quency of the carbon–halogen bond, ν, according to

$$\Delta G^{\ddagger}_{0,\mathrm{iso}} = \mathrm{Cst}\, \nu^2 \, (\Delta d^{\ddagger})^2$$

where $\Delta d^{\ddagger}$ is the difference in the carbon–halogen distance between the initial and the transition states. It is seen that the ratio of $\Delta G^{\ddagger}_{0,\mathrm{iso}}$ over ν^2 (Table III) is about constant in all series of butyl halides. The ease of stretching of the carbon–halogen bond thus appears as the dominant factor governing the rate of the reductive cleavage. (The relative variation of location of the transition state vis-à-vis the initial state is less than 20% in the series.)

Concluding Remarks

The main conclusions that emerge from the preceding results and discussion are the following. The kinetics of the heterogeneous and homogeneous reductive cleavage of the carbon–halogen bond in simple aliphatic halides are governed by the same activation–driving force free-energy relationship. It is consistent with a concerted electron transfer–bond breaking mechanism implying that the origin of the driving force scale is the standard potential of the $RX/R\cdot + X^-$ couple and not that of the $RX/RX^{-}\cdot$ couple. The activation–driving force relationship is nonlinear. It can be approximated by a quadratic equation of the Hush–Marcus type. Not unexpectedly, some deviation vis-à-vis this behavior appears for very large values of the driving force.

Experimental Section

Chemicals. The DMF was from commercial origin (Merck) and was vacuum-distilled before use. The supporting electrolyte (Fluka puriss.) was used as received. The butyl halides, from commercial origin, were distilled before use, and the mediators were used as received.

Instrumentation. The electrochemical cell was equipped with a water jacket, allowing the temperature to be fixed by means of a thermostat (10 °C with the *t*- and *sec*-Bu halides and 20 °C with the *n*-butyl halides). For direct electrochemical experiments, the working electrode was in all cases a glassy carbon (IMC Industry, Japan—Grade CG-A) disc of 3-mm diameter. This was polished by using a 1-μm diamond paste and ultrasonically rinsed in ethanol before use. Several control experiments were carried out with a gold disc electrode (1-mm diameter) pretreated in the same way. A mercury drop suspended from a 1-mm gold disc was used as the working electrode for the mediated electrochemical reduction experiments. It was checked with several mediator–alkyl halide couples that the results are the same as with a glassy carbon electrode. The counterelectrode was a mercury pool and the reference electrode an aqueous SCE in all cases.

The cyclic voltammetry apparatus was composed of a home-built solid-state amplifier potentiostat equipped with positive feedback *iR* drop compensation and a PAR (Model 175) function generator. The voltammograms were displayed on a chart recorder (Ifelec 2502) for sweep rates below 0.5 V.s^{-1}. For higher sweep rates, a Nicolet (3091) allowing the automatic determination of peak heights and peak potential was used.

The numerical calculations were carried out on a MINI 6 BULL computer and all the figures (with the exception of Figures 1 and 2) were directly drawn on a 1102 Benson plotter.

Acknowledgment. The attribution of a fellowship to I. G. by the Ministerio de Educación y Ciencia is gratefully acknowledged. Discussions with Prof. L. Nadjo (Université de Nancy, France) during the initial stage of this work were very fruitful.

Registry No. *n*-BuI, 542-69-8; *n*-BuBr, 109-65-9; *sec*-BuI, 513-48-4; *t*-BuI, 558-17-8; *sec*-BuBr, 78-76-2; *t*-BuBr, 507-19-7; *n*-BuCl, 109-69-3; *sec*-BuCl, 78-86-4; *t*-BuCl, 507-20-0.

Supplementary Material Available: Kinetic data for the reduction of butyl halides, i_p/i_p° vs. γ plots of mediators, and λ_1 and ρ parameter fittings of each butyl halide (76 pages). Ordering information given on any current masthead page.

