

Photodegradation of 1,3,5-Trichlorobenzene in Aqueous Surfactant Solutions

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Recent environmental concerns have led to the demand for development of new methods of eliminating chlorinated aromatics in polluted water and soil. Chu et al. (Chu and Jafvert 1994; Chu et al. 1998) proposed a surfactant-extraction method for soil remediation, including the capture and decomposition of polychlorobiphenyls by surfactants, as a promising tool. This is based on the result of the increased photodechlorination of chlorinated aromatics in surfactant solutions (Epling et al. 1988). Several groups have investigated the photolyses of polychlorobenzenes, polychlorobiphenyls, and other chlorinated aromatics in surfactant solutions (Chu and Jafvert 1994; Chu et al. 1998; Chu and Kwan 2002; Epling et al. 1988; Shi et al. 2000; Tanaka et al. 1984). Direct and indirect photodechlorination of these compounds has been performed in the absence and presence of additives. However, the understanding of the "micellar effect" on the photolysis seems to be insufficient. In addition, the experimental conditions have been limited: in most cases diluted solutions of substrates were photolyzed (usually much less than $10^{-4} M$ in concentration), unless higher concentrations of surfactants ($> 0.1 M$) were added or substrates with hydrophilic substituents and/or a small number of chloride groups were used. This may be mainly due to the limited solubility of substrates in surfactant solutions. From a practical point of view, however, pollutants in wide concentration ranges should be examined because the concentration effect of substrates and surfactants may affect their photoreactivity.

In the present study, the photolysis of a moderate concentration (0.5 mM) of 1,3,5-trichlorobenzene (TCB) has been examined in various surfactant solutions. We used TCB as a substrate because of the followings: (i) trichlorobenzene is one of precursors of polychlorobiphenyls (Liu 2001), although it is less toxic than the higher chlorinated benzenes and polychlorobiphenyls (IPCS 1991); (ii) TCB is expected to have a moderate solubility in aqueous surfactant solutions; (iii) photoproducts of TCB are expected to include no structural isomers, facilitating the analysis of the photolysis. We find that the product distribution markedly depends on the type of surfactants.

Table 1. Surfactant characteristics^a.

Surfactant	Abbreviation	CMC ^b (mM)	n	HLB ^c
Cetyltrimethylammonium chloride	CTAC	1.3	81 ^d	
Dodecyltrimethylammonium chloride	DTAC	20	44 ^d	20 ^e
Dodecylammonium chloride	DAC	15	80 ^d	
Sodium dodecylsulfate	SDS	8.1	68 ^d	40
Sodium dodecylsulfonate	SDSO ₃	9.8	54 ^e	
Sodium laurate	SL	24	56 ^e	
Polyoxyethylene(4) lauryl ether	Brij 30	0.040	>100 ^f	10
Polyoxyethylene(23) lauryl ether	Brij 35	0.060	40 ^e	17
Polyoxyethylene(20) cetyl ether	Brij 58	0.0039	70 ^e	16

^a The literature values reported under slightly different conditions.

^b Mukerjee et al. 1971.

^c Horiguchi 1975.

^d Ikeda 1991.

^e Fendler and Fendler 1975.

^f JOCS 2001.

MATERIALS AND METHODS

Polychlorobenzenes (DCB, TCB, TeCB) (reagent grade) and polychlorobiphenyls (TCBP, TeCBP) (analytical standard) were purchased from Tokyo Kasei (Tokyo) and Wako Chemicals (Osaka), respectively, and used without further purification. Cationic and anionic surfactants were reagent grade (Tokyo Kasei) and nonionic surfactants were commercial grade (Wako Chemicals), which were used as received. All solutions were made with distilled water. Characteristics of the surfactants, including critical micelle concentration (CMC), aggregation number (n), and hydrophile-lipophile balance (HLB), are summarized in Table 1.

Sample solutions were prepared as follows. A solution of TCB (10 μ mol) in CH₂Cl₂ (5 ml) was placed in a flask and the solvent was evaporated slowly at room temperature. To the residue a 20 ml of surfactant solution was added and then sonicated gently for 15 min. A 4 ml of the resulting transparent supernatant was transferred to a quartz tube (13 mm ϕ) and then irradiated for 5 min at 25 °C under aerated condition with all light emitted from a 500-W high-pressure mercury lamp (EHB-W-500) (Eikohsha, Osaka) in a merry-go-round apparatus. The intensity of the incident light observed at 265 nm was 8×10^{-6} einstein L⁻¹sec⁻¹.

