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Degradation of phenylarsonic acid and its derivatives into arsenate by hydrothermal treatment and photocatalytic reaction

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The degradation of phenylarsonic acid (PA) and its derivatives by hydrothermal treatment (HTT) was examined, especially focusing on the effect of adding H_2O_2 upon the degradation efficiency. The degradation was assessed by the generation of arsenate resulting from the cleavage of As–C bonds in the PA derivatives. When PA (without substituents) was subjected to an HTT with H_2O_2 (H_2O_2-HTT; 0.5–1% H_2O_2) at 175–200 °C, PA was almost completely degraded into arsenate, whereas an HTT with NaOH (NaOH-HTT; 3 M NaOH) at the temperatures provided almost no degradation. The H_2O_2-HTT also worked well for the degradation of PA derivatives with hydroxy and/or nitro groups on the phenyl ring. However, the degradation of aminophenylarsonic acids was not favorably performed by the H_2O_2-HTT. The effect of the structure of PA derivatives upon the degradation susceptibility was discussed. A photocatalytic reaction using TiO_2 was also attempted for the degradation of PA derivatives. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: phenylarsonic acid; derivatives; degradation; hydrothermal treatment; H_2O_2; TiO_2-photocatalytic reaction

INTRODUCTION

Arsenic is present in natural waters in both inorganic and organic forms. Although the inorganic species are predominant in natural waters, the presence of organoarsenic compounds, such as methylated and phenylated arsenic compounds, has been reported.[1,2] Organoarsenic compounds, including phenylated arsenic compounds, are used in agriculture, especially in the USA, and these compounds may contaminate agricultural wastewaters.[3,4] Recently, it has been found in some places, including in Japan, that serious arsenic pollution of soil and ground water is caused by the presence of phenylated arsenic compounds that may be produced from chemical warfare agents; these were prepared during World Wars I and II and discarded there.[5–7]

Katrizky *et al.*[8] reported the degradation of several organoarsenic compounds, including 4-aminophenylarsonic acid (4-NH_2-PA) and 4-nitrophenylarsonic acid (2-NO_2-PA), by a hydrothermal treatment (HTT) for the purpose of providing background information for the detoxification of chemical warfare agents. However, they used only water for the reaction solvent of HTT, and the improvement of degradation efficiency was not attempted. In a previous paper,[9] we described the efficient degradation of 4-NH_2-PA by an HTT with 3 M NaOH, and the degradation of dimethylarsinic acid (DMA) by a TiO_2-photocatalytic reaction. Also, we developed a novel removal system for DMA in which DMA was degraded into arsenate, which was adsorbed by a suitable adsorbent, such as activated alumina.[10] It has been reported that the degradation of some organic compounds is greatly improved by the addition of H_2O_2 into HTT systems.[11–15] However, the application of the HTT with H_2O_2 to the degradation of organoarsenic compounds has not yet been done.

From the viewpoint of arsenic removal from aqueous media, the conventional arsenic removal methods, i.e. precipitation–coagulation and adsorption, are not good for organoarsenic compounds.[16–19] Therefore, the degradation of organoarsenic compounds, such as phenylated arsenic compounds, is important from the aspects of both detoxification

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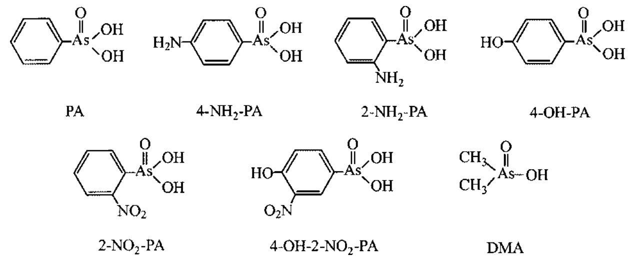

Figure 1. Organoarsenic compounds used in this study.

and removal. So far, there have been no systematic studies concerning the degradation of organoarsenic compounds, i.e. the cleavage of As–C bonds, under various conditions.

In this study, we examined the degradation of commercially available phenylarsonic acid (PA) and its derivatives having various substituents on the phenyl ring as well as DMA by HTT systems, especially focusing on the effect of adding H_2O_2 upon the degradation efficiency. Also, the degradation susceptibilities of various organoarsenic compounds for HTT and TiO_2-photocatalytic reaction were systematically evaluated. Figure 1 presents the structures of the organoarsenic compounds used in this study, i.e. PA, 4-NH_2-PA, 2-aminophenylarsonic acid (2-NH_2-PA), 4-hydroxyphenylarsonic acid (4-OH-PA), 2-NO_2-PA, 4-hydroxy-3-nitrophenylarsonic acid (4-OH-3-NO_2-PA), and DMA.

