

Photoreductive Dehalogenation of Halogenated Benzene Derivatives Using ZnS or CdS Nanocrystallites as Photocatalysts

HENGBO YIN, YUJI WADA,
TAKAYUKI KITAMURA, AND
SHOZO YANAGIDA*

Material and Life Science, Graduate School of Engineering,
Osaka University, Suita, Osaka 565-0871, Japan

ZnS nanocrystallites (nc-ZnS) prepared in *N,N*-dimethylformamide (DMF) photocatalyze dehalogenation of halogenated benzenes to benzene as the final product from chlorinated benzenes and to difluorobenzenes from fluorinated benzenes in the presence of triethylamine (TEA) as an electron donor under UV light irradiation ($\lambda > 300$ nm). When CdS nanocrystallites (nc-CdS) are used as a photocatalyst ($\lambda > 400$ nm), halogenated benzenes are photoreductively dehalogenated, yielding trichlorobenzene from hexachlorobenzene and tetrafluorobenzene isomers from hexafluorobenzene as the final products. Photoformed electrons on nc-ZnS and nc-CdS have such negative reduction potentials that these electrons reduce polyhalogenated benzenes, leading to the successive dehalogenation. nc-ZnS exhibits higher photocatalytic activity than nc-CdS due to the more negative potential of the electrons on nc-ZnS than that on nc-CdS. The higher activities of nc-ZnS and nc-CdS compared to their bulk forms are explained as being due to their quantum size effects and the adsorptive interaction between the substrates and the nanosized photocatalysts.

Introduction

Photocatalytic reactions have attracted the attention of scientists in the fields of photosynthesis (1, 2) and pollutant treatment (1, 3–15). In particular, with respect to the environmental protection issues, halogenated chemicals, such as pesticides, halogenated benzenes, and halogenated aliphatic hydrocarbons, are difficult to decompose completely to CO₂, H₂O, and HCl by incineration, and toxic chemicals such as dioxins are detected in incinerator fields. Recently, many researchers have devoted their efforts to performing the photodehalogenation of polyhalogenated compounds under mild conditions (11, 13, 14, 16). There exist two pathways for photocatalytic dehalogenation in which semiconductor particles are used as photocatalysts; one is photocatalytic oxidation using nanosized TiO₂ as a catalyst under atmospheric conditions (3, 4, 7–10), and the other is photocatalytic reduction using semiconductors as catalysts and some electron donors (11, 13, 14). In general, the oxidation potentials of the halogenated compounds are highly positive, suggesting difficulty of oxidation in nature. Furthermore, in photocatalytic oxidation, the hydroxyl radical plays a domi-

nant role in the dehalogenation process, yielding intermediary aldehyde and carboxylic acids which still contain carbon–chlorine bonds (3, 4, 7–10, 17).

On the other hand, the excited electrons on nc-ZnS and nc-CdS exhibit highly negative reduction potentials, and the nanocrystallites are effective photocatalysts for the photoreduction of CO₂, aromatic ketones, amides, and electron-deficient alkenes under UV or visible light irradiation (1a, h, j) when triethylamine (TEA) is employed as an electron donor. In our previous communication, the high activity of nc-ZnS for dechlorination of chlorinated benzene was reported briefly (1f). Keeping these facts in mind, we thoroughly investigated photocatalytic dehalogenation of halogenated benzenes using nc-ZnS or nc-CdS under UV and visible light irradiation, respectively, in the presence of TEA as an electron donor. The present paper deals with photoreductive dehalogenation using nc-ZnS or nc-CdS as a photocatalyst, by taking into account the fact that the toxicity of organic halides can be decreased by decreasing the halogen content in compounds (18).

Experimental Section

Materials. Halogenated benzenes were obtained from the following sources: monochlorobenzene, dichlorobenzenes, trichlorobenzenes, tetrachlorobenzenes, 1,4-difluorobenzene, and 1,2,3,4-tetrafluorobenzene from Wako Pure Chemicals Industries; pentachlorobenzene, hexachlorobenzene, 1,2-difluorobenzene, 1,3-difluorobenzene, 1,2,4-trifluorobenzene, 1,3,5-trifluorobenzene, and hexafluorobenzene from Tokyo Kasei Organic Chemicals; and 1,2,3-trifluorobenzene, 1,2,3,5-tetrafluorobenzene, 1,2,4,5-tetrafluorobenzene, and pentafluorobenzene from Aldrich Chem. Co. Zinc perchlorate and cadmium perchlorate (from Mitsuwa) were used as received. Triethylamine (TEA) (from Wako) was used after fractional distillation. *N,N*-Dimethylformamide (DMF) (from Wako) was used as delivered. All chemicals mentioned above are guaranteed reagent grade. Highly pure CdS (99.99%, particle size 2.5 μ m) and ZnS (99.9%, particle size 3 μ m) bulk powders were commercially purchased from Furuuchi Pure Chemicals and Nacalai Tesque, respectively, and in this paper, they are called the bulk powders.

