Photoreductive dechlorination of chlorinated benzene derivatives catalyzed by ZnS nanocrystallites

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ZnS nanocrystallites effectively enhanced photo-reduction of chlorinated benzene derivatives in the presence of triethylamine as a sacrificial electron donor under UV irradiation (λ > 300 nm), leading to selective and stepwise dechlorination to give benzene at the final stage.

Photochemical detoxification of halogenated compounds, such as PCB, dioxin, and DDT, has been attracting much attention because this can be regarded as a promising process to eliminate C–Cl bonds under environmentally relevant and mild conditions. In particular, TiO_2-catalyzed photoprocesses involving oxidation and reduction in aqueous systems have been extensively investigated.[1] In such systems, however, photooxidation proceeds through the formation of hydroxyl radical (HO•), leading to unavoidable formation of unknown photoproducts especially from polychlorinated compounds.[2,3] Further, the rate of such photodegradation often slows in the case of polychlorinated compounds because they are electron-deficient molecules, *i.e.* their oxidation potentials are very positive in nature, showing resistance to the electrophilic attack of HO•.[4] Therefore, reductive processes with semiconductors should be investigated practically for the purpose of detoxification of chemicals.[5,6]

In this paper, we show that photoreduction induces selective dehalogenation of chlorinated benzene derivatives, providing more favorable dehalogenation processes than the photooxidative ones. In particular, ZnS nanocrystallites stabilized in *N,N*-dimethylformamide (DMF)[7] catalyze photoreduction of chlorinated benzene derivatives, leading to their step-wise dechlorination under UV-irradiation at ambient temperature.

A DMF solution of ZnS nanocrystallites was prepared by the reaction of $Zn(ClO_4)_2$ with H_2S under cooling with ice and water as described elsewhere.[7] Photoreactions were carried out under cooling with water by UV irradiation of a DMF solution (2 ml) containing a substrate (25 mM), ZnS nanocrystallites (2.5 mM in diatomic concentration as ZnS) and triethylamine (TEA, 1 M) in a Pyrex glass tube using a 500 W high pressure mercury lamp. The reaction mixtures were analyzed by gas chromatography with a fused silica capillary column (HiCap-CBP20, 25 m × 0.2 mm, Shimadzu) using dodecane as an internal standard.

Fig. 1 shows time conversion plots of the photoreaction of 1,4-dichlorobenzene. The concentration of 1,4-dichlorobenzene decreased during irradiation with and without ZnS nanocrystallites. However, the rate of the conversion in the presence of ZnS nanocrystallites was twice that at the beginning and several times faster at the later stages than that in the absence of ZnS crystallites. In parallel with the consumption of 1,4-dichlorobenzene the formation of chlorobenzene was observed and benzene was formed at the final stage, *i.e.* after the induction period of 1 h with the decreased rate of formation of chlorobenzene, indicating that 1,4-dichlorobenzene is dechlorinated successively to benzene through chlorobenzene. Hydrogen was formed competitively but in a small amount (2–3 μmol in 5 h) in the presence of ZnS nanocrystallites. No other byproducts, such as biphenyl derivatives and chlorophenol, were detected by GC analysis, showing a consistent material balance between the consumed substrate and the products.

The dechlorination proceeded at a relatively high rate even without ZnS nanocrystallites. The absorption spectrum measured for the mixture of 1,4-dichlorobenzene and TEA showed the appearance of a shoulder at the long wavelength edge of the absorption of 1,4-dichlorobenzene, suggesting the formation of the exciplex between the two compounds. The formation of the exciplex should contribute to the photochemical dechlorination without the catalyst.[8,9] On the other hand, the photocatalytic dechlorination in the presence of ZnS nanocrystallites should mainly proceed through the excitation of ZnS, since ZnS nanocrystallites absorb most light in this region when they are present in the system.