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Semiconductor Photocatalysis.[1] Cis–Trans Photoisomerization of Simple Alkenes Induced by Trapped Holes at Surface States

Shozo Yanagida,* Kunihiko Mizumoto, and Chyongjin Pac

Contribution from Chemical Process Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan. *Received May 13, 1985*

Abstract: The use of ZnS or CdS as photocatalysts induces an efficient cis–trans photoisomerization of simple alkenes, e.g., the 2-octenes, 3-hexen-1-ols, and methyl 9-octadecenoates in photostationary cis–trans ratios almost identical with the thermodynamic equilibrium ratios achieved by the phenylthio radical. Quantum yields for the cis–trans photoisomerization, ϕ_{c-t}, exceed largely over unity. Mechanistic studies involving Stern–Volmer analyses, quenching effect of oxygen, and ESR analyses under band-gap irradiation of ZnS in methanol demonstrate that the photoisomerizations take place with high turnover numbers at active sites where trapped holes at surface states, i.e., sulfur radicals arising from Zn vacancies and/or interstitial sulfur on sulfide semiconductors, play decisive roles. A highly efficient catalysis occurs with ZnS sols prepared from polysulfide-containing Na_2S solution. The trapped-hole mechanism is further supported by the enhanced effect of water acting as a good electron acceptor as well as the quenching effect of diethylamine acting as an electron donor.

Photoreactions at semiconductor/liquid or vapor interface are generally discussed based on the separation of electrons and holes upon absorption of photons.[2] The separated electron and hole are considered to migrate to the surface of the irradiated semiconductor on which photoredox reactions occur. Our recent studies revealed that not only the reductive H_2 generation but also sequential two-electron reductions of organic substrates occur efficiently on ZnS without noble metal modification and that the one-hole oxidation which leads to carbon–carbon bond formation or the two-hole oxidation through intermediary carbocation is observable depending on organic substrates and reaction conditions.[3] On the other hand, photoinduced organic reactions without

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net oxidations at dispersed semiconductor interface were also elucidated by several research groups, including photocycloreversions of strained cage molecules[4] and dianthracene,[5] and photodimerization of phenyl vinyl ether[6] by ZnO and CdS which are enhanced by coexistence of oxygen molecule. These reactions were suggested to involve radical cations generated by the electron transfer between substrates and irradiated semiconductors.

Although photooxidation of olefins in the semiconductor–oxygen system was first reported by Tokumaru et al.[7] and extensively investigated by Fox et al.,[8] little attention has been paid on their cis–trans photoisomerizations.[9] Recently de Mayo and his group[10] reported CdS-photocatalyzed cis–trans equilibrium of styrene derivatives through the radical cations generated by electron transfer from the olefins to the photogenerated holes on the semiconductor. On the other hand, we found that ZnS and CdS sols efficiently catalyze photochemical cis–trans isomerization of methyl 9-octadecenoates (oleate and elaidate).[11] Prominently, quantum yields of the photoisomerization exceed largely over unity for several simple alkenes using suitably prepared ZnS sols.

In this paper, we report in detail ZnS- or CdS-catalyzed cis–trans photoequilibrations of simple alkenes in which trapped-holes arising from surface defects or impurities might play essential roles.