Samples were analysed on a Jasco liquid chromatography system equipped with a UV detector (UV-975) (Jasco, Tokyo) and a reversed-phase C₁₈ column (MG-120) (Shiseido, Tokyo). Methanol-water (80:20) was employed as the eluent. GC/MS analysis was carried out as described previously (Itoh et al. 1998).

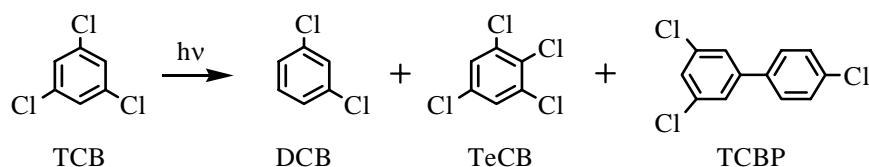


Figure 1. Products for photolysis of TCB.

RESULTS AND DISCUSSION

Irradiation of TCB in surfactant solutions for 5 min gave three major products, which were identified by HPLC and GC/MS (Figure 1). Most plausible pathways for the formation of these products are shown in Figure 2. 1,3-Dichlorobenzene (DCB) and 1,2,3,5-tetrachlorobenzene (TeCB) will be derived from dechlorination and chlorination of TCB, respectively. A phenyl dimer, 3,4',5'-trichlorobiphenyl (TCBP), will be derived from dechlorination of a coupling product between DCB radical and TCB, 2,3',4,5',6-pentachlorobiphenyl (PeCBP). In fact, the production of PeCBP and its dechlorinated product, 2,3',4,5'-tetrachlorobiphenyl (TeCBP), was confirmed by HPLC and GC/MS. Their yields were, however, found to be low and not to be reproducible. This may not be surprising because of the higher photoreactivity of ortho-chlorine in polychlorobiphenyls (Ruzo et al. 1974); i.e., rapid dechlorination of PeCBP and TeCBP to TCBP would occur during photolysis. No attempt was then made to quantify PeCBP, TeCBP, and other minor products such as monochlorobenzene (MCB), benzene, and high molecular-weight products. The results of the photolyses are summarized in Table 2.

A 10 mM of CTAC solution (above the CMC) could dissolve 0.5 mM of TCB almost quantitatively and could photolyze it efficiently. On the other hand, the limited solubility of TCB in DTAC and DAC solutions (below the CMCs) decreased the conversion yields. These results clearly indicate the “micellar effect” on the photolysis of polychloroaromatics (Epling et al. 1988). It should be noted that the conversion yield of TCB in organic solvents obtained under the similar condition decreased in the order: cyclohexane (71 %) > methanol (63 %) > acetonitrile (28 %). This suggests that the less polar environment and/or the presence of hydrogen sources contribute to the enhanced photolysis in surfactant systems. The irradiation of TCB in CTAC solution gave not only a dechlorinated product (DCB) but also a chlorinated one (TeCB) and polychlorobiphenyls such as TCBP, as described above. The latter products, being more toxic than TCB (IPCS 1991), would be formed in micelles containing plural TCBs. The average number of TCB solubilized per micelle (N_{TCB}) was estimated roughly by:

$$N_{\text{TCB}} = \{ [\text{TCB}]_0 \times \text{Sol.} - [\text{TCB}]_w \} / \{ ([\text{surfactant}] - \text{CMC}) / n \} \quad (1)$$

where $[\text{TCB}]_0$ is the initial molar concentration of TCB, Sol. is the solubility of TCB in the surfactant solution in %, $[\text{TCB}]_w$ is the molar solubility of TCB in water ($2.2 \times 10^{-5} \text{ M}$ at 25 °C) (IPCM 1991), $[\text{surfactant}]$ is the surfactant concentration in M , and n is the aggregation number, respectively. Using the literature data in Table 1, N_{TCB} in 10 mM CTAC solution was determined to be