Preparations of nc-ZnS and nc-CdS in DMF. ZnS and CdS nanocrystallites were prepared in DMF using the methods similar to those described in previous studies (1f, k). A DMF solution 5 mL of Zn(ClO₄)₂·6H₂O (5 mM) or Cd(ClO₄)₂·6H₂O (5 mM) was taken into a Pyrex tube, and then the solution was flushed with nitrogen for 15 min. After oxygen purging, H₂S was introduced into the DMF solution under stirring and cooling in an ice–water bath for 30 or 8 s to prepare nc-ZnS or nc-CdS, respectively. The particle size ranges of nc-ZnS and nc-CdS in DMF were 1.6–2.7 and 2–5 nm, respectively (1f, k). The concentrations of the colloidal solutions of the nanocrystallites are denoted as those of the formulas of ZnS and CdS, which are called the diatomic concentration.

Procedure for ZnS- or CdS-Photocatalyzed Dehalogenation of Halogenated Benzene. To 1 mL of nc-ZnS or nc-CdS (5 mM) DMF solution in a Pyrex tube (diameter 8 mm) was added 1 mL of a DMF solution of halogenated benzene containing TEA (2 M) and dodecane as an internal standard. The photocatalytic reaction mixture was degassed again using nitrogen for 15 min in order to purge dissolved oxygen. The reaction tube was closed using a rubber plug and irradiated under magnetic stirring using a high-pressure mercury lamp ($\lambda > 300$ nm, 500 W) when nc-ZnS was used as a photocatalyst, or a tungsten halogen lamp through a saturated aqueous

* Corresponding author phone: +81-66879-7924; fax: +81-66879-7875; e-mail: yanagida@chem.eng.osaka-u.ac.jp.

TABLE 1. Dechlorination of Chlorinated Benzenes Photocatalyzed by nc-ZnS under UV Light^a

react.	$E_{red.}$ (V vs SCE) ^b	catalyst	react. time (h)	conv. (%)	composition of reaction mixtures (mol %)								
					ben	m	1,2-di	1,3-di	1,4-di	1,2,3-tri	1,2,4-tri	tetra	
m	-2.44	nc-ZnS	4.2	31	32	69							
m		none	4	9	9	91							
1,2-di	-2.22	nc-ZnS	4	59	4.3	64	41						
1,3-di	-2.20	nc-ZnS	4	56	2.9	58		44					
1,4-di	-2.20	nc-ZnS	4	73	8	64			27				
1,2,3-tri	-1.96	nc-ZnS	3.9	90	trace	36	34	21		10			
1,2,4-tri	-2.00	nc-ZnS	5	69	trace	15	4	9	39		31		
tetra	-1.76	nc-ZnS	4	75	trace	1.6	1.6	2	7.8	6.9	44	25	
tetra		bulk ZnS	5	26					trace	trace	26	74	
tetra		none	5	23					2.7	trace	24	77	

^a Reaction conditions: reactant (25 mM), TEA (1 M), and nc-ZnS (diatomic concentrated 2.5 mM) or bulk ZnS (5 mg) in 2 mL of DMF. Abbreviations: tetra, 1,2,3,4-tetrachlorobenzene; 1,2,4-tri, 1,2,4-trichlorobenzene; 1,2,3-tri, 1,2,3-trichlorobenzene; 1,4-di, 1,4-dichlorobenzene; 1,3-di, 1,3-dichlorobenzene; 1,2-di, 1,2-dichlorobenzene; m, chlorobenzene; ben, benzene. ^b From ref 19 in DMSO.

