衛生化学
EISEI KAGAKU
30 (6) 377-383 (1984)

Studies on the Photochemical Decomposition of Dodecylbenzenesulfonate by Ultraviolet Irradiation

ATSUKO ADACHI and TADASHI KOBAYASHI

*Kobe Women's College of Pharmacy, Motoyamakitamachi
4-chome, Higashinada-ku, Kobe 658, Japan*

(Received June 7, 1984)

The effect of wavelength on the photochemical decomposition of dodecylbenzenesulfonate (LAS) and the decomposition process were investigated. When LAS in water was subjected to monochromatic irradiation between 200 and 700 nm from a spectroirradiator equipped with a Xe arc lamp, the largest decomposition rate was observed at 215 nm. Thus a low-pressure mercury lamp providing radiation mainly in the lower ultraviolet (UV) range was chosen as a light source for the photochemical reaction. LAS in various kinds of water samples, *e.g.*, city sewage, treated sewage water, river water, sea water and others, was found to be rapidly decomposed by irradiation with the light source and there was little difference among water samples. Since formaldehyde and formic acid were identified among the photochemically decomposed products of LAS, it is suggested that LAS is photochemically decomposed through formaldehyde and formic acid.

Keywords — photochemical decomposition; anionic surfactant; formic acid; formaldehyde; dodecylbenzenesulfonate

Introduction

Water pollution by surfactants has become a serious problem. In order to eliminate such pollutants in public sewage and industrial waste water, aggregation precipitation, absorption on activated carbon or biochemical decomposition by activated sludge have been predominantly used. Photochemical decomposition by ultraviolet (UV) irradiation was also reported,^{1,2)} and since UV irradiation can almost completely destroy surfactants in water, this might be useful as a method of tertiary treatment of waste water on an industrial scale. However, few detailed investigations have been made on the photochemical decomposition. Therefore we studied the effect of wavelength, irradiation energy and other factors on the decomposition, and investigated the decomposition process by means of GC-MS and spectrophotometric analyses. The results

are presented here.

Experimental

1. Reagents—1) Sodium *n*-dodecylbenzenesulfonate (LAS) and sodium dodecyl sulfate (SDS): Guaranteed reagents of Wako Pure Chem. Ind. Ltd. were used.

2) Sodium di-(2-ethylhexyl) sulfosuccinate (SSS): Guaranteed reagent of Nakarai Chem. Ind. Co. was used. Other reagents were also of guaranteed reagent grade.

2. Apparatus — 1) Spectroirradiator: A JASCO (Japan Spectroscopic Co. Ltd., Tokyo) CRM-FA spectroirradiator with a Xe arc lamp as a light source was used. Monochromatic irradiation in the range of 200–700 nm is possible with this apparatus.

2) Photochemical reaction apparatus: A Taika HLV-B photochemical reaction apparatus (Taika Ind. Co., Tokyo) with a low-pressure mercury lamp (5 W) was used.

3) Atomic absorption spectrophotometry: A

Shimadzu AA-620 atomic absorption spectrophotometer with a graphite furnace atomizer (Shimadzu Co. Ltd., Kyoto) was used.

4) Gas chromatography-mass spectrometry (GC-MS): GC-MS was performed on a Hitachi M-80 gas chromatography double-focussing mass spectrometer (Hitachi Co. Ltd., Ibaragi). A glass column (0.3×300 cm i.d.) packed with 3% SE-30 on Gas-chrom Q (80–100 mesh) was run at 180°C with a helium flow of 40 ml/min for the identification of dodecylbenzene. On the other hand, a glass column (0.3×300 cm i.d.) packed with Unisol F-200 was run at 105°C with a helium flow of 40 ml/min for the identification of formic acid.

3. Ultraviolet Irradiation of Anionic Surfactant Solutions—1) Procedure for irradiation of anionic surfactants with monochromatic UV light: A solution of 1 mg/l of anionic surfactant (LAS, SDS, SSS) in water was used. Four ml of the solution was taken in a quartz cell (10×10×40 mm) and placed in the spectroirradiator. After setting the wavelength and integrator to the desired settings, irradiation was carried out. The slit width was fixed at 10 mm. The irradiated solution was then transferred into a separation funnel and rinsed with 2–3 ml of water several times. The resulting solution was designated as a sample solution and used in the determination of anionic surfactants.

2) Procedure for irradiation of LAS with a low-pressure mercury lamp: A solution of LAS (1 mg/l) in one of various kinds of water samples (e.g., city sewage treated sewage water, river water, sea water, buffer solution, etc.) was irradiated in the photochemical apparatus with a low-pressure mercury lamp for a desired time. Two ml of the irradiated solution was transferred into a separation funnel. The resulting solution was designated as a sample solution and was used in the determination of LAS.

