APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **13**, 121–125 (1999)

Degradation of Organoarsenic Compounds by a Hydrothermal or Photo-oxidation Process

Shigeru Maeda, Akira Ohki,* Takanori Kawabata and Mayumi Kishita
Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

The degradation of organoarsenic compounds by a hydrothermal process and by photo-oxidation was studied. When 4-aminophenylarsonic acid (4-APA) was treated hydrothermally, almost complete degradation into an inorganic arsenic compound (arsenate, IA) was attained by use of 1.0–3.0 M NaOH solution at 200 °C. Phenylarsonic acid derivatives which had nitro or hydroxy substituents on the phenyl ring were rather more efficiently degraded than those with amino-substituents. Compared with phenylarsonic acid derivatives with those functional groups, phenylarsonic acid (PA) and dimethylarsinic acid (DMA) were hard to degrade. On the other hand, DMA was effectively degraded into IA by TiO_2-catalyzed photo-oxidation, whereas for PA and 4-APA the photo-oxidation treatment was not efficient. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: organoarsenic; phenylarsonic acid derivatives; dimethylarsinic acid; degradation; hydrothermal treatment; photo-oxidation

Received 26 January 1998; accepted 26 May 1998

INTRODUCTION

There are many arsenic-containing chemical-weapon reagents which were prepared during World Wars I and II; typical compounds in this category are shown in Fig. 1. Destruction and disposal of these compounds, which have been stored and abandoned in many places around the world, are urgently need but are not easy to accomplish.[1–4] All of the compounds shown in Fig. 1 are organoarsenic compounds in which chloro or cyano substituents are attached to the arsenic atom. When such organoarsenic compounds are decomposed by hydrolysis, alkyl- or phenyl-arsonic acids (or arsinic acids) are obtained.

Compared with the inorganic arsenic compounds (i.e. arsenate, IA), it is not easy to recover arsonic acids and arsinic acids from aqueous phases by conventional arsenic-recovery methods, which include precipitation–coagulation by use of iron(III) salts with lime and adsorption by the correct adsorbents.[5] Thus it is important to decompose arsonic acids and arsinic acids into IA. Degradation of these compounds has been studied for the purpose of measurement.[6,7] However, there have been almost no studies which relate to such a degradation from the viewpoint of disposal.

In the present study, we have examined the degradation of commercially available organoarsenic compounds (arsonic acids and arsenic acids) by a hydrothermal process and a photo-oxidation process. The organoarsenic compounds include phenylarsonic acid (PA), 2-aminophenylarsonic acid (2-APA), 4-aminophenylarsonic acid (4-APA), 4-hydroxyphenylarsonic acid (HPA), 2-nitrophenylarsonic acid (NPA), 4-hydroxy-3-nitrophenylarsonic acid (HNPA), and dimethylarsinic acid (DMA) (Fig. 2).

EXPERIMENTAL

Chemicals

Organoarsenic compounds, PA, 4-APA, and DMA and anatase-type TiO_2 were purchased from Wako Pure Chemical Industries Ltd (Osaka, Japan), while 2-APA, HPA, NPA and HNPA were from Tokyo Chemical Industry Co. Ltd (Tokyo, Japan).

Hydrothermal reaction

An alkaline solution (100 ml) containing the organoarsenic compound ($1000\ \mathrm{mg\ As\ l^{-1}}$) and

---

* Correspondence to: Akira Ohki, Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan. E-mail: ohki@apc.eng.kagoshima-u.ac.jp.

CCC 0268–2605/99/020121–05 $17.50

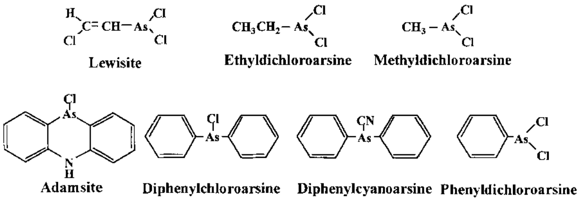

Figure 1 Arsenic-containing chemical weapon reagents.

the correct concentration of NaOH was placed in a 200 ml autoclave (200 H; Suzuki Seisakusho, Tokyo, Japan). The atmosphere in the autoclave was purged by N_2 and a 3 kg cm^{-2} pressure was provided by N_2. The autoclave was heated at a rate of 3–4 °C min^{-1} to the desired temperature and the temperature was kept for a definite period. Then the autoclave was cooled by a fan and the resulting reaction mixture was taken out and analyzed.