EXPERIMENTAL

Chemicals

Organoarsenic compounds (PA, 4-NH_2-PA, and the acid form of DMA), H_2O_2 (30% solution), and TiO_2 powder (anatase type) were purchased from Wako Pure Chemical Industries, Ltd (Osaka, Japan). Other organoarsenic compounds (2-NH_2-PA, 4-OH-PA, 2-NO_2-PA, and 4-OH-2-NO_2-PA) were obtained from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan).

Hydrothermal treatment

An aqueous H_2O_2 or NaOH solution (100 ml) containing the organoarsenic compound ($[\mathrm{As}] = 1000\ \mathrm{mg\ l^{-1}}$) was placed in a 200 ml autoclave (200H, Suzuki Seisakusho, Tokyo, Japan). The atmosphere in the autoclave was purged by nitrogen. The autoclave was heated at a rate of 3–4 °C $\mathrm{min^{-1}}$ to the desired temperature and the temperature was maintained for a definite period. The autoclave was then cooled by a fan and the resulting reaction mixture taken out and analyzed.

Photocatalytic reaction

An aqueous TiO_2 suspension was prepared by adding 0.1 g of TiO_2 powder to a Pyrex round-bottomed flask with 100 mg $\mathrm{l^{-1}}$ (as arsenic) of organoarsenic compound solution (100 ml). The flask was externally irradiated by a 500 W xenon lamp (USH-500D, Ushio Denki, Ltd, Tokyo, Japan) while the suspension was stirred with a magnetic stirrer at 24–25 °C. Light intensity was measured by an illuminometer (Minolta Camera T-1). At given irradiation time intervals, 3 ml aliquots were collected and centrifuged to remove the suspended particulates, and the supernatant was analyzed.

Fractional determination of arsenic species in the reaction mixture

The fractional determination of arsenic species in the reaction mixture was carried out by an off-line combination of high-performance liquid chromatography (HPLC) and graphite furnace atomic absorption spectrophotometry (GFAAS) as reported in our previous paper.[9] The HPLC was performed with a Shimadzu LC-6A pump equipped with a Hamilton PRP-X100 anion-exchange column (150 mm × 5.0 mm). For the separation between a PA derivative and arsenate, a buffered aqueous solution containing 6 mM potassium hydrogenphthalate (pH 4.0) was used, and 15 mM ammonium carbonate (pH 8.5) was used for DMA and arsenate separation. The eluent was collected at fixed intervals by a fraction collector. The arsenic concentration of each fraction was determined by a GFAAS instrument (Nippon Jarrel Ash AA-890 spectrometer with FLA-1000 flameless atomizer unit). The total arsenic concentration in the reaction mixture was also measured to confirm the mass balance of arsenic.

RESULTS AND DISCUSSION

Degradation of PA by HTT

The degradation of PA by HTT was examined under various conditions. An aqueous solution of PA ($[\mathrm{As}] = 1000\ \mathrm{mg\ l^{-1}}$) was subjected to the HTT procedure in the presence of NaOH or H_2O_2, and the resulting solution was analyzed for the fractional determination of arsenic species. The concentration of PA adopted was similar to those described in the literature for the purpose of providing basic information about the degradation of organoarsenic compounds.[8,9] The degradation was assessed by the generation of arsenate, resulting from the cleavage of As–C bonds in the PA molecule; no arsenic species other than unreacted PA and arsenate were detected in the reaction mixture. For each case, the mass balance of arsenic was confirmed; almost all arsenic initially added (>98%) was recovered in the reaction mixture.