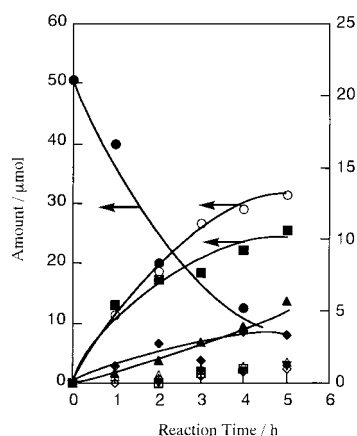


FIGURE 1. nc-ZnS-catalyzed photodechlorination of 1,2,3,4-tetrachlorobenzene in DMF. Conditions are as listed in Table 1. Symbols: ● 1,2,3,4-tetrachlorobenzene, ■ 1,2,4-trichlorobenzene, ◆ 1,2,3-trichlorobenzene, ▲ 1,4-dichlorobenzene, ▼ 1,2-dichlorobenzene, □ 1,3-dichlorobenzene, ◇ chlorobenzene, △ hydrogen, and ○ diethylamine.

sodium nitrite solution filter ($\lambda > 400$ nm, 300 W) when nc-CdS was used as a photocatalyst. The lamps were cooled by water, and the reaction tube was maintained in a water bath (298 K) during irradiation.

For the commercially available ZnS or CdS bulk powder-photocatalyzed dehalogenation, all of the procedures were the same as mentioned above, except that the nanocrystallites were replaced by the bulk powder.

Determination of Apparent Quantum Yields. The quantum yields for dechlorination of 1,2,3,4-tetrachlorobenzene (6.25 mM) photocatalyzed by nc-ZnS (2.5 mM) and nc-CdS (2.5 mM) were determined under irradiation with monochromatic lights at 313 and 405 nm, respectively, by using 2 mL of a DMF solution containing TEA (1 M) in a 4 mL quartz cell. The monochromatic lights (313 and 405 nm) were obtained by using a Xe lamp (TRIAX 180, Instrument S. A., Inc. Edison NJ). The intensity of incident light was monitored by the conventional actinometry method using tris(oxalate) iron(III).

Analysis. The liquid-phase reaction mixtures were analyzed by gas chromatography using a fused silica capillary column (HiCap-CBP20, 25 m \times 0.2 mm, Shimadzu) and a flame ionization detector. Dodecane was used as an internal standard sample. The concentrations of the halogenated benzenes were determined using the ratios of the peak areas of halogenated benzene to those of dodecane. Hydrogen was analyzed by gas chromatography using a Shimadzu GC-8A apparatus equipped with a thermal conduction detector and a column packed with active carbon.

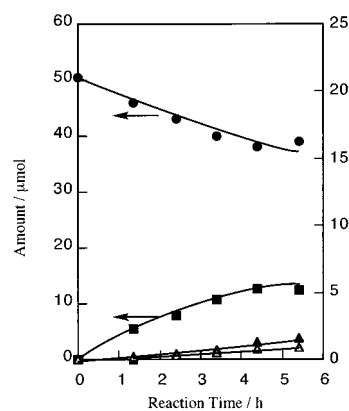


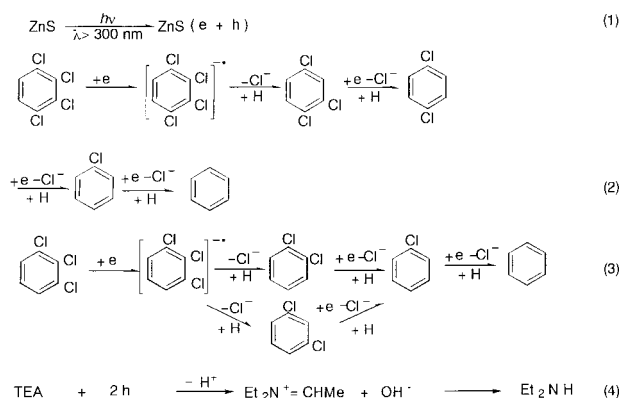
FIGURE 2. Photodechlorination of 1,2,3,4-tetrachlorobenzene with TEA in DMF. Conditions are identical to those in Figure 1, except for the absence of nc-ZnS. Symbols: ● 1,2,3,4-tetrachlorobenzene, ■ 1,2,4-trichlorobenzene, ▲ 1,4-dichlorobenzene, and △ hydrogen.

Spectral analyses of ZnS, CdS, and their interaction with the chlorine-containing compounds were performed using Hitachi U-3300 spectrometer. The diffusion reflectance spectra of nc-ZnS and nc-CdS were measured for the samples obtained by depositing freshly prepared nanocrystallites on filter papers.