In our earlier report, ZnS nanocrystallites prepared in DMF act as a photocatalyst for the two-electron reduction of CO_2 to HCOOH or CO in the presence of triethylamine.[7] The photogenerated electrons on ZnS nanocrystallites possess such a high reducing power (< -2.2 V *vs.* SCE) that the substrates are subject to successive two-electron reduction, causing the stepwise dechlorination. This fact suggests that the anion radicals first formed should be readily dechlorinated to the radicals, which may undergo further reduction and protonation. The electrons can be supplied by photooxidation of TEA. The resulting $TEA^{+\bullet}$ works as a proton source giving $[Et_2NHCHCH_3]^\bullet$ which can also function as a good electron source in the system.[7]

In Table 1 are listed the conversions and the product distributions for the photodechlorination of various chlorobenzene derivatives observed in the presence of ZnS nanocrystallites with their reduction potentials.[10,11] The distribution of the products observed for the reactions of polychlorobenzenes well confirmed the successive and stepwise dechlorination reactions. For example, in the reaction of 1,2,3,4-tetrachlorobenzene, 1,2,4-trichlorobenzene formed preferentially is dechlorinated at the 2 position giving 1,4-di-

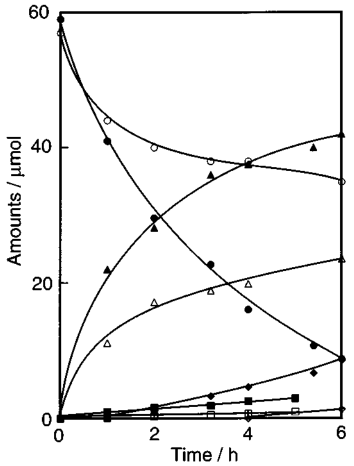

Fig. 1 Time profile of the photocatalytic dechlorination of 1,4-dichlorobenzene by ZnS nanocrystallites. In the presence of ZnS: 1,4-dichlorobenzene (●), chlorobenzene (▲), benzene (◆), hydrogen (■); in the absence of ZnS: 1,4-dichlorobenzene (○), chlorobenzene (△), benzene (◇), hydrogen (□).

Table 1 Dechlorination of various chlorobenzenes by ZnS–DMF[a]

Substrate[b]	E_{red}[c]/V *vs.* SCE	t[d]/h	Conv.[e] (%)	Composition of reaction products/mol%							
				ben	m	1,2-di	1,3-di	1,4-di	1,2,3-tri	1,2,4-tri	tetra
m	−2.44	4.2	31	32	69	—	—	—	—	—	—
1,2-di	−2.22	4.0	59	4.3	64	41	—	—	—	—	—
1,3-di	−2.20	4.0	56	2.9	58	—	44	—	—	—	—
1,4-di	−2.20	4.0	73	7.9	64	—	—	27	—	—	—
1,2,3-tri	−1.96	3.9	90	Trace	36	34	21	0	10	—	—
1,2,4-tri	−2.00	5.0	69	Trace	15	4.0	9	39	—	31	—
tetra	−1.76	4.0	75	Trace	1.6	1.6	2	7.8	6.9	44	25

[a] Reaction solution containing substrate (25 mM), TEA (1 M) and ZnS (2.5 mM) in DMF was irradiated with UV light ($\lambda > 300$ nm) under N_2. Abbreviations: ben, benzene; m, chlorobenzene; 1,4-di-, 1,4-dichlorobenzene; 1,3-di, 1,3-dichlorobenzene; 1,2-di, 1,2-dichlorobenzene; 1,2,3-tri, 1,2,3-trichlorobenzene; 1,2,4-tri, 1,2,4-trichlorobenzene; tetra, 1,2,3,4-tetrachlorobenzene. [b] Starting substrates. [c] From ref. 9 and 10; measured in DMSO solution containing TEABr (0.1 M) as electrolyte. [d] Irradiation time. [e] Conversion of substrates.

chlorobenzene as the predominant product in the isomers of dichlorobenzene, and is further dechlorinated to benzene through chlorobenzene.

The order of the photocatalytic dechlorination rates was 1,2,3-trichlorobenzene > 1,4-dichlorobenzene > 1,2,3,4-tetrachlorobenzene > 1,2,4-trichlorobenzene ≈ 1,3-dichlorobenzene ≈ 1,2-dichlorobenzene >> chlorobenzene. This order is roughly explained by the order of the redox potentials shown in Table 1, in other words, ease of reduction of the substrates.

In conclusion, the reduction of polychlorobenzene photocatalyzed by ZnS nanocrystallites gives selective and successive dechlorination without formation of any unidentified byproducts containing chlorine atoms. This photoreduction should provide a new strategy for detoxification of hazardous chlorinated aromatics under minimum-energy conditions.

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