As shown in Fig. 2, no degradation of PA occurred up to 300 °C, when an HTT with 3 M NaOH (NaOH-HTT) was carried out; 84% of PA was degraded into arsenate at 350 °C. However, the addition of H_2O_2 in the HTT system (H_2O_2-HTT) resulted in a great improvement in the PA degradation. When the H_2O_2-HTT (1% H_2O_2) was performed, 60% of PA was degraded into arsenate, and almost all PA was degraded above 175 °C. The use of 0.5% H_2O_2 led to some decrease in the degradation efficiency at 125–150 °C, but the degradation

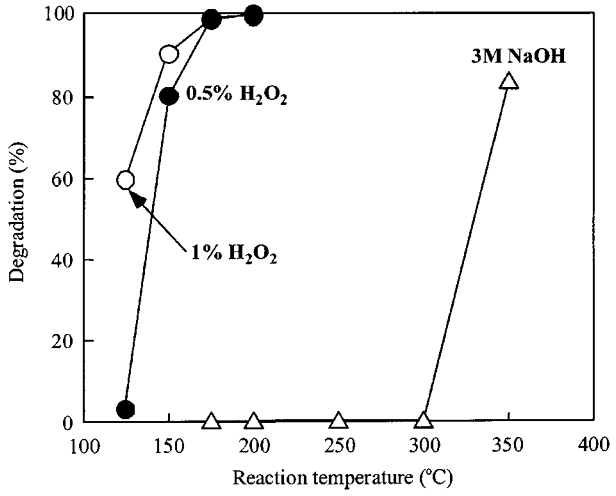

Figure 2. Degradation of PA by HTT (PA, [As] = 1000 mg l^{-1}; 3 h).

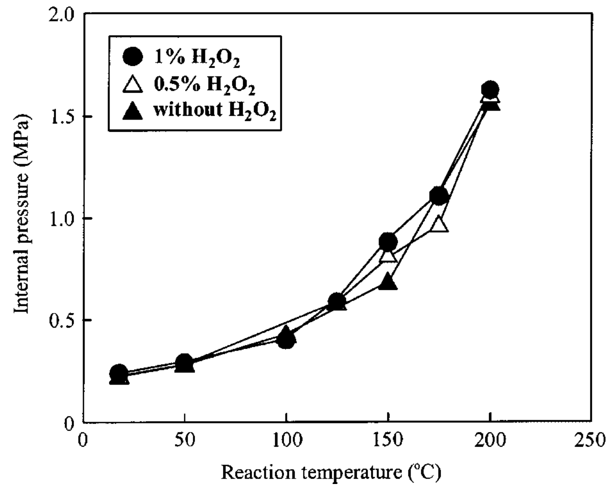

Figure 3. Plot of internal pressure versus reaction temperature for H_2O_2-HTT.

was almost completed above 175 °C, similarly to the use of 1% H_2O_2.

Figure 3 shows the plot of the internal pressure of the autoclave against the HTT temperature. There is almost no significant difference between the pressures observed in the presence of H_2O_2 and those in the absence of H_2O_2. Consequently, it is proposed that the enhancement observed in the PA degradation for the H_2O_2-HTT is not due to the pressure increase, but probably due to the promotion of the degradation reaction, which involves radicals produced from H_2O_2.

The effect of reaction time is presented in Fig. 4. When the H_2O_2-HTT was carried out at 200 °C, a 1 h reaction time provided an almost complete degradation. As the reaction temperature was decreased, the time needed for the complete degradation became longer.

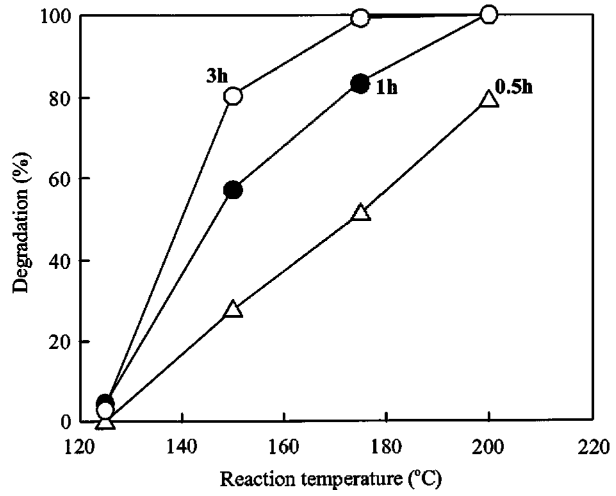

Figure 4. Effect of reaction time on the degradation of PA by H_2O_2-HTT (PA, [As] = 1000 mg l^{-1}; 0.5% H_2O_2).