Experimental Section

Materials. Alkenes were obtained from the following sources: *cis*-2-pentene (Extra pure (EP) grade), *cis*-2-octene (EP grade), *cis*-3-hexen-1-ol (EP grade), *trans*-2-hexene (Guaranteed reagent (GR) grade), and *trans*-2-octene (GR grade) from Tokyo Kasei, *cis*-2-hexene (EP grade) and *trans*-2-hexene (GR grade) from Nakarai Chemicals, *trans*-2-pentene (GR grade) from Wako Pure Chemical Industries, methyl *cis*-9-octadecenoate (99%) from Sigma, and methyl *trans*-9-octadecenoate (standard for GLC) from Merck. The EP grade cis alkenes were all purified by fractional distillation and were determined to include the respective trans isomer as follows: *cis*-2-pentene (2.7% trans), *cis*-2-hexene (17% trans), *cis*-2-octene (4.9% trans), and *cis*-3-hexen-1-ol (2.4% trans). Sodium sulfide, zinc sulfate, and mercuric chloride were GR grade of Wako, sodium chlorate and ammonium hexafuluorophosphate were GR grade of Nakarai, and cadmium perchlorate was GR grade of Mitsuwa Chemicals. ZnS (GR grade, Nakarai), ZnS for electroluminescence (Mitsuwa), CdS (Aldrich Gold label), CdS (GR grade, Nakarai), ZnSe (GR grade, Nakarai), TiO_2 (Anatase, Merck), ZnO (GR grade, Wako), and SnO_2 (Aldrich Gold label) were used after being degassed in vacuo. Solvents used were all GR grade chemicals and were used after distillation. Diphenyl sulfide (GR grade) was obtained from Nakarai Chemicals. Platinum black was obtained from Nippon (Japan) Engelhard.

Analyses. The determination of the cis–trans ratio of the simple alkenes (and of detection of positional isomers) was carried out by gas chromatography on a Shimadzu GC-7AF apparatus equipped with flame ionization detectors and the following columns: a 3 m × 3 mm column packed with 25% β,β'-oxydipropionitrile on Shimalite (NAW) (60–80 mesh) for 2-pentenes, 2-hexenes, 3-hexenes, and 2-octenes; a 3 m × 3 mm column packed with 25% polyethylene glycol 20 M on Shimalite (NAW) (60–80 mesh) for 3-hexen-1-ol. Decrease of *cis*-2-octene was monitored by using a 2 m × 3 mm column of 5% Ucon LB 550X on Uniport B (60–80 mesh) and ethyl acetate or methyl hexanoate as an internal reference. H_2 evolution was analyzed by GLC with use of an active carbon column (2 m × 3 mm) on Shimadzu GC-3BT at 100 °C as reported in the preceeding paper.[3] The cis–trans ratio of the methyl 9-octadecenoates was determined by high-pressure liquid chromatography on Yanapak ODS-T 25 cm × 4 mm with UV detector of Yanagimoto M-315.

Photoacoustic spectra were recorded by using an EDT Reserch Model OAS 400 spectrometer and UV spectra with Hitachi 220A spectrophotometer.

ESR Measurements. The ESR spectra were recorded at liquid nitrogen temperature at X band with 100-KHz modulation on a JEOL JS-ME-2X spectrometer. Prior to measurements all samples were thoroughly deoxygenated by the freeze–pump–thaw technique and irradiated for 10 min within a cryostat cavity (filled with liquid nitrogen) with UV light from a 100-W high-pressure mercury lamp. A sample of ZnS-2 sols in methanol was also irradiated at room temperature for 30 min with the UV lamp which was filtered through a Pyrex filter.

Preparation and Classification of Semiconductor Sols. ZnS sols were prepared in situ by mixing equal amounts of methanolic or aqueous solutions (0.04 M, 1 mL) of sodium sulfide and zinc sulfate with magnetic stirring at room temperature (20–25 °C). It was confirmed that the influence of excess ions (Zn^{2+} or S^{2-}) was negligible in the photoisomerization. Similarly CdS and HgS sols were prepared by using solutions of $Cd(ClO_4)_2$ and $HgCl_2$.

Methanolic and aqueous ZnS sols revealed identical optical absorption spectra from which the apparent molar absorption coefficient was estimated to be 200 M^{-1} cm^{-1} in methanol at 313 nm. Transmission electron micrographs showed that the particle sizes are less than 10 nm, comparable with those of the aqueous ZnS sols.[12]

Since activities of ZnS sols depend on periods of time for storage of methanolic Na_2S solutions, the ZnS sols were classified as follows. ZnS-1: the ZnS sols prepared by using a methanolic Na_2S solution which was left standing for 2 weaks after preparation to contain white precipitates. ZnS-2: ZnS sols prepared by using a fresh Na_2S solution. Aqueous ZnS sols and methanolic CdS sols were also classified in a similar manner. ZnS-2 sols used for the photoisomerization of methyl 9-octadecenoates were prepared from methanolic solution (0.02 M) of anhydrous yellowish Na_2S obtained by vacuum drying.