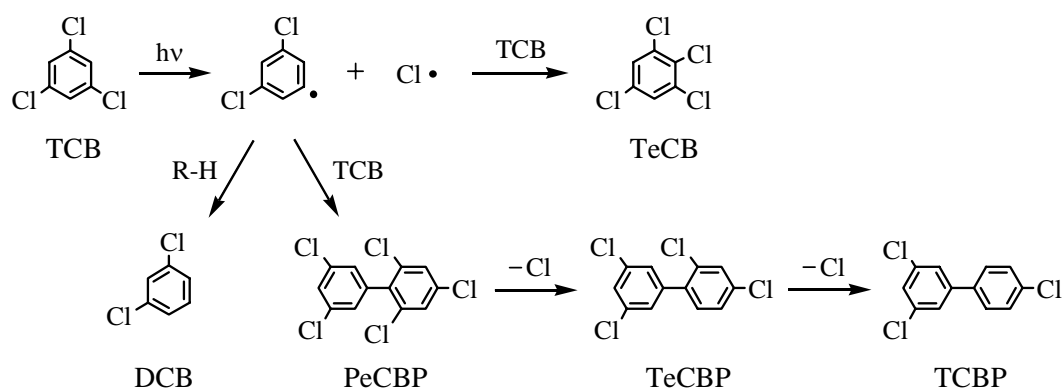


Figure 2. Plausible mechanism for formation of photoproducts.

Table 2. Photolysis of TCB in surfactant solutions^a.

Surfactant	Micelle ^b	Sol. ^c (%)	Conv. ^d (%)	Product yield ^e (%)			N _{TCB} ^f
				DCB	TeCB	TCBP	
CTAC		91	54	33	33	3.1	4.0
DTAC	×	24	29	73	trace ^g	trace ^g	<1
DAC	×	40	28	11	1.5	trace ^g	<1
SDS		32	55	24	29	2.3	5.0
SDSO ₃		24	53	9	trace ^g	trace ^g	<1
SL	×	43	57	8	4.0	0.6	<1
Brij 30		90	61	34	60	1.9	>4.6
Brij 35		92	63	27	9.0	0.4	1.8
Brij 58		92	66	31	10	0.4	3.1

^a [TCB]=0.5 mM; [surfactant]=10 mM; irradiation time, 5 min.

^b - [surfactant] > CMC, - [surfactant] ≅ CMC, × - [surfactant] < CMC.

^c Solubility of TCB in surfactant solutions.

^d Conversion yield of TCB.

^e Yields of products based on TCB consumed.

^f Calculated by eq 1.

^g Yield < 0.4 %.

4.0. This high value is responsible for the preferential formation of TeCB and TCBP. In fact, the product yields depended on the surfactant concentration (see below). It is interesting to note that the yields of TeCB and TCBP were remarkably decreased to negligibly small values in DTAC and DAC solutions below the CMCs. Most of the TCB molecules may be dispersed mono-molecularly in these solutions and may thus be photolyzed to give monomeric products predominantly. We also note that the photolysis in DTAC produced DCB preferentially while that in DAC gave some of unidentified products other than DCB.

All anionic surfactants, whether their concentrations were above the CMCs or below, solubilized TCB less efficiently compared with CTAC, which reflected the lower solubilizing power of anionic surfactants (Kile and Chiou 1989). It is anticipated from the large values of CMC and HLB (Table 1) that the anionic surfactants are essentially hydrophilic. Nevertheless, the apparent conversion yields of the solubilized TCB were relatively high, which were comparable with that for CTAC and somewhat smaller than those for nonionic surfactants. It seems likely that a hydrophobic substrate, TCB, is solubilized in the nonpolar inner core of the micelles just as a pyrene molecule (Kalyanasundaram and Thomas 1977), increasing its photoreactivity. In contrast, Chu and Kwan (2002) reported the remarkably decreased degradation of 4,4'-dichlorobiphenyl in SDS compared with that in nonionic surfactants. We speculate that the biphenyl molecule is too large to be solubilized in the inner core of the SDS micelles, increasing the polarity of the "microenvironment" and thus decreasing the degradability. Anyhow it can be safely said that the overall degradability of TCB in anionic surfactants is rather low because of their lower solubilizing power. Undesirable products, TeCB and TCBP, were formed efficiently in the SDS micelles with a high N_{TCB} , just as in CTAC. In contrast, the yields largely decreased in SDSO₃ and SL solutions of the CMC concentration or below. The yields of DCB, however, were not increased in the latter cases (see below).

