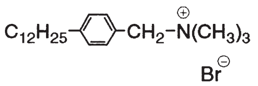
Photodegradative Surfactants: Photolysis of *p*-Dodecylbenzyltrimethylammonium Bromide in Aqueous Solution

Yoshihiro Itoh,* Kenji Yamamoto, and Hirofusa Shirai
Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567

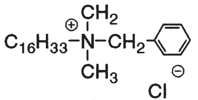
(Received October 1, 2002; CL-020844)

Upon UV irradiation, a benzyl-containing cationic surfactant, *p*-dodecylbenzyltrimethylammonium bromide, has been converted to a nonsurfactant, which can be separated from the aqueous solution by coprecipitation with $CaSO_4$.

Photodegradative surfactants have become of great interest because of not only environmental concerns but also promising applications such as photosensitive emulsifiers.[1] Although several kinds of photodegradative surfactants have been synthesized, there are only a few compounds with a leaving hydrophilic head group and with a similarity to commercial products (e.g., alkyl- and alkoxy-phenyldiazosulfonates).[2,3] These surfactants are expected as 'environmentally-benign' alternatives because the hydrophobic moieties, which may contaminate the hydrosphere, would be removed quickly after photolysis. As part of our continuing interest in photochemistry of benzyl compounds,[4–6] we are now synthesizing a series of benzyl-containing surfactants. The present communication compares the photolyses of *p*-dodecylbenzyltrimethylammonium bromide **1** and benzylcetyldimethylammonium chloride **2**, known as disinfectant detergents.[7] The UV irradiation of **1** in aqueous solution results in almost perfect separation of hydrophobic and ionic moieties.



1



2

The surfactant **1** was easily prepared by bromomethylation[8] of dodecylbenzene followed by quarternization with trimethylamine.

Critical micelle concentrations (CMC) of the surfactants were determined photometrically by observing the vibrational peak ratio (I_3/I_1) of pyrene fluorescence;[9] the CMCs for **1**, **2**, and cetyltrimethylammonium chloride (CTAC) at 25 °C were 5.0×10^{-4}, 4.3×10^{-4}, and 1.5×10^{-3} M (mol dm^{-3}), respectively.[10] The presence of the hydrophobic benzene ring in **1** and **2** may be responsible for their decreased values. Judging from the higher value of I_3/I_1 for **1** (0.95, 0.90, and 0.90 in the above order),[11] **1** would provide more hydrophobic microenvironment for the solubilized pyrene.

Aqueous solutions of **1** and **2** (1.0×10^{-2} M) were irradiated with a low-pressure mercury lamp (30 W) under aerated conditions. The reactions were traced by HPLC and NMR spectroscopy. Figure 1 illustrates the dependence of the conversions of **1** and **2** on the irradiation time. The transmittances of the solutions observed at 500 nm were also plotted. The degradations of both surfactants proceeded promptly and similarly, which were faster than that of benzyltrimethylammonium chloride.[12,13] It should be noted that after irradiation for 20 min the solution of **1** became turbid (Figure 1), indicating the aggregation of water-insoluble photoproducts. While the suspension for **1** yielded no bigger coagulations even after aging overnight (particle size, ca. 240 nm),[14] the addition of proper amounts of aqueous solutions of Na_2SO_4 and $CaCl_2$ in order, yielding the precipitate of $CaSO_4$, could coprecipitate the water-insoluble photoproducts.[15] In fact, the supernatant solution after irradiation exhibited negligible absorption around 255 nm due to the benzyl group (Figure 2); the absorption band around 275 nm may be assigned to trace amounts of oxides.[16]

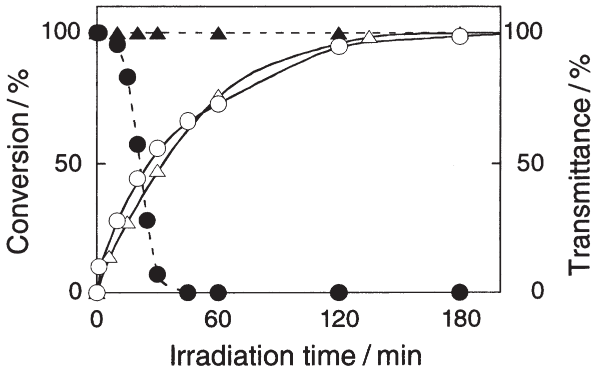


Figure 1. Conversions of **1** and **2** and transmittances of their solutions versus irradiation time: [surfactant] = 1.0×10^{-2} M; circle, **1**; triangle, **2**; open symbols, conversion; closed symbols, transmittance at 500 nm.