Photo-oxidation

An aqueous solution containing the organoarsenic compound (100 mg As l^{-1}) and powdery TiO_2 (100 mg) was placed in a vessel (a stoppered Pyrex tube with 50 ml capacity). The vessel was irradiated externally by a 500 W xenon lamp (UXL-500D; Ushio Denki Ltd, Tokyo, Japan) while the solution was stirred magnetically at room temperature (24–26 °C). At a definite interval, a portion of the solution was taken and analyzed.

Analysis of reaction mixture

The reaction mixture after the hydrothermal treatment or the photo-oxidation was analyzed by HPLC and AA spectroscopy.[8] The HPLC was carried out with a Shimadzu LC-6A pump equipped with a Hamilton PRP-X100 anion-exchange column (150 mm × 5.0 mm) and a Rheodyne injector; the mobile phase was a buffered aqueous solution containing 6 mM potassium hydrogenphthalate (pH 4.0) except for DMA, for which a buffered aqueous solution containing 15 mM ammonium carbonate (pH 8.5) was used. The flow rate was 0.5 ml min^{-1} and the eluent was collected at a fixed interval by a fraction collector. The arsenic concentration of each fraction was determined by an AA spectrometer (Japan Jarrel Ash AA-890) with a flameless atomizer (FLA-1000).

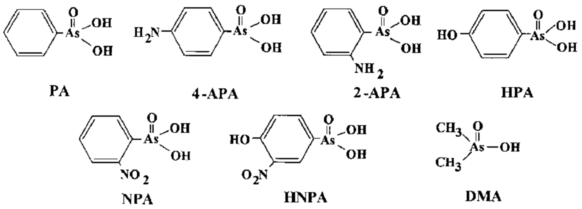

Figure 2 Organoarsenic compounds used in this study.

RESULTS AND DISCUSSION

Determination of organoarsenic compounds and IA

When phenylarsonic acid derivatives, such as PA, 2-APA, 4-APA, HPA, NPA and HNPA, are degraded, IA is the most likely arsenic-containing degradation product. Thus, we tried to determine each of the phenylarsonic acid derivatives in the presence of IA. Figure 3 shows a chromatogram when an aqueous solution containing 4-APA and IA is injected. Other phenylarsonic acid derivatives provided similar chromatograms. Calibration curves for those arsenic compounds were made.

When DMA is degraded, methylarsonic acid (MMA) is produced in addition to IA. Figure 4

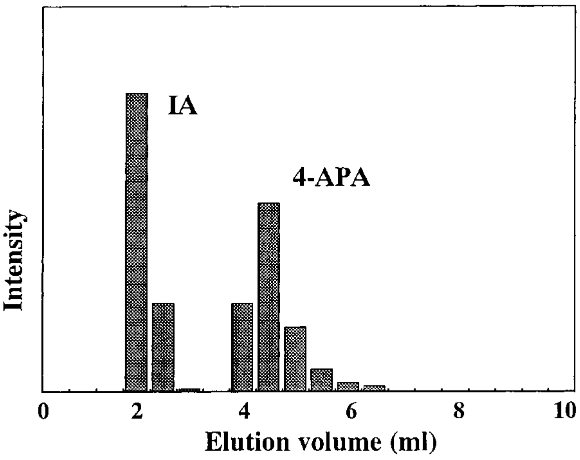

Figure 3 Chromatogram for 4-APA and IA. An aqueous solution (20 µl) containing equal concentrations of 4-APA and IA (2.0 mgAs l^{-1} each) was injected. HPLC conditions are given in the text. Intensity is in arbitrary units.

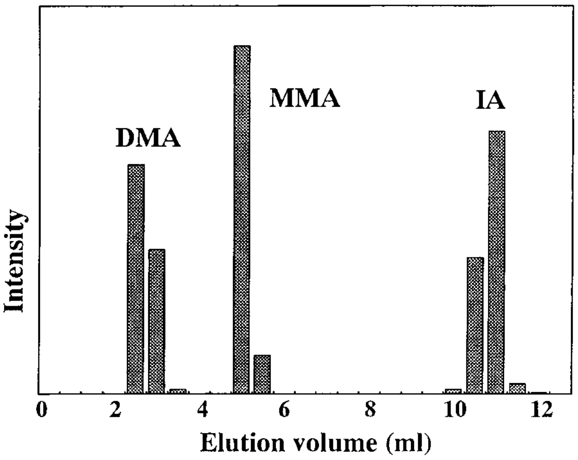

Figure 4 Chromatogram for DMA, MMA and IA. An aqueous solution (20 μl) containing equal concentrations of DMA, MMA, and IA (2.0 mgAs l^{-1} each) was injected. HPLC conditions are given in the text. Intensity is in arbitrary units.

shows a chromatogram when an aqueous solution containing DMA, MMA and IA is injected. Calibration curves for these arsenic compounds were also prepared.