Results and Discussion

Photodechlorination Using ZnS. When nc-ZnS was used as a photocatalyst, chlorinated benzenes were successively dechlorinated to benzene at the final stage. The amounts of consumed substrates were in balance with those of the products, indicating that stoichiometric dechlorination occurred in this system. No other byproducts other than the partially dechlorinated benzenes were detected, indicating that this catalytic reaction was very selective. The conversions and the product distributions for dechlorination under various conditions are listed in Table 1. Under UV light irradiation without nc-ZnS, the photodechlorination rate was much lower than that with nc-ZnS. Under visible light ($\lambda > 400$ nm) irradiation, no dechlorination took place even in the presence of nc-ZnS. The commercially available ZnS bulk powder exhibited little activity for the dechlorination of tetrachlorobenzene, even compared to the blank experiment, and the final dechlorinated product was 1,4-dichlorobenzene.

Figures 1 and 2 show the time profiles of the dechlorination of 1,2,3,4-tetrachlorobenzene in the presence and the absence of nc-ZnS, respectively. Although the photocatalytic dechlorination of 1,2,3,4-tetrachlorobenzene clearly showed higher rate than that in the blank experiment, the product distributions were similar for the two systems, i.e., the predominant

SCHEME 1


products were 1,2,4-trichlorobenzene in the trichlorobenzene derivatives and 1,4-dichlorobenzene in the dichlorobenzene derivatives, suggesting the formation of common intermediates in the dechlorination processes for the photocatalytic and photochemical systems. Tetrachlorobenzene was selectively and stepwise dechlorinated to form less-chlorinated homologues, through trichlorobenzene, dichlorobenzene, and monochlorobenzene to benzene as the final product. Diethylamine was formed as an oxidation product from TEA as the reaction progressed. Hydrogen was also competitively formed in the photocatalysis. In addition, the main products were found to be 1,4-dichlorobenzene and 1,2-dichlorobenzene for dechlorination of 1,2,4-trichlorobenzene and 1,2,3-trichlorobenzene, respectively (see Table 1). The main pathways in the photoreductive dechlorination catalyzed by nc-ZnS are demonstrated in Scheme 1. Chlorinated benzenes combine with electrons from the conduction bands of nc-ZnS to form corresponding radical anions, and TEA should transfer their electrons to the holes formed in the valence bands of nc-ZnS under UV light irradiation (1*k*). The electron-transfer process in the catalysis process should be different from that in the photochemical process in which chlorinated benzene radical anion is generated through the direct transfer of an electron from TEA to an excited state of chlorinated benzene as described by Freeman et al. (16*a, c, d*). However, the common intermediates, i.e., the radical anion of the substrate, are formed for the two systems. Hydrogen atoms which replace chlorine atoms should come from TEA. The chloride anions formed from chlorinated benzene derivatives should combine with protons from TEA to form HCl as confirmed by Freeman et al. (16*c, d*).

The apparent quantum yield for dechlorination of 1,2,3,4-tetrachlorobenzene to 1,2,4- and 1,2,3-trichlorobenzene by nc-ZnS irradiated by monochromatic light (313 nm, 5.430 × 10⁻⁹ einstein/min) was 8.6%.

Photodechlorination Using CdS. When nc-CdS was used as a photocatalyst under visible light irradiation ($\lambda > 400$ nm), chlorinated benzenes were photoreductively dechlorinated, yielding trichlorobenzene without further dechlorination (Table 2). The final product in the dechlorination

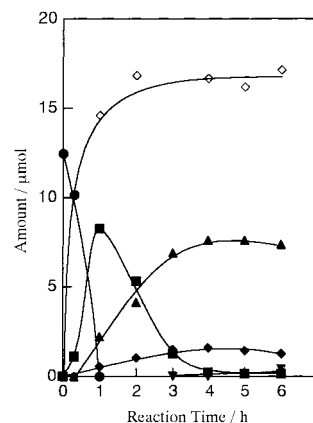


FIGURE 3. nc-CdS-catalyzed photodechlorination of hexachlorobenzene in DMF. Conditions are as listed in Table 2. Symbols: ● hexachlorobenzene, ■ pentachlorobenzene, ▲ 1,2,4,5-tetrachlorobenzene, ◆ 1,2,3,4-tetrachlorobenzene, ▼ 1,2,4-trichlorobenzene, and ◇ diethylamine.

of hexachlorobenzene was pentachlorobenzene when bulk CdS was used in place of nc-CdS, suggesting that the photocatalytic activity of nc-CdS was much higher than that of the bulk CdS. No photodechlorination took place without CdS nanocrystallites.