Photoisomerization Using Freshly Prepared Semiconductor Sols. To 2 mL of methanolic ZnS (0.04 mmol) suspensions in a Pyrex tube (8 mm in diameter) was added a pure alkene or an alkene of a given isomer composition in an amount to make a 0.05 M solution. The resulting methanolic solution was flushed with argon gas under cooling on an ice bath and then irradiated at 25 °C with a 500-W high-pressure mercury lamp fitted with an aqueous potassium chromate solution filter. Stirring was accomplished by using a magnetic stir-bar (5 mm × 2 mm). The cis–trans ratios were determined by periodic GLC analyses.

Typical procedures for photoisomerization in mixture solvents are as follows. MeOH/H_2O (10:1 v/v): to the methanolic ZnS suspensions containing 0.04 mmol of ZnS sols were added 200 μL of water and the resulting mixture was used after removing 200 μL from it. H_2O/MeOH (1:9 v/v): the ZnS suspension containing 0.4 mmol of ZnS was prepared from 1 mL of an aqueous Na_2S solution (0.4 M) and 1 mL of an aqueous $ZnSO_4$ solution (0.4 M), and then 200 μL of the suspension were mixed with 1.8 mL of methanol. The resulting ZnS suspension was used for photoisomerization.

Photoisomerization Using Semiconductor Powders. All reactions were performed in a Pyrex tube with 1 mL of a methanolic alkene solution (0.05 M) and a semiconductor (40 mg). The mixture was sonicated for 10 min, flashed with argon gas, and then irradiated as described for the photoisomerization with the sols.

Photoisomerization in the Presence of Diphenyl Sulfide. A cyclohexane or benzene solution (2 mL) of alkene and diphenyl sulfide (10^{-4} mol) was irradiated with a 500-W high-pressure mercury lamp fitted with an aqueous potassium chromate solution filter. Prior to irradiation the sample was flushed with argon gas.

Blank Experiments. In the absence of photocatalysts, none of the alkenes was isomerized under irradiation of 313-nm light. In addition, no isomerization was observed by refluxing a methanolic solution of *cis*-2-octene (0.04 M) and ZnS sols (0.04 mmol) for 9.5 h. *cis*-2-Octene photoisomerized in a methanolic Na_2S solution (0.04 M) which had been stored about 2 weeks and then contained white precipitates, but in a very low quantum yield (0.006 at 313 nm).

Determination of Quantum Yields. The quantum yields for the isomerization were determined at 313 nm. The monochromatic light was isolated from a 500- or 300-W high-pressure mercury lamp with use of the following filter: aqueous potassium chromate solution filter (313-F)[13a] in combination with Toshiba UV-29 glass filter[13b] (313-nm light) for ZnS-catalyzed photoisomerization, 313-F solution filter combined with Toshiba UV-D33S glass filter (313 nm light) for CdS- and HgS-catalyzed photoisomerization.[13b] The intensity of incident light was

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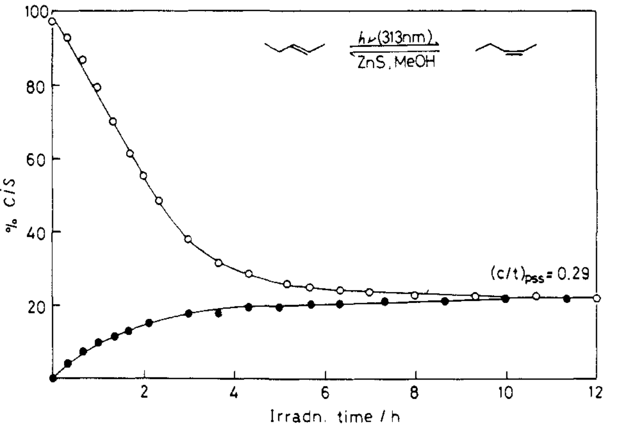

Figure 1. ZnS-catalyzed cis–trans photoequilibration of the 2-pentenes: ○, starting from *cis*-2-pentene; ●, starting from *trans*-2-pentene. Conditions: ZnS-1, 0.04 mmol; 2-pentene, 0.05 M; solvent, methanol; volume of solution, 2 mL; 313-nm irradiation.