4. Procedure for Determination of Anionic Surfactants—Anionic surfactants were determined by means of the atomic absorption spectrophotometric method reported previously.⁹⁾

5. Procedure for Identification of Dodecyl-

benzene—A solution of LAS in water (3.3 mg/l) was irradiated in a photochemical apparatus with a low-pressure mercury lamp for 1 h. After being adjusted to pH 2–3 with hydrochloric acid, the irradiated solution was transferred to a separation funnel. The fraction which might contain dodecylbenzene was extracted twice with 100 ml each of ethyl ether by vigorous shaking. The extract was evaporated to dryness under reduced pressure below 40°C and the resulting residue was dissolved in 0.5 ml of acetone. The sample solution obtained thus was subjected to the GC-MS as described in "Experimental."

6. Procedure for Identification of Formic Acid—A solution of LAS in water (3.3 mg/l) was irradiated in a photochemical apparatus with a low-pressure mercury lamp for 1 h. The irradiated solution was transferred to a round-bottomed flask and the solvent was evaporated off under reduced pressure. The residue was dissolved in 0.5 ml of ethanol. The sample solution thus obtained was subjected to GC-MS as described in "Experimental."

7. Identification of Formaldehyde—Formaldehyde was identified according to the test methods for the industrial waste water described in JIS K0102.⁴⁾

Results and Discussion

1. Effect of Wavelength on the Photochemical Decomposition of Anionic Surfactants

Samples of 4 ml of anionic surfactant solutions (LAS, SDS, SSS) in water (1 mg/l) were individually irradiated with monochromatic light in the range of 200–700 nm according to the method described in "Experimental." Figures 1 and 2 show the decomposition rates of LAS when UV irradiation was performed at a fixed irradiation energy of 3.5×10^8 erg/cm² (the irradiation period was changed appropriately) or by fixing the irradiation period at 5 h respectively. The latter experiment was carried out to compare the results with those of Murakami *et al.*¹⁾ Both ex-

Fig. 1. Photodecomposition of Anionic Surfactants

Anionic surfactant solutions in water (1 mg/l) were subjected to monochromatic UV irradiation in the range of 200–700 nm (3.5×10^8 erg/cm²).
 LAS: Sodium *n*-dodecylbenzenesulfonate,
 SDS: Sodium dodecyl sulfate,
 SSS: Sodium di-(2-ethylhexyl) sulfosuccinate.
 ●—●: LAS, ○—○: SDS, □—□: SSS.

Fig. 2. Photodecomposition of LAS
 LAS in water (1 mg/l) was subjected to monochromatic UV irradiation for 5 h.

periments gave very similar results, showing maximal decomposition rates at 215 nm (Figs. 1 and 2). However, Murakami *et al.*¹⁾ reported that the maximum decomposition rate was observed at 270 nm (they used the same type of spectroirradiator as ours). Murakami *et al.*¹⁾ determined total organic carbon (TOC) for measuring remaining LAS, whereas we assayed LAS itself by the proposed atomic absorption spectrophotometric method. TOC might include not only LAS but also other organic compounds, and therefore their result may not be reliable. It was thus concluded

Fig. 3. Effect of pH on the Photodecomposition of LAS

LAS in buffer solution (1 mg/l) was irradiated with a low-pressure mercury lamp for 30 min.

Fig. 4. Photodecomposition of LAS in Various Kinds of Water Samples

Various kinds of water samples containing LAS (1 mg/l) were irradiated with a low-pressure mercury lamp.

●—●: City sewage,
 ○—○: Treated water from sewage treatment plant,
 ■—■: Untreated water from chemical laboratories,
 □—□: Treated water from chemical laboratories,
 ▲—▲: River water,
 △—△: Sea water,
 ×—×: Distilled water.

that the maximum decomposition rate of LAS was obtained on irradiation not at 270 nm but at 215 nm. No change was observed on irradiation at above 290 nm, while the decomposition rates gradually increased below 290 nm and reached a maximum at 215 nm (Fig. 1). Since a lamp with peak output at 215 nm is not available, a low-pressure mercury lamp having a high output at 254 nm was selected for the irradiation at study. The following studies on a large scale were

Fig. 5. GC-MS of Irradiated LAS, Non-irradiated LAS and Dodecylbenzene

- (a) Mass chromatogram of irradiated LAS,
- (b) Mass chromatogram of non-irradiated LAS,
- (c) Mass chromatogram of dodecylbenzene,
- (d) Mass spectrum of dodecylbenzene.

performed in a Taika photochemical reaction apparatus with this lamp.