Degradation of 4-APA by a hydrothermal process

In Fig. 5 is shown the degradation of 4-APA when the organoarsenic compound is hydrothermally treated at 200 °C under various alkaline conditions, for which 1.0–9.0 M NaOH solutions were used. In all cases, the arsenic-containing compound produced by the degradation of 4-APA was IA only, and the mass balance was confirmed.

When 3.0 M NaOH solution was used, 78% of the 4-APA initially added was degraded after 3 h of reaction whereas almost all the 4-APA was decomposed after 10 h of reaction. For 1.0 M and 6.0 M NaOH solutions 37% and 71%, respectively, of the 4-APA added initially were degraded after 3 h of reaction. These results suggest that the use of 3.0 M NaOH is most efficient. The autoclave pressures observed when 3.0 M, 6.0 M, and 9.0 M NaOH solutions were used at 200 °C were 14.5, 13.2 and 12.0 kg cm^{-1}, respectively. Therefore it is proposed that the lowering in degradation efficiency observed when high NaOH concentrations were used is caused by the decrease in the autoclave pressure.

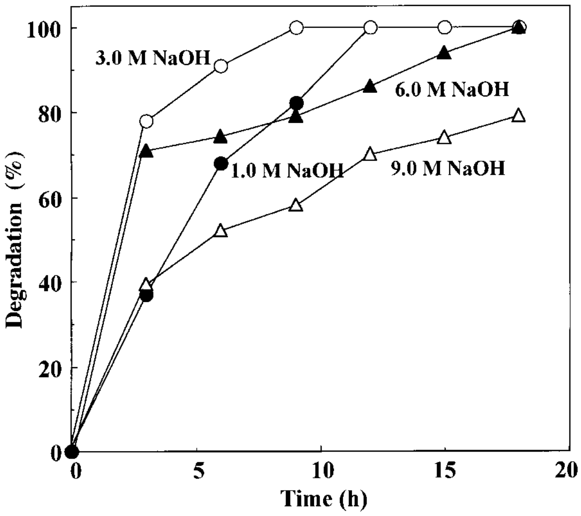

Figure 5 Time course of the degradation of 4-APA (autoclave temperature 200 °C).

Effect of temperature

Figure 6 indicates the degradation of 4-APA when the organoarsenic compound was treated hydrothermally at 100–200 °C for 12 h under various alkaline conditions.

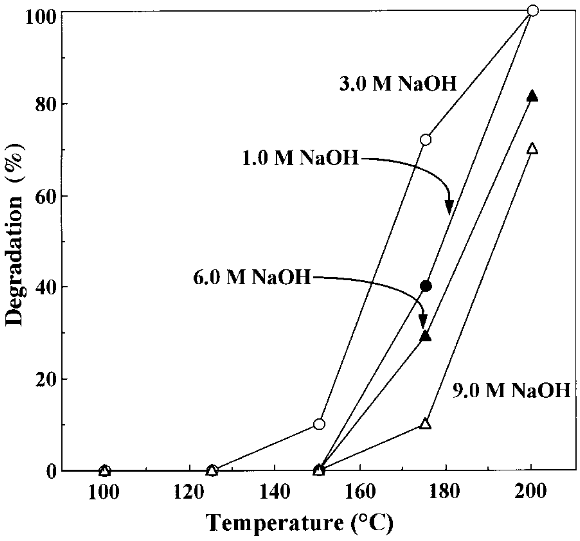

Figure 6 Effect of temperature on the degradation of 4-APA (reaction time 12 h).

When 3.0 M NaOH solution was used, no degradation of 4-APA occurred up to 125 °C; the degradation gradually increased as the temperature was raised above 125 °C, reaching almost complete decomposition at 200 °C. When 1.0 M NaOH solution was used, no degradation of 4-APA took place up to 150 °C, then it gradually increased, becoming almost 100% at 200 °C. However, for 6.0 M and 9.0 M NaOH solutions degradation of 4-APA was 81% and 70%, respectively, even at 200 °C. Consequently, it is shown that 200 °C is needed to attain complete degradation of 4-APA when 1.0 M or 3.0 M NaOH solution is used.