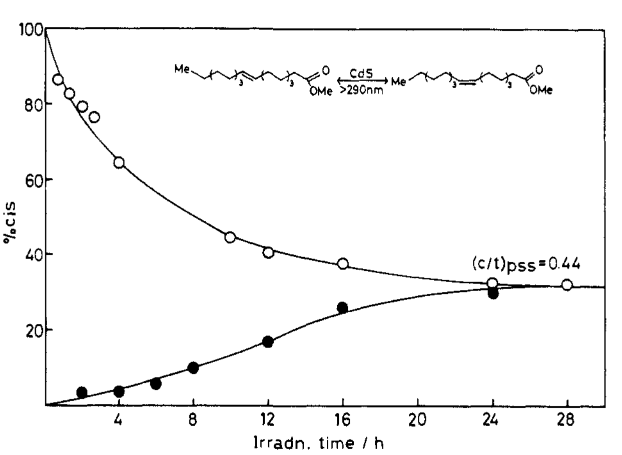

Figure 2. CdS-catalyzed cis–trans photoequilibration of the methyl 9-octadecenoates: ○, starting from the cis isomer; ●, starting from the trans isomer. Conditions: CdS-2, 0.04 mmol; methyl 9-octadecenoate, 0.05 M; >290-nm irradiation; for other conditions see Figure 1.

monitored by 2-hexanone actinometry.

Toshiba UV-35 and UV-D36C glass filters were used for photoisomerization under the 366-nm light, aqueous sodium nitrite solution filter being used to obtain the >400-nm light.[13]

Results and Discussion

Photoisomerization with ZnS and CdS Sols. Figure 1 shows the sequence of photoisomerization of the 2-pentenes occurring upon >290-nm irradiation of freshly prepared ZnS suspensions (ZnS-1) in methanol. After 10 h, cis–trans equilibration was attained from either the cis or trans isomer. The comparable photoisomerization was also induced by CdS sols as shown in Figure 2 for the methyl 9-octadecenoates, in which the cis–trans ratio at the photostationary state is 0.44. Freshly prepared HgS also showed a catalytic activity under the comparable condition with 313-nm light, but with very low efficiency.

The irradiation light for the photoisomerization should be higher in energy than the band-gap, since no photoreaction occurred upon irradiation of ZnS solutions at ≥366 nm. With CdS sols, irradiation at 366 nm or at ≥400 nm also induced the photoisomerization. In the absence of the sols, however, none of the alkenes was isomerized under >290-nm light irradiation. Under 313-nm light irradiation of *cis*-2-octene in the presence of Na_2S, photoisomerization was observed but with a very low efficiency (see Experimental Section).

The photoisomerizations proceed very cleanly. During irradiation, neither double-bond migration nor hydrogenation occurred in any cases. In addition, the disappearance of starting alkenes was negligible even after the equilibrium had been reached. The methyl octadecenoates and 3-hexen-1-ols were consumed only in small amounts, and HPLC analysis indicated the formation of a negligible amount of positional isomers in the former case.