Degradation of PA derivatives with some substituents by HTT

For the PA derivative 4-OH-2-NO_2-PA, which has both hydroxyl and nitro groups on the phenyl ring, the H_2O_2-HTT was reasonably superior to the NaOH-HTT in terms of the degradation efficiency, as shown in Fig. 5. As the concentration of H_2O_2 was raised, the degradation efficiency increased. As seen in Fig. 6, for 4-OH-PA, i.e. a PA derivative with a hydroxyl group but no nitro group, the H_2O_2-HTT was much better than the NaOH-HTT. In contrast, when 2-NO_2-PA was degraded, i.e. a PA derivative with a nitro group but no hydroxyl group, the efficiency of the H_2O_2-HTT was comparable to that of the NaOH-HTT.

Table 1 summarizes the degradation of the various organoarsenic compounds by HTT. The use of H_2O_2-HTT

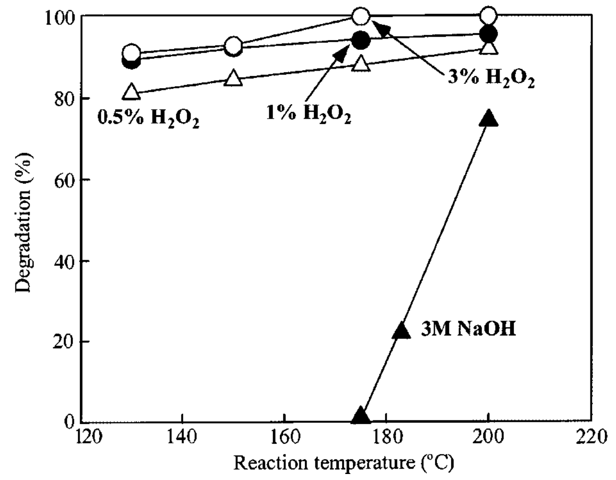

Figure 5. Degradation of 4-OH-2-NO_2-PA by HTT (4-OH-2-NO_2-PA, [As] = 1000 mg l^{-1}; 1 h).

Table 1. Degradation of organoarsenic compounds by HTT

Compound ([As] = 1000 mg l^{-1})	Degradation (%) 1% H_2O_2 (200 °C, 1 h)	3 M NaOH (200 °C, 3 h)	3 M NaOH (200 °C, 1 h)	3 M NaOH with 5% CH_3OH (200 °C, 1 h)
PA	>99	<1	<1	<1
4-NH_2-PA	8	76, >99[a]	56	43
2-NH_2-PA	9	33, 89[a]		
4-OH-PA	>99	>99	69	95
2-NO_2-PA	96	98	87[c]	>99[c]
4-OH-2-NO_2-PA	96	>99	74	84
DMA	14	41[b]		

[a] Reaction temperature, 250 °C.
[b] Reaction temperature, 350 °C.
[c] Reaction temperature, 150 °C.

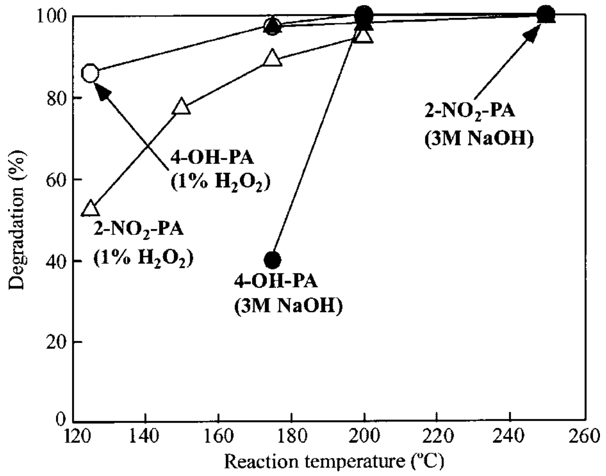

Figure 6. Degradation of 4-OH-PA and 2-NO_2-PA by HTT (4-OH-PA or 2-NO_2-PA, [As] = 1000 mg l^{-1}; 1 h for H_2O_2-HTT and 3 h for NaOH-HTT).

led to effective degradation of PA, 4-OH-PA, 2-NO_2-PA, and 4-OH-2-NO_2-PA, whereas the degradation of 4-NH_2-PA and 2-NH_2-PA was quite poor. On the other hand, for the NaOH-HTT, 4-NH_2-PA and 2-NH_2-PA showed considerable susceptibilities to degradation, although the susceptibilities were lower than those of the PA derivatives having hydroxyl and nitro substituents. Consequently, the H_2O_2-HTT is effective except for NH_2-PA compounds, whereas the NaOH-HTT is good except for PA. The degradation of a methylated arsenic compound, DMA, was not so effective by either the H_2O_2-HTT or NaOH-HTT; even at 350 °C, the NaOH-HTT resulted in just 41% degradation of DMA.