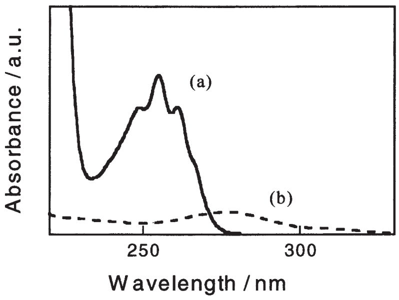
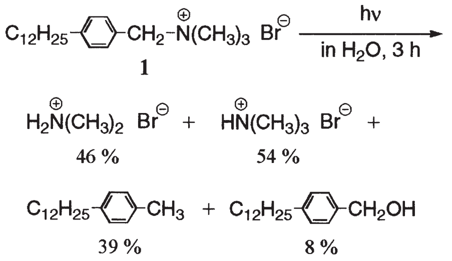


Figure 2. Absorption spectra of **1** in aqueous solution (1.0×10^{-2} M) before and after irradiation: (a) the sample solution before irradiation; (b) the supernatant after irradiation followed by copreipitation.

By contrast, no apparent change in transmittance was observed for the solution of **2** (Figure 1). It is anticipated from the product analysis (see below) and the foaming ability that its surface activity will not be lost after photolysis.

It has been reported that benzyltrimethylammonium salts in aqueous solution underwent homolytic and heterolytic cleavage of the C–N bond to give radical (homolytic) and ionic (heterolytic) products, respectively.[17] The same type of photoproducts were obtained for **1** and **2**. As for **1**, after irradiation for 3 h (100% conversion) followed by coprecipitation, the obtained supernatant and the extracts from the precipitate into chloroform were analyzed by ^{1}H NMR spectroscopy:



As expected, the supernatant hardly contains any product except for quantitative amounts of secondary and tertiary ammonium salts (homolytic and heterolytic products, respectively).[17] The precipitate gave *p*-dodecyltoluene (homolytic product) and *p*-dodecylbenzyl alcohol (heterolytic one), as main products. The relative yields of homolytic products increased for **1** and **2** compared with for benzyltrimethylammonium chloride, which may be partially due to the less polar environments of the surfactants.[13]

These observations clearly indicate that insertion of a benzyl moiety between the hydrophobic chain and ionic group in surfactants leads to efficient separation of the hydrophobic moieties from aqueous solution by photodegradation. In this connection, we found that alkylbenzyl-sulfonates and sulfates are photolyzed, forming nonsurfactants.[13] Further studies directed towards syntheses of surfactants with different polar head groups of the present type as well as their applications are currently in progress in our laboratory.

This work was supported partially by a Grant-in-Aid for COE Research (10CE2003) from the Ministry of Education, Science, Sports and Culture of Japan.

References and Notes

1 P.-E. Hellberg, K. Bergstrom, and K. Holmberg, *J. Surf. Deterg.*, **3**, 81 (2000).

2 O. Nuyken, K. Meindl, A. Wokaun, and T. Mezger, *J. Photochem. Photobiol., A*, **81**, 45 (1994); O. Nuyken, K. Meindl, A. Wokaun, and T. Mezger, *J. Photochem. Photobiol., A*, **85**, 291 (1995).

3 I. R. Dunkin, A. Gittinger, D. C. Sherrington, and P. Whittaker, *J. Chem. Soc., Perkin Trans. 2*, **1996**, 1837.

4 T. Goshima, Y. Itoh, M. Kojima, and T. Karatsu, *J. Photochem. Photobiol., A*, **127**, 75 (1999).

5 T. Goshima, Y. Itoh, H. Shirai, and M. Kojima, *J. Photochem. Photobiol., A*, **141**, 139 (2001).

6 Y. Itoh, T. Goshima, and H. Shirai, *J. Appl. Polym. Sci.*, **82**, 2227 (2001).

7 I. Nishi, T. Imai, and M. Kasai, ‘‘Handbook of Surface Active Agents,’’ Sangyo Tosho, Tokyo (1960), p 737.

8 G. Kubiczek and L. Neugebauer, *Monatsh. Chem.*, **81**, 917 (1950).

9 K. Kalyanasundaram and J. K. Thomas, *J. Am. Chem. Soc.*, **99**, 2039 (1977).

10 The CMCs for **2** and CTAC were reported to be 4.0×10^{-4} and 1.1×10^{-3} M, respectively, in the literature: L. T. Okano, F. H. Quina, and O. A. El Seoud, *Langmuir*, **16**, 3119 (2000).

11 The values were determined from the uncorrected fluorescence spectra.

12 The quantum yields of degradation for **1** and **2** were determined to be 0.45 and 0.44, respectively, based on that for chlorobenzene (0.14): T. Ichimura, M. Iwai, and Y. Mori, *J. Phys. Chem.*, **92**, 4047 (1988).

13 Y. Itoh and K. Yamamoto, unpublished results: the detailed study on the effect of alkyl chain length of **1** and **2** on the photolysis is now in progress.

14 Estimated by light scattering experiments.

15 The experimental conditions have not been optimized and we are now exploring suitable flocculants.

16 Judging from the absorbance of the solution, the yields of oxides seem to be much less than 1%.

17 D. C. Appleton, D. C. Bull, R. S. Givens, V. Lillis, J. McKenna, J. M. McKenna, S. Thackeray, and A. R. Walley, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 77.