Table I. Photostationary Cis–Trans Ratios of Alkenes Induced by Semiconductors, Triplet Sensitizers, and Diphenyl Sulfide

alkene[a]	ZnS(sol)[b]	CdS(sol)[b]	benzene[c]	acetone[d]	PhSPh[e]
2-pentene	0.29	0.29	1.10[f]	0.66[f]	0.29
2-hexene	0.29	0.29	1.0[g]		0.29
3-hexen-1-ol	0.22	0.39	0.74		0.23
3-hexene	0.17	0.35	0.97		0.22
2-octene	0.29	0.30[h]	1.00[i]	0.59	0.30
methyl oleate	0.20	0.44	0.76	0.45	0.22

[a] At 0.05 M. [b] For 2 mL of methanol solution in the presence of 0.04 mmol of the sols irradiated at 313 nm. [c] Irradiation in neat benzene at 254 nm. [d] Irradiation in neat acetone at 313 nm. [e] Irradiation of a cyclohexane or benzene solution at 313 nm. [f] See ref 16. [g] See ref 17. [h] A similar photostationary ratio was obtained by 366-nm irradiation. [i] See ref 18.

Table II. Quantum Yields of Photocatalytic Isomerization of Alkenes under 313-nm Irradiation[a]

alkene	catalyst[b]	ϕ_{c-1}	ϕ_{1-c}
2-pentenes	ZnS-1	3.3	1.3
2-hexenes	ZnS-1	3.1	1.1
2-octenes	ZnS-1	2.2	0.78
2-octenes	ZnS-2	0.60	0.21
2-octenes	CdS-2	0.36	0.18
methyl 9-octadecenoates	ZnS-1	0.77	0.18

[a] At 0.05 M. [b] Catalyst = 0.04 mmol/2 mL.

Table I shows the cis–trans ratios at the photostationary state attained from either cis or trans isomer by irradiated ZnS or CdS. CdS sols also gave a photostationary ratio, 0.29, for the 2-octenes under 366-nm or >400-nm light. It is known that phenylthio radical produced thermally or photochemically from diphenyl sulfide effects rapid isomerization of alkenes to give a thermodynamic equilibrium without double bond migration.[14] The ratios were thus obtained by irradiating alkene solutions in the presence of diphenyl sulfide and are shown in Table I together with those of ZnS- or CdS-catalyzed photoisomerization and the triplet-sensitized isomerization. It becomes apparent that the present cis–trans photoisomerization is thermodynamically controlled in most cases. It is noteworthy, however, that the cis–trans ratios of functional alkenes obtained in the presence of CdS sols are larger than those of 2-alkenes and different from those attained by ZnS sols and that they deviate from the thermodynamic ratios as well as that of 3-hexene attained in the presence of ZnS sols.[15]

Quantum Yields. As shown in Table II, the ZnS sols are superior to the CdS sols in efficiency at 313-nm light. Interestingly, the quantum yields with ZnS-1 exceed over unity for the *cis*-2-alkene photoisomerization. Catalytic activities of ZnS-1, which was prepared from a methanolic Na_2S solution stored for 2 weeks is much higher (about 4 times) than ZnS-2 which was prepared from fresh solutions. A similar observation was confirmed for aqueous ZnS sols; ZnS-1 was about seven times as active as ZnS-2. Although ZnS-1 gave stable dispersion in methanol better than ZnS-2, their photoacoustic spectra which were measured after drying to powder were almost identical.

The Na_2S solution used for the preparation of ZnS-1 was exposed to air for a long period of time to form some precipitates. Chen and Gupta[19] reported that a Na_2S solution undergoes partial

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(13) (a) Murov, S. L. "Handbook of Photochemistry"; Mercel Dekker: New York, 1973. (b) Since 230-nm light and visible light with the wavelength longer than 400 nm pass through the 313-F filter, the glass filters were used combined with it for the respective purpose.

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Table III. Comparison between Photocatalyzed and Photosensitized Isomerization of Methyl 9-Octadecenoates and 2-Octenes[a]

alkene	catalyst	band gap or Et energy (eV)	ϕ^{∞}_{c-t}	ϕ^{∞}_{t-c}	$\alpha/1-\alpha$	$\phi(c/t)_{pss}$
methyl 9-octadecenoates	ZnS-2	3.66	0.72	0.23	0.29	0.20
	acetone	3.47	0.57	0.40	0.71	0.45
	acetophenone	3.21	0.84	0.16	0.19	0.64
2-octenes	ZnS-1	3.66	4.4	2.7		0.29
	benzene	3.83	0.50	0.50	1.0	1.0
	acetone	3.47	0.50	0.50	0.99	0.59

[a] Reaction conditions: see Table I.