It has been reported that the degradation of organic matter by the NaOH-HTT is promoted by the addition of organic solvents, such as methanol.[20] Thus, the addition of methanol into the NaOH-HTT system was attempted in order to improve the degradation efficiency. As also seen in Table 1, the addition of methanol into the NaOH-HTT system promoted the degradation of 4-OH-PA, 2-NO_2-PA, and 4-OH-2-NO_2-PA by 10–26%. However, the degradation of 4-NH_2-PA was somewhat retarded by the addition of methanol, probably due to the low solubility of 4-NH_2-PA to methanol.

Degradation of organoarsenic compounds by TiO_2-photocatalytic reaction

In a previous paper,[9] the degradation of methylated arsenic compounds, such as DMA, was efficiently performed by use of a photocatalytic reaction with TiO_2 suspension. When the TiO_2-photocatalytic reaction was carried out at 1.5 × 10^5 lx, DMA was degraded by 84% after 12 h, as shown in Fig. 7; the degradation was also assessed by the generation of arsenate. The degradation of DMA proceeded via the formation of monomethylarsonic acid; the mass balance of

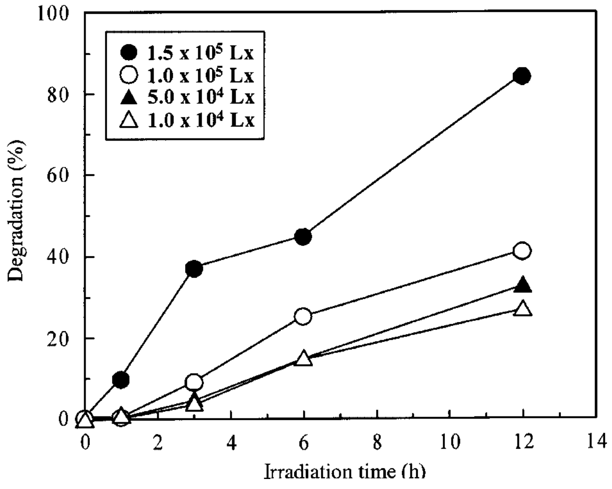

Figure 7. Degradation of DMA by TiO_2-photocatalytic reaction (DMA, [As] = 100 mg l^{-1}; 1.0 g l^{-1} TiO_2).

arsenic was already described in our previous paper,[9] and the adsorption of arsenic species on TiO_2 was negligible (<2%). The degradation of DMA was retarded as the illuminance was lowered, suggesting that the reaction is undoubtedly driven by photo-irradiation.

Figure 8 shows the degradation of PA when it is subjected to the same photocatalytic reaction. PA was degraded by 38% even for 1.5×10^5 lx irradiation for 12 h. Also for PA, the degradation decreases as the illuminance is decreased, suggesting that the degradation of PA also proceeds by the photocatalytic reaction. The degradation of 4-NH_2-PA was much less than that of PA, as seen in Fig. 9. Consequently, it is found that the degradation susceptibility for the photocatalytic reaction decreases in the order DMA > PA > 4-NH_2-PA.

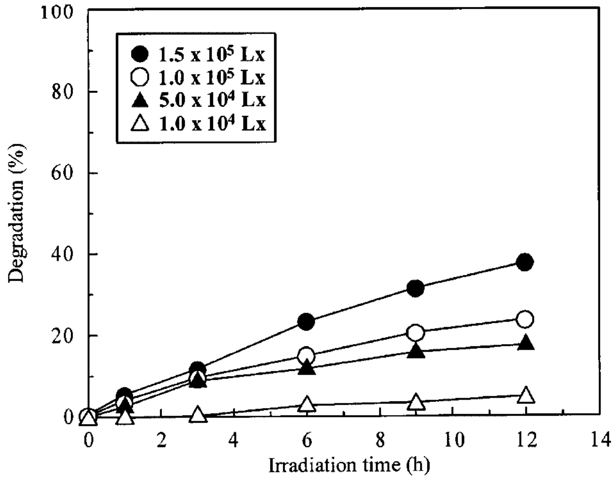

Figure 8. Degradation of PA by TiO_2-photocatalytic reaction (PA, [As] = 100 mg l^{-1}; 1.0 g l^{-1} TiO_2).