The nc-CdS-catalyzed photodechlorination of hexachlorobenzene (Figure 3) demonstrated that hexachlorobenzene was completely dechlorinated to form less-chlorinated benzene derivatives in 1 h. Pentachlorobenzene, which was first formed with the elapse of time, reached a maximum after hexachlorobenzene was completely dechlorinated, undergoing further dechlorination. After a short induction time, 1,2,4,5(1,2,3,4)-tetrachlorobenzene appeared, but the formation of 1,2,4-trichlorobenzene required a long induction time. Among the photoformed tetrachlorobenzene isomers, the main product was 1,2,4,5-tetrachlorobenzene, and further photocatalytic dechlorination yielded only 1,2,4-trichlorobenzene as the final dechlorinated product. As shown in Table 2, the amounts of consumed substrates were in balance with those of the products, indicating that stoichiometric dechlorination also occurred for nc-CdS. Diethylamine was also formed as an oxidation product as the reaction progressed. The main photoreductive pathways are demonstrated in Scheme 2.

The apparent quantum yield for dechlorination of 1,2,3,4-tetrachlorobenzene to 1,2,4- and 1,2,3-trichlorobenzene by nc-CdS irradiated by monochromatic light (405 nm, 1.897 × 10⁻⁸ einstein/min) was 1.4%.

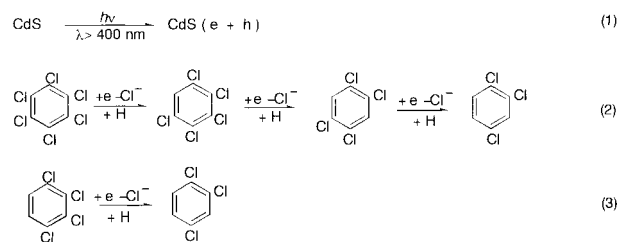
Photodefluorination Using nc-ZnS and nc-CdS. The photocatalysis using nc-ZnS was successfully extended to defluorination of fluorinated benzene derivatives. (Table 3) The defluorination proceeded even in the absence of nc-ZnS, but the defluorination rate in the presence of nc-ZnS was much faster than that in the absence of nc-ZnS. The conversion of hexafluorobenzene or 1,2,4-trifluorobenzene in the presence of nc-ZnS after 4-h irradiation was six and

TABLE 2. Dechlorination of Chlorinated Benzenes Photocatalyzed by nc-CdS under Visible Light^a

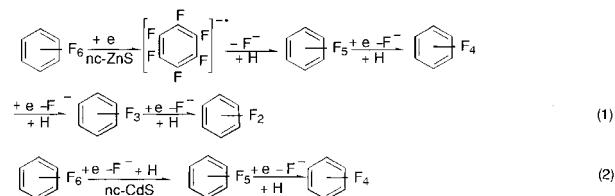
react.	E_{red} (V vs SCE) ^b	catalyst	react. time (h)	conv. (%)	composition of reaction mixtures (mol %)				
					1,2,4-tri	1,2,4,5-tetra	1,2,3,4-tetra	PCB	HCB
HCB	-1.32	nc-CdS	6	100	4	80	14	2	0
HCB		bulk CdS	6	20				20	80
1,2,3,4-tetra		nc-CdS	6	36	36		64		

^a Reaction conditions: reactant (6.25 mM), TEA (1 M), and nc-CdS (diatomic concentrated 2.5 mM) or bulk CdS (5.5 mg) in 2 mL of DMF. Abbreviations: HCB, hexachlorobenzene; PCB, pentachlorobenzene; 1,2,3,4-tetra, 1,2,3,4-tetrachlorobenzene; 1,2,4,5-tetra, 1,2,4,5-tetrachlorobenzene; 1,2,4-tri, 1,2,4-trichlorobenzene. ^b From ref 19 in DMSO.

SCHEME 2



SCHEME 3



four times higher, respectively, than that in the absence of nc-ZnS. After 4-h irradiation, hexafluorobenzene, pentafluorobenzene, tetrafluorobenzene, and trifluorobenzene were defluorinated to form less fluorinated derivatives, but difluorobenzene was not defluorinated any further. The commercially available ZnS bulk powder was of little activity for the defluorination of hexafluorobenzene compared to the blank experiment. The amounts of the consumed substrates were in balance with those of products. The photocatalytic defluorination was a successive process similar to that of chlorinated benzene, and the final product was the difluorinated derivatives (Scheme 3(1)).

