. The photo-desulfonation was also observed in the photolysis of *p*-toluenesulfonic acid with titanium dioxide as a photocatalyst, yielding *p*-cresol [18]. If these reactions were dominant in the photolysis of pyrenesulfonate, we could expect that PO$^-$ and pyrene (and/or bipyrene) were formed as the major photoproducts from desulfonylation and desulfonation, respectively. The experimental evidence mentioned above, however, showed that the dominant process was the activation process of C–H bond on the pyrenyl frame, leading to the formation of PSOH (PSO$^-$ in alkaline solution). This reaction was suggested to occur via the cation radical of PS$^-$ ($P^{\bullet +}S^-$) because the formation of PSO$^-$ was markedly suppressed in the presence of iodide anion. Only

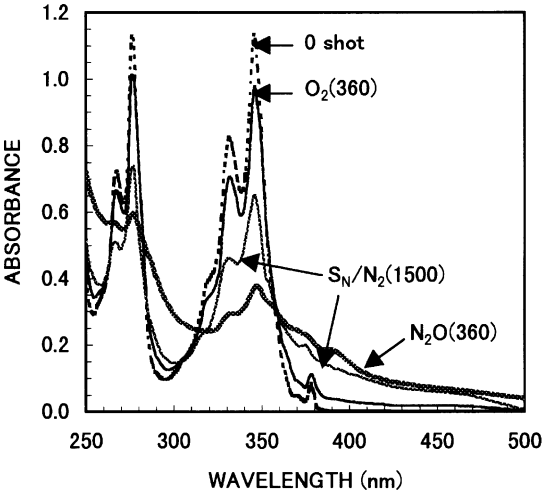

Fig. 7. Photolysis of PS$^-$ in neutral aqueous solution under N_2, O_2 and N_2O. The S_N shows the absorption spectrum of PS$^-$ in neutral solution after 1500 shots of laser pulses were irradiated as gently bubbling nitrogen gas.

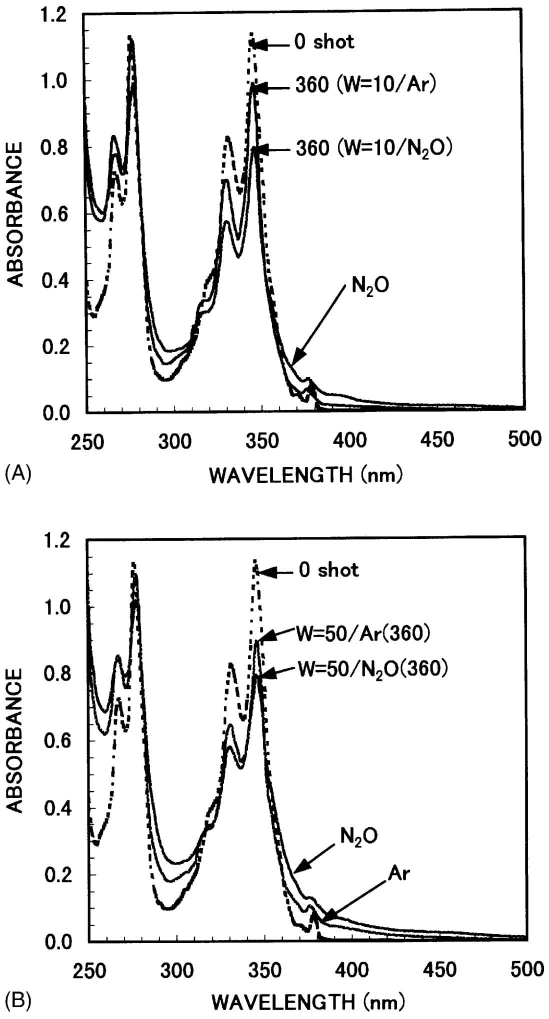

Fig. 8. Photolysis of PS$^-$ in reverse micellar solutions with $W = 10$ (top; A) and $W = 50$ (bottom; B) under different gaseous environments. All the spectra were observed after irradiation with 360 laser shots.

a small increase in absorbance at 416 nm (<0.1) associated with about 10% reduction in PS^- was observed even after irradiation with 600 laser shots in 0.1 M NaOH solution containing 1×10^{-3} M of KI. A similar hydroxylation reaction through the activation of C–H bond without loss of substituents ($-SO_3^-$, $-NO_2$) were also observed in the steady-state photolysis of naphthoquinone sulfonate [9] and nitropyrene [13,14].

The photoreaction of PS^- proceeded much less efficiently in neutral or acidic solution than in alkaline solution. The spectrum S_N in Fig. 7 suggests that about half of the PS^- molecules remained unchanged even after 1500 shots of laser pulses were irradiated in neutral solution under N_2. A long absorption tail extending to 500 nm, attributable to the photoproducts, appeared in this spectrum. This tail was little changed by adding 0.1 M NaOH solution. The photoreaction in the neutral or acidic solution occurred efficiently under N_2O but appeared to proceed in more complicated ways. The hydroxyl radical and/or hydroxyl anion produced through the electron-trapping reaction by N_2O may participate as the reactant in this reaction [16].

The photolysis of PS^- was markedly suppressed within the water pool as shown in Fig. 8. Such a suppressive micellar effect can be explained on the basis of the following experimental results: (1) the pH in the water pool of the AOT reverse micelle is weakly acidic [19], (2) the photolysis of PS^- less efficiently occurs in neutral or acidic aqueous solution mentioned above. The former was consistent with the fact that the observed spectrum of pyranine photochemically formed in the water pool showed the acid form, that is, the absorption maximum was found at 405 nm as shown in Fig. 3B.

4. Conclusion

In this study, we identified the final products produced in the laser photolysis of Na_4PS_4 and NaPS in aqueous solution under different conditions: pH, dissolved gases and the presence of several quenchers. The primary reaction was commonly presented by laser-induced formation of the corresponding cation radicals followed by hydroxylation of them. In the case of PS_4^{4-}, pyranine was efficiently and highly selectively formed, possibly via desulfonation of the cation radical, $P^{\bullet +}S_4^{4-}$, and then hydroxylation. On the other hand, from PS^-, hydroxypyrenesulfonate was initially formed in alkaline solution. These findings are the first examples of the photochemical hydroxylation via the cation radicals of pyrene derivatives. These photoreactions in bulk solution were markedly suppressed within a small water pool of the AOT reverse micelle. The observed micellar effects could be explained based on the pH of water pool and the nature of the cation radicals in it.

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