Nonionic surfactants (10 mM) dissolved TCB almost quantitatively. These data are not in conflict with the "general" order of the solubilizing power for organic solutes in surfactant micelles that have the same length of nonpolar chains: nonionic > cationic > anionic (Kile and Chiou 1989). The conversion yields of TCB were also higher in nonionic surfactants. Surfactants, Brij 35 and Brij 58, had decreased yields of TeCB and TCBP. Since the N_{TCB} values are estimated to be still higher than one, the formation of these toxic products is possible to occur in these surfactants. A plausible reason is that nonionic surfactants have good hydrogen sources, as pointed out by Chu et al. (Chu and Jafvert 1994; Chu et al. 1998). It should be, however, noted that the yields of a hydrogenated product, DCB, in these surfactants, are as small as those in other ionic micelles and thus that the total yields of the main products in the nonionic surfactants are much smaller than 100 %. We speculate the preferential formation of coupling products between reaction intermediates and surfactant molecules. In this regard, the following observations would be important: (i) Brij 30 with a short polyoxyethylene chain had remarkably increased yields of TeCB and TCBP and a somewhat higher yield of DCB compared with Brij 35 and Brij 58. (ii) the photolysis of TCB in an ether solvent, 1,2-dimethoxyethane, gave coupling products between the solvent molecule and the DCB or MCB radicals, as main products, despite their fine structures having not been specified. We thus conclude that the polyoxyethylene chains in nonionic surfactants play an important role in the photolysis of TCB. It should be pointed out again that the formation of DCB was not necessarily facilitated in both ionic and nonionic micelles showing the decreased yields of TeCB and TCBP. Such surfactants might have a reactive site in each molecule.

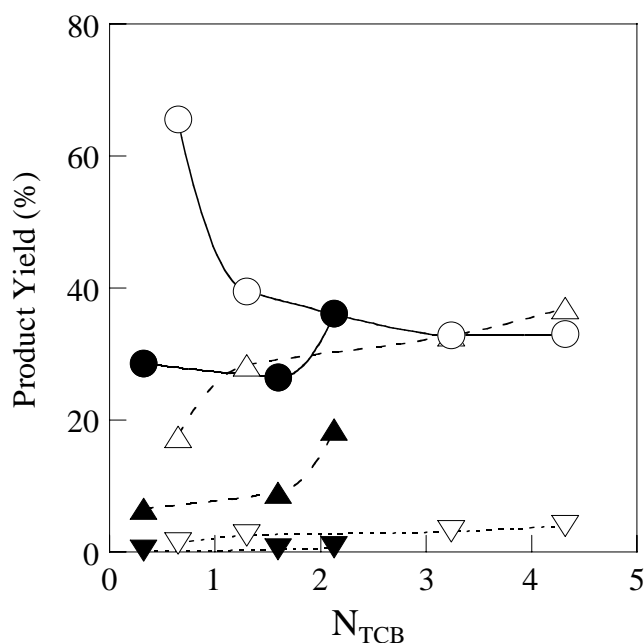


Figure 3. Product yields for photolysis of TCB in CTAC and Brij 35 solutions as a function of N_{TCB} : [TCB]=0.5 mM; [surfactant]=7.5-50 mM; open symbols, CTAC; closed symbols, Brij 35; DCB (,); TeCB (,); TCBP (,).

Since the N_{TCB} values were crucial for the product distribution as described above, the photolysis was examined at various concentrations (7.5-50 mM) of CTAC and Brij 35. Increasing the surfactant concentration solubilized TCB perfectly and increased the conversion yield slightly (data not shown). In Figure 3, the product yields are plotted against N_{TCB} . As expected, with decreasing N_{TCB} for CTAC, the yields of TeCB and TCBP decreased and that of DCB increased. The formation of the former toxic products, however, could not be inhibited at N_{TCB} below one. As for Brij 35, the yield of DCB even at lower N_{TCB} was not increased apparently. This result strongly suggests the formation of the above-mentioned “coupling products”.

The present study demonstrated that a moderate concentration (0.5 mM) of TCB could be readily photodegraded in surfactant solutions. The overall degradability decreased in the following order reflecting the solubilizing power of surfactants: nonionic > cationic > anionic. Not only dechlorination but also bimolecular reactions, chlorination and dimerization, and other side reactions occurred during photolysis, which depended on the surfactant type. Decreasing N_{TCB} retarded the chlorination and dimerization, but did not necessarily facilitate the dechlorination. In nonionic surfactants, the formation of coupling products between reaction intermediates and surfactant molecules was suggested. These are probably because radical intermediates formed by homolytic cleavage can react readily with the surrounding molecules. It would be thus said that the direct photolysis in surfactant micelles is unsatisfactory as a “remediation” tool

for chlorinated aromatic compounds. In this context, we recently found that the addition of some electron donors is quite effective for photodechlorination of TCB in surfactant solutions.

Acknowledgements. This work was supported by Grants-in-Aid for COE Research (10CE2003) and 21st Century COE Program by the Ministry of Education, Culture, Sports, Science, and Technology.

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