When nc-CdS was used as a photocatalyst, hexafluorobenzene was photodefluorinated to form tetrafluorobenzene isomers as the final products via pentafluorobenzene (Table 3). No defluorination of hexafluorobenzene took place under dark or in the absence of nc-CdS. The commercially available CdS bulk powder did not show any photocatalytic activity for the defluorination of hexafluorobenzene. The amount of defluorinated hexafluorobenzene was in balance with that of the produced pentafluorobenzene and tetrafluorobenzene, supporting successive and selective defluorination, as shown in Scheme 3(2).

Mechanism of Photocatalytic Dechlorination. The onsets of the diffusion reflectance UV–visible absorption of commercially available micron-size ZnS and CdS were observed at 375 and 550 nm, respectively. However, the freshly prepared nc-ZnS and nc-CdS exhibited the absorption onsets

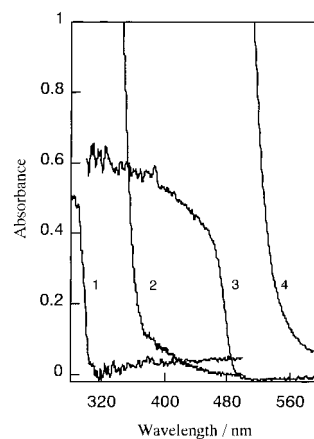


FIGURE 4. Diffusion reflectance spectra of ZnS and CdS: (1) nc-ZnS deposited on filter paper, (2) bulk ZnS, (3) nc-CdS deposited on filter paper, and (4) bulk CdS.

at 310 and 490 nm, respectively (Figure 4). The blue shift in absorption of the freshly prepared sulfide nanocrystallites compared to that of the bulk sulfides is explained as being due to the quantum size effect. The higher photocatalytic activities of nc-ZnS and nc-CdS than their bulk forms should be ascribed to the quantum size effects of nanocrystallites.

The quantum size effect gives rise to electrons having highly negative reduction potential. The conduction band energy of nc-ZnS was estimated to be -2.3 V vs SCE, whereas bulk ZnS was estimated to be -2.0 vs SCE (1g). The conduction band energy of bulk CdS was reported to be -1.90 V vs SCE (1f). However, the photoexcited nc-CdS was estimated to produce electrons having a potential of -2.21 V vs SCE in DMF (1f). The more negative conduction band energy of nc-ZnS than that of nc-CdS and the more negative conduction band energies of nc-ZnS and nc-CdS than those of their corresponding bulk forms should explain the reason nc-ZnS is of higher catalytic activity than nc-CdS and why the nanosized sulfides are of higher activities than their bulk forms.

Figure 5 shows that the absorption onset of the mixture of tetrachlorobenzene and nc-ZnS (spectrum 3) exhibited red-shift, compared to that of only nc-ZnS (spectrum 1) or tetrachlorobenzene (spectrum 2) in DMF. The absorption onsets of the mixtures of hexafluorobenzene and nc-CdS (Figure 6, spectrum 2) and tetrachlorobenzene and nc-CdS (Figure 6, spectrum 3) also exhibited red-shift, compared to that of nc-CdS alone in DMF (Figure 6, spectrum 1). These

TABLE 3. Defluorination of Fluorinated Benzenes Photocatalyzed by nc-ZnS^a and nc-CdS^b

react.	$E_{\text{red.}}$ (V vs SCE) ^c	catalyst	react. time (h)	conv. (%)	composition of reaction mixtures (mol %)					
					DFB	TrFB	TeFB	PFB	HFB	
HFB	-2.11	nc-ZnS	4	64				trace	60	40
HFB		none ^d	4	11					11	89
HFB		bulk ZnS	4	14					14	86
PFB	-2.35	nc-ZnS	4	57		8	44		48	
1,2,4,5-TeFB	-2.40	nc-ZnS	4	37	4	33	63			
1,2,3,4-TeFB		nc-ZnS	4	44	5	35	60			
1,2,4-TrFB	-2.40 to -2.64	nc-ZnS	4	36	37	63				
1,2,4-TrFB		none ^d	4	9	9	91				
HFB		nc-CdS	6	38				trace	38	62
HFB		none ^e	6	0						100
HFB		bulk CdS	6	0						100

^a Reaction conditions: reactant (25 mM), TEA (1 M), and nc-ZnS (diatomic concentrated 2.5 mM) or bulk ZnS (5.2 mg) in 2 mL of DMF. Abbreviations: HFB, hexafluorobenzene; PFB, pentafluorobenzene; TeFB, tetrafluorobenzene isomers; TrFB, trifluorobenzene isomers; DFB, difluorobenzene isomers. ^b Reaction conditions: reactant (6.51 mM), TEA (1 M), and nc-CdS (diatomic concentrated 2.5 mM) or bulk CdS (6 mg) in 2 mL of DMF. ^c From ref 20 in DMF. ^d Blank experiments, other conditions are the same as that with nc-ZnS as a catalyst. ^e Blank experiment, other conditions are the same as that with nc-CdS as a catalyst.