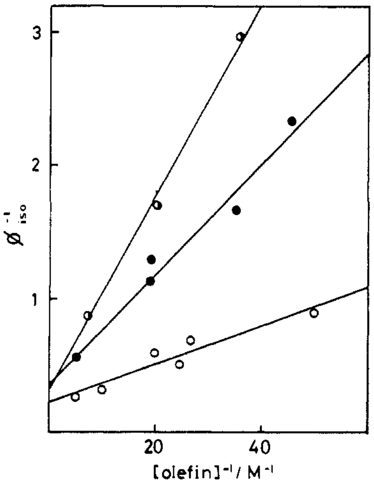

Figure 3. Reciprocal quantum yield of photoisomerization vs. reciprocal alkene concentration in the ZnS-1-catalyzed photoisomerization of cis- (○) and *trans*-2-octene (●) in methanol and (◐) the ZnS-2-catalyzed photoisomerization of *cis*-octene. Reaction conditions: see Figure 1.

oxidation by dissolved air to give polysulfide anions such as S_4^{2-} and S_5^{2-} through S_2^{2-} and S_3^{2-}. Accordingly, it is reasonable to presume that ZnS includes polysulfides as impurities which are probably responsible for high catalytic activities. On the other hand, CdS-1 and CdS-2 showed the comparable activities without such distinguishing difference.

Double-reciprocal plots of quantum yields vs. alkene concentrations give linear correlations for the photoisomerization of 2-octenes with the ZnS-1 sols (Figure 3). The intercepts give the limiting quantum yields $\phi^{\infty}_{c-t} = 4.4$ and $\phi^{\infty}_{t-c} = 2.7$. Figure 3 includes a similar plot for the *cis*-2-octene/ZnS-2 system and gives the limiting quantum yield $\phi^{\infty}_{c-t} = 3.1$. These facts suggest that, as was reported for the CdS-potocatalyzed cis–trans isomerization,[10] Langmuir–Hinshelwood kinetics are appropriate in this photoisomerization and it should be a surface reaction occurring at an active site with a high turnover number.

In the case of the methyl 9-octadecenoates, a similar linear Stern–Volmer correlation was also obtained, the sum ϕ^{∞}_{c-t} and ϕ^{∞}_{t-c} being less than unity and comparable with those obtained by using triplet sensitizers. In order to know whether or not the triplet energy transfer mechanism participates in this photoisomerization, a simple, general reaction scheme was applied to the present inhomogeneous ZnS system by assuming that adsorption and desorption are not rate-determining as shown below:

$$\mathrm{ZnS} \xrightarrow{h\nu} {}^*\mathrm{ZnS}$$

$$^*\mathrm{ZnS} + \mathrm{C} \xrightarrow{k_1} {}^*\mathrm{X}$$

$$^*\mathrm{ZnS} + \mathrm{T} \xrightarrow{k_2} {}^*\mathrm{X}$$

$$^*\mathrm{ZnS} \xrightarrow{k_3} \mathrm{ZnS}$$

$$^*\mathrm{X} \rightarrow \alpha\mathrm{C} + (1-\alpha)\mathrm{T}$$

$$([\mathrm{C}]/[\mathrm{T}])_{pss} = (k_2/k_1)[\alpha/(1-\alpha)]$$

$$1/\phi_{c-t} = [1/(1-\alpha)](1+k_3)/(k_1[\mathrm{C}])$$

$$1/\phi_{t-c} = [1/\alpha](1+k_3)/(k_2[\mathrm{T}])$$

In the above scheme, *X represents an unspecified intermediate, and other symbols and equations have their usual meaning.[16a]

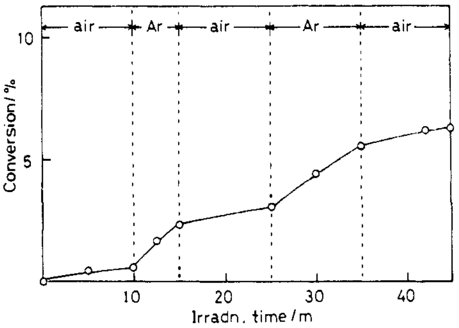

Figure 4. ZnS-catalyzed photoisomerization of *cis*-2-octene in an air or argon atmosphere. Reaction conditions: see Figure 1.