Degradation of various phenylarsonic acid derivatives

Figure 7 shows the degradation of various phenylarsonic acid derivatives (PA, 2-APA, 4-APA, HPA, NPA and HNPA) when these compounds are hydrothermally treated for 3 h by using 3.0 M NaOH solution. For 175 °C, NPA, HPA, and 4-APA were degraded by 98%, 39% and 15%, respectively, whereas almost no degradation was observed in the case of 2-APA, HNPA and PA. When these organoarsenic compounds were treated at 200 °C, HNPA, HPA, NPA, 4-APA, 2-APA and PA were degraded by 100%, 99%, 98%, 76%, 33% and *ca* 0%, respectively. For PA, which has no substituent on the phenyl ring, almost no degradation took place up to 300 °C, but 84% was decomposed when the temperature was 350 °C.

It appears that the attachment of nitro or hydroxy substituents to the phenyl ring greatly enhances degradation; that of amino substituents also promotes the degradation, although the efficiency is somewhat inferior to that for nitro and hydroxy substituents. The detection of degradation products other than IA was not successful, probably because the aromatic part of the organoarsenic compounds undergoes complex reactions. Both electron-withdrawing groups, (such as nitro) and electron-donating groups (such as hydroxy and amino) enhance the degradation. This result suggests that degradation does not proceed via a simple ionic mechanism. The detailed mechanism is now under study.

Degradation of DMA

As shown in Fig. 8, when DMA was treated hydrothermally at 350 °C for 3 h under three sets of alkaline conditions for which 0.5–1.0 M NaOH solutions were used, both MMA and IA were detected as degradation products. The use of 3.0 M NaOH solution led to production of 40% MMA and 41% IA (percentages of the equivalent of DMA initially added). Compared with phenylarsonic acid derivatives which have nitro, hydroxy or amino substituents, DMA is hard to degrade, probably

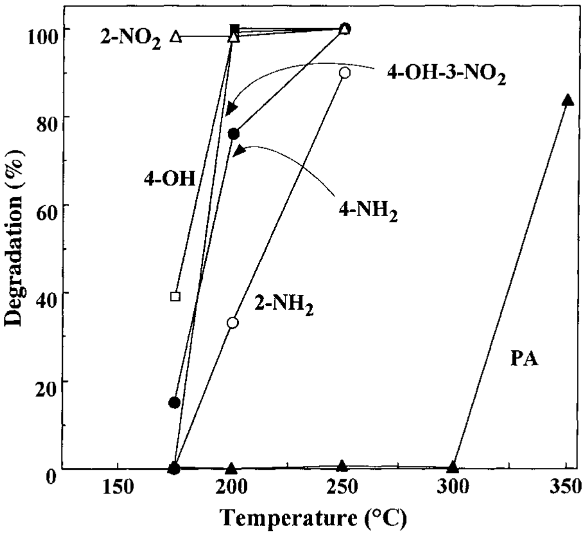

Figure 7 Degradation of PA and its derivatives (reaction time 3 h; 3.0 M NaOH solution was used).

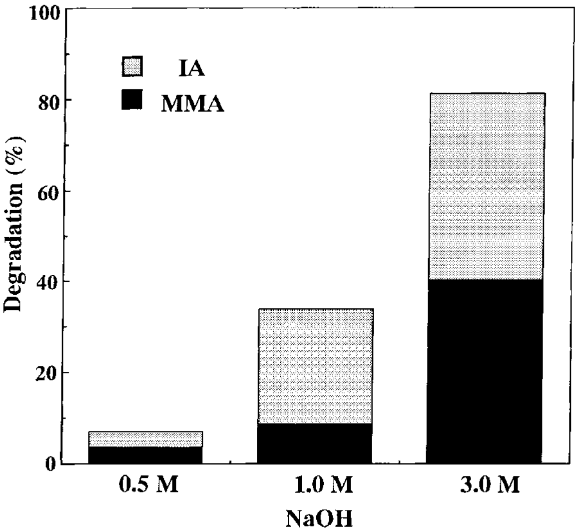

Figure 8 Degradation of DMA (reaction time 3 h; autoclave temperature 350 °C).