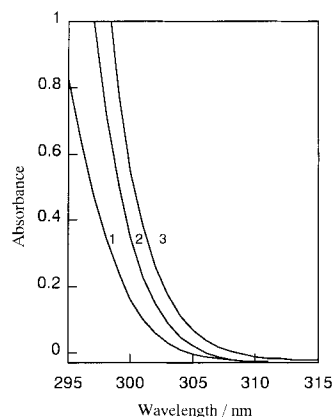


FIGURE 5. UV-vis spectra of nc-ZnS-catalyzed system in DMF: (1) nc-ZnS, (2) 1,2,3,4-tetrachlorobenzene (TeCB), and (3) mixture of TeCB and nc-ZnS. The concentrations are the same as that in nc-ZnS-catalyzed system.

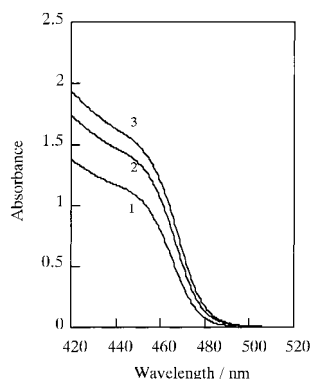
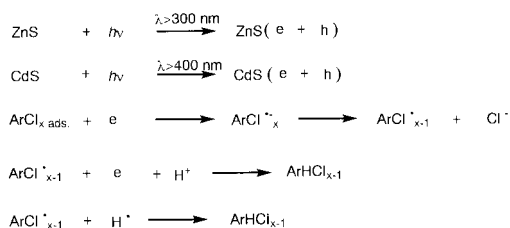


FIGURE 6. UV-vis spectra of nc-CdS-catalyzed system in DMF: (1) nc-CdS, (2) mixture of nc-CdS and HFB, and (3) mixture of nc-CdS and TeCB. The concentrations are identical to that in the nc-CdS-catalyzed system.

SCHEME 4



findings suggest the existence of adsorptive interaction between halogenated benzenes and sulfide nanocrystallites. Such chemisorption should contribute to lowering of the electron-transfer barrier and to sequential electron transfer, as observed in the CO_2 photoreduction (1f, g).

Taking into account the strong adsorptive interaction between sulfide nanocrystallites and substrates, the mechanism of photocatalytic dechlorination by nc-ZnS or nc-CdS is depicted in Scheme 4. The valence band electrons of nc-ZnS and nc-CdS are excited by light irradiation to their conduction bands, giving rise to the formation of electron and hole pairs. The conduction band electrons are transferred to chlorinated benzenes which are adsorbed on the surfaces of the nanocrystallites, resulting in the selective dehalogenation. TEA, as a sacrificial electron donor, is effectively oxidized to DEA, supplying an electron to the hole in the valence band in nc-ZnS or nc-CdS in the dehalogenation processes.

The photocatalytic dehalogenation that occurs under the conditions examined in the present study is a consecutive

and selective reduction process. Since no byproducts are formed in the present dehalogenation processes, the extension of these processes will provide a new concept for the detoxification of highly toxic polyhalogenated aromatics such as dioxin at ambient temperature.

Acknowledgments

This work was partly supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan (Nos. 09490023, 11358006) and "Research for the Future" Program, JSPS 96P00305. We gratefully acknowledge useful discussion with Drs. Hiroaki Fujiwara and Kei Murakoshi, and H. Y. gratefully thanks Mr. Sadao Murasawa for his financial support in Japan.