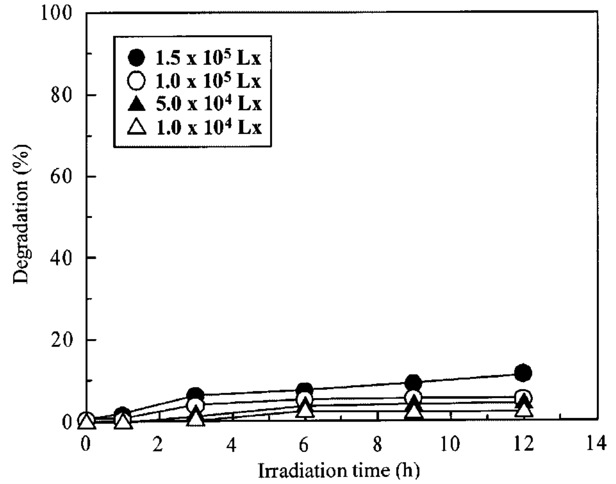

Figure 9. Degradation of 4-NH_2-PA by TiO_2-photocatalytic reaction (4-NH_2-PA, [As] = 100 mg l^{-1}; 1.0 g l^{-1} TiO_2).

Susceptibility of organoarsenic compounds to degradation

The following has been found in this study: (i) when PA derivatives have hydroxyl and/or nitro groups on the phenyl ring, both the H_2O_2-HTT and NaOH-HTT are effective; (ii) the H_2O_2-HTT works well for PA without any substituents, whereas it is not good for PA derivatives with an amino group; (iii) in contrast, the NaOH-HTT works favorably for the latter compounds, whereas it gives poor results for the former compound; (iv) the degradation of DMA is not carried out successfully by either the H_2O_2-HTT or NaOH-HTT, whereas the TiO_2-photocatalytic reaction works well for DMA.

The detection of reaction products other than arsenate was not successful. Thus, it is not possible to discuss the reaction mechanisms clearly. However, some prospects will be described about the degradation susceptibilities of various organoarsenic compounds for HTT and TiO_2-photocatalytic reaction.

Katrizky *et al.*[8] described that the degradation of 4-NH_2-PA, (which has an electron-donating group) by an HTT with only water was better than that of 2-NO_2-PA (which has an electron-withdrawing group), suggesting that this reaction proceeds through an ionic reaction. However, it has been found in this study that there is no such substituent effect for either the NaOH-HTT or H_2O_2-HTT, which indicates that even the NaOH-HTT involves radical reactions. The degradation susceptibility of PA for the NaOH-HTT is quite low, probably because some substituents on the phenyl ring are needed for the stabilization of the phenyl radical produced. Even for the H_2O_2-HTT, the degradation susceptibility of PA is lower than those of PA derivatives with some substituents on the phenyl ring. The H_2O_2-HTT gives quite poor results for the degradation of PA derivatives with an amino group. This may be because the amino group is protonated, resulting in a decrease in the electron density in the phenyl ring, which retards the formation of phenyl radicals; for the NaOH-HTT, such a protonation does not occur, so that NH_2-PA compounds are degraded appreciably. The degradation susceptibility of the methylated arsenic compound DMA is quite low for both the NaOH-HTT and H_2O_2-HTT. Consequently, it is found that the cleavage of a phenyl–arsenic bond is easier than that of a methyl–arsenic bond for these HTT reactions.

However, for the photocatalytic reaction, the degradation susceptibility of DMA is higher than those of PA derivatives, suggesting that the factors determining the reaction rate are different from those for the HTT reactions. It appears that the affinity of reaction species to the catalyst surface is another factor in degradation susceptibility.

CONCLUSION

The degradation of PA, its derivatives, and DMA was examined by use of the H_2O_2-HTT, NaOH-HTT, and a photocatalytic reaction. It has been found that the degradation susceptibility, i.e. the susceptibility of As–C bond cleavage, for each degradation method is greatly dependent upon the structure of PA and its derivatives. The H_2O_2-HTT was quite effective for the degradation of those compounds, except for NH_2-PA compounds and DMA. The NH_2-PA compounds are favorably degraded by the NaOH-HTT, whereas the photocatalytic reaction was good for the degradation of DMA. The detailed mechanism for each degradation method is still not clear, and this is now being studied. Thus, the H_2O_2-HTT is proved to be a good method for the degradation of PA without any substituents on the phenyl ring. This method will hopefully be applied to the degradation of diphenylarsinic acid, which has been found in Japan, presumably as a consequence of long-ago discarded chemical warfare agents.

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