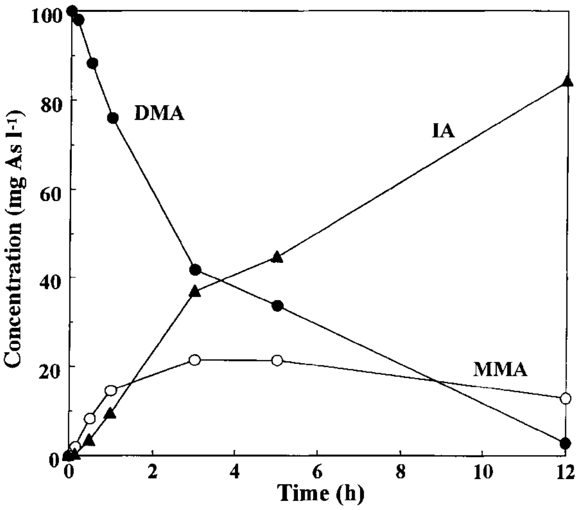

Figure 9 Degradation of DMA by photo-oxidation.

because, similarly to PA, it has no substituents which can promote the degradation.

Degradation by photo-oxidation

A photo-oxidation with a TiO_2 catalyst was attempted in order to degrade the organoarsenic compounds. When an aqueous solution containing 100 mg As l^{-1} of DMA was irradiated in the presence of TiO_2 powder, the concentration of DMA in the aqueous solution decreased gradually and the degradation was almost complete after a 12 h reaction (Fig. 9). On the other hand, the concentration of MMA increased up to 3 h of reaction and then decreased slightly, reaching 13 mg As l^{-1} after a 12 h reaction; meanwhile the concentration of IA increased continuously becoming 84 mg As l^{-1}. These results suggest that a large proportion of DMA is degraded to IA. However, for PA and 4-APA, degradation by photo-oxidation under the same conditions was only 18% and 15%, respectively, after a 12 h reaction.

It is known that generation of the hydroxyl radical is usually involved in photo-oxidation processes using the TiO_2 catalyst.[9] Thus, it is anticipated that the degradation mechanism is different from that for the hydrothermal process, which may lead to a difference in the susceptibility to degradation of DMA and phenylarsonic acids between the photo-oxidation process and the hydrothermal process.

CONCLUSION

Degradation of organoarsenic compounds was performed by a hydrothermal process and by photo-oxidation. For phenylarsonic acid derivatives which have nitro, hydroxy and amino substituents on the phenyl ring, hydrothermal treatment using 3.0 M NaOH solution was quite effective, and thus these compounds were degraded up to 250 °C. However, when PA was treated, 350 °C was needed to attain efficient degradation. For DMA, considerable amounts of undegraded compounds, including MMA and unreacted DMA, remained after even the 350 °C reaction. On the other hand, when a TiO_2-catalyzed photo-oxidation was performed, DMA was degraded effectively. However, phenylarsonic acid derivatives were not easy to degrade by photo-oxidation.

REFERENCES

1. C. E. Stewart and J. B. Sullivan, Military munitions and antipersonnel agents. In: *Hazardous Materials Toxicology: Clinical Principals of Environmental Health*, Sullivan, J. B. and Krieger, G. R. (eds), Williams and Wilkins, Baltimore, 1992, pp. 986–1014.
2. J. F. Bunnet, *Science* **263**, 1205 (1994).
3. R. G. Manley, The problem of old chemical weapons which contain mustard gas or organoarsenic compounds: an overview. In *Chemical Problems Associated with Old Arsenical and Mustard Munitions, NATO Advanced Research Workshop Proceedings, Lodz, Poland*, 1996.
4. H. Martens, Recovered old arsenical and mustard munitions in Germany: technologies, plans, and problems. In: *Chemical Problems Associated with Old Arsenical and Mustard Munitions, The NATO Advanced Research Workshop Proceedings, Lodz, Poland*, 1996.
5. A. Ohki, K. Nakayachigo, K. Naka and S. Maeda, *Appl. Organometal. Chem.* **10**, 747 (1996).
6. W. R. Cullen and M. Dodd, *Appl. Organometal. Chem.* **2**, 1 (1988).
7. R. Rubio, J. Alberti and G. Rauret, *Int. J. Environ. Anal. Chem.* **52**, 203 (1993).
8. J. Gailer and K. J. Irgolic, *Appl. Organometal. Chem.* **8**, 129 (1994).
9. H. Hidaka, J. Zhao, E. Pelizzaetti and N. Serpone, *J. Phys. Chem.* **96**, 2226 (1992).