Literature Cited

- (1) (a) Shiragami, T.; Ankyu, H.; Fukami, S.; Pac, C.; Yanagida, S.; Mori, H.; Fujita, H. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1055. (b) Shiragami, T.; Fukami, S.; Pac, C.; Yanagida, S. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1857. (c) Shiragami, T.; Fukami, S.; Wada, Y.; Yanagida, S. *J. Phys. Chem.* **1993**, *97*, 12882. (d) Shiragami, T.; Pac, C.; Yanagida, S. *J. Phys. Chem.* **1990**, *94*, 504. (e) Shiragami, T.; Fukami, S.; Pac, C.; Wada, Y.; Yanagida, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2461. (f) Yanagida, S.; Kanemoto, S.; Ishibara, K.; Wada, Y.; Sakata, T.; Mori, H. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2063. (g) Kanemoto, M.; Shiragami, T.; Pac, C.; Yanagida, S. *J. Phys. Chem.* **1992**, *96*, 3521. (h) Yanagida, S.; Yoshiya, M.; Shiragami, T.; Pac, C. *J. Phys. Chem.* **1990**, *94*, 3104. (i) Wada, Y.; Yin, H.; Kitamura, T.; Yanagida, S. *Chem. Commun.* **1998**, 2683. (j) Kanemoto, M.; Shiragami, T.; Pac, C.; Yanagida, S. *Chem. Lett.* **1990**, 931. (k) Kanemoto, M.; Hosokawa, H.; Wada, Y.; Murakoshi, K.; Yanagida, S.; Sakata, T.; Mori, H.; Ishikawa, M.; Kobayashi, H. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2401. (l) Shiragami, T.; Pac, C.; Yanagida, S. *Chem. Commun.* **1989**, 831.
- (2) Fox, M. A.; Dulay, M. T., *Chem. Rev.* **1993**, *93*, 341.
- (3) Theurich, J.; Lindner, M.; Bahnemann, D. W. *Langmuir* **1996**, *12*, 6368.
- (4) Choi, W.; Hoffmann, M. R. *J. Phys. Chem.* **1996**, *100*, 2161.
- (5) Bunce, N. J.; Gallagher, J. C. *J. Org. Chem.* **1982**, *47*, 1955.
- (6) Villenave, E.; Orkin, V. L.; Huie, R. E.; Kurylo, M. *J. Phys. Chem.* **1997**, *101*, 8513.
- (7) Calza, P.; Minero, C.; Pelizzetti, E. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3765.
- (8) Stafford, U.; Gray, K. A.; Kamat, P. V. *Res. Chem. Intermed.* **1997**, *23*, 355.
- (9) Calza, P.; Minero, C.; Pelizzetti, E. *Environ. Sci. Technol.* **1997**, *31*, 2198.
- (10) Mas, D.; Pichat, P.; Gullard, C. *Res. Chem. Intermed.* **1997**, *23*, 275.
- (11) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
- (12) Mills, A.; Davies, R. H.; Worsley, D. *Chem. Soc. Rev.* **1993**, 417.
- (13) Kuchmii, S. Y.; Korzhak, A. V.; Kulik, S. V.; Belous, A. I.; Kryukov, A. I. *Theoretical Exptl. Chem.* **1994**, *30*, 30.
- (14) Choi, W.; Hoffmann, M. R. *Environ. Sci. Technol.* **1995**, *29*, 1646.
- (15) Schmelling, D. C.; Gray, K. A.; Kamat, P. V. *Environ. Sci. Technol.* **1996**, *30*, 2547.
- (16) (a) Freeman, P. K.; Ramnath, N. *J. Org. Chem.* **1988**, *53*, 3, 148. (b) Freeman, P. K.; Ramnath, N.; Richardson, A. D. *J. Org. Chem.* **1991**, *56*, 3643. (c) Freeman, P. K.; Ramnath, N. *J. Org. Chem.* **1991**, *56*, 3646. (d) Freeman, P. K.; Srinivasa, R.; Campbell, J. A.; Deinzer, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 5531.
- (17) Minero, C.; Maurino, V.; Pelizzetti, E. *Res. Chem. Intermed.* **1997**, *23*, 291.
- (18) Pelizzetti, E.; Serphone, N. *Homogeneous and Heterogeneous Photocatalysis*; D. Reidel Publishing Company: Dordrecht, Holland, 1986; p 619.
- (19) Bard, A. J.; Lund, H. *Encyclopedia of Electrochemistry of the Elements, Organic Section*; Marcel Dekker: New York, 1980; Vol. XI, p 182.
- (20) Loutfy, R. O. *Can. J. Chem.* **1976**, *54*, 1454.

Received for review March 20, 2000. Revised manuscript received October 3, 2000. Accepted October 9, 2000.

ES001114D