2. Effect of pH on the Photochemical Decomposition of LAS

The effect of pH on the photochemical decomposition was investigated by using a Taika HLV-B photochemical reaction apparatus with a low-pressure mercury lamp according to the method described in "Experimental." Glycine hydrochloric acid buffer, glycine sodium hydroxide solution or 0.1 M phosphate buffer solution was used. As shown in Fig. 3, there was little change in the range of pH 1–10, but the decomposition rate gradually increased in the range above pH 10.

The results suggest that the pH has very little effect on the decomposition.

3. Photochemical Decomposition of LAS in Various Kinds of Water Samples

City sewage, treated water from sewage treatment plants, untreated and treated water from chemical laboratories, river water and sea water were used. As shown in Fig. 4, LAS in various kinds of water sample solutions was found to be rapidly decomposed by irradiation and there was little difference among water samples.

Yamada *et al.*⁵⁾ investigated the photochemical decomposition of anionic surfactants in city sewage or hot spring water and their

Fig. 6. GC-MS of Irradiated LAS and Formic Acid

- (a) Mass chromatogram of irradiated LAS,
- (b) Mass spectrum of peak B,
- (c) Mass chromatogram of formic acid,
- (d) Mass spectrum of peak B'.

results were similar to ours. Waste water generally contains various kinds of organic compounds and ions, but these have little effect on the photochemical decomposition of LAS. Presumably the concentration of such contaminants is too low to reduce the UV intensity significantly or the compounds might have little ability to absorb UV light.

4. Studies on the Mechanism of Photochemical Decomposition of LAS

Photochemical decomposition of organic compounds sometimes produces toxic substances. Therefore studies on the mechanism of photochemical decomposition of anionic

surfactants are important. Watanabe⁶⁾ reported that dodecylbenzene was formed as an intermediate during UV irradiation of LAS. On the other hand, Matsuura *et al.*⁷⁾ identified formic acid and formaldehyde, which were finally oxidized to carbon dioxide, as photochemical decomposition products of LAS by GLC method. We tried to identify dodecylbenzene, formaldehyde and/or formic acid in the photochemical decomposition products of LAS by GC-MS. The experiment was carried out according to the method described in "Experimental." Figures 5a, 5b and 5c show the mass chromatograms of irradiated LAS,

Fig. 7. Absorption Spectra of Irradiated LAS, Non-irradiated LAS and Formaldehyde by Acetylacetone Spectrophotometric Method

- (a) Irradiated LAS,
(b) Non-irradiated LAS,
(c) Formaldehyde.

non-irradiated LAS and a reference standard of dodecylbenzene, respectively, based on the total ion collector (TIC) or the base peak (m/e 119). Figure 5d shows the mass spectrum of a reference standard of dodecylbenzene. As shown in Fig. 5a, no peak due to dodecylbenzene was observed in the mass chromatogram measured at the base peak (m/e 119), as in the case of non-irradiated LAS (Fig. 5b). The results indicate that the UV irradiation of LAS does not produce dodecylbenzene. Figure 6a shows the mass chromatograms of irradiated LAS in terms of TIC or the molecular ion (m/e 46), while Fig. 6b shows the mass spectrum of the eluate at peak B in Fig. 6a. On the other hand, Figs. 6c and 6d show the mass chromatograms of a reference standard of formic acid and the mass spectrum of peak B', respectively.

Although the retention times of the peaks A or B and A' or B' in the mass chromatograms differed slightly (Figs. 6a and 6c), the

shapes of the two chromatograms were similar and the fragmentation patterns in the mass spectra of peaks B and B' were essentially the same. Therefore, the formation of formic acid from irradiated LAS was confirmed. Formaldehyde was also identified in the irradiated LAS by a spectrophotometric method (Fig. 7). Watanabe⁶⁾ identified dodecylbenzene as a photochemical decomposition product of LAS simply on the basis of the retention time in GLC method. However, dodecylbenzene was not detected in our GC-MS experiment. We concluded that LAS was photochemically decomposed not through dodecylbenzene, but through formaldehyde and formic acid.

Conclusions

Photochemical decomposition of anionic surfactants was investigated and the following results were obtained.

1. It was found that 215 nm was the most effective wavelength for the photochemical decomposition.
2. The photochemical decomposition of anionic surfactants, was almost independent of pH from pH 1 to pH 10, but the decomposition rates gradually increased in the range above pH 10.
3. Anionic surfactants in various kinds of water samples (city sewage, treated sewage water, river water, sea water and others) were found to be rapidly decomposed by irradiation and there was little difference among water samples.
4. Formic acid and formaldehyde were identified as decomposition products of LAS by GC-MS and spectrophotometric methods, respectively.

Acknowledgement We wish to thank Miss Torei Sai, Kobe Women's College of Pharmacy, for performing the GC-MS.

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