The decay and excitation ratios for an intermediate (*X) with either ZnS or triplet sensitizers were obtained from the slopes and the intercepts in the double reciprocal plots of quantum yields vs. alkene concentration. The results are shown in Table III together with those determined by using two typical triplet sensitizers. Similar calculations were also applied to the 2-octenes and the results are shown together in Table III for comparison. As the decay ratios and the cis–trans ratios at the photostationary state are quite different from those for triplet sensitizers, it is concluded that a triplet energy transfer mechanism is not involved in the ZnS-photocatalyzed isomerization of the methyl octadecenoates.

Effect of Oxygen on ZnS-Catalyzed Photoisomerization. Figure 4 shows the ZnS-1-induced photoisomerization of *cis*-2-octene which was alternately continued under deaerated or aerated conditions, indicating that the photoisomerization was quenched by air. It was further confirmed that the photoisomerization in the oxygen-saturated solution was quenched to about a hundredth of that in the argon-purged system. The catalytic activities were mostly recovered by deaeration after the irradiation under air, but the recovered activities decreased with the increase in the number of cycles of alternating aeration and deaeration. These observations can be easily interpreted by assuming the participation of both reversible and irreversible mechanisms in the oxygen quenching. The former might involve the preferential capture of active sites by O_2 or $O_2^{-}\cdot$ whereas the latter might occur through the lasting degradation of active sites via photooxidation of ZnS to $ZnSO_4$.[12,20]

With regard to oxygen behavior in the irradiated semiconductor system, Fox et al.[8] examined closely the TiO_2/O_2 system in relation with oxidative olefin cleavage and clarified the participation of molecular oxygen and/or superoxide ($O_2^{-}\cdot$) and the cation radicals from olefins. However, no oxidative degradation of alkenes was observed in the present ZnS/O_2 system, indicating that the behavior of O_2 in the ZnS-induced photoisomerization should be different from that in the olefin/TiO_2/O_2 system.

Effect of Water on the ZnS-Catalyzed Photoisomerization. The photoisomerization of *cis*-2-octene in a methanolic ZnS dispersion system remarkably depends on water contents as shown in Figure 5. The enhancing effect of water would arise from increasing adsorption of octene molecules on the hydrophobic ZnS surface. However, the quantum yields obtained are far more than the limiting quantum yields ($\phi^{\infty}_{c-t} = 4.4$) which corresponds to the maximum efficiency attained at the complete coverage of the olefin

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[20] Platz, H.; Schenk, P. W. *Angew. Chem.* **1936**, *49*, 822.

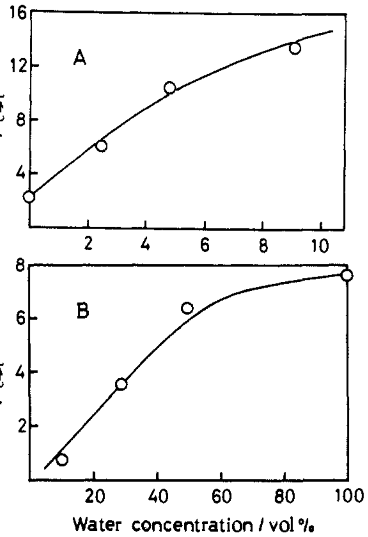

Figure 5. Effect of water on ZnS-catalyzed photoisomerization: (A) *cis*-2-octene in methanol, (B) 3-hexen-1-ol in water. ZnS-1 sols were prepared from aqueous $ZnSO_4$ and Na_2S. Reaction conditions: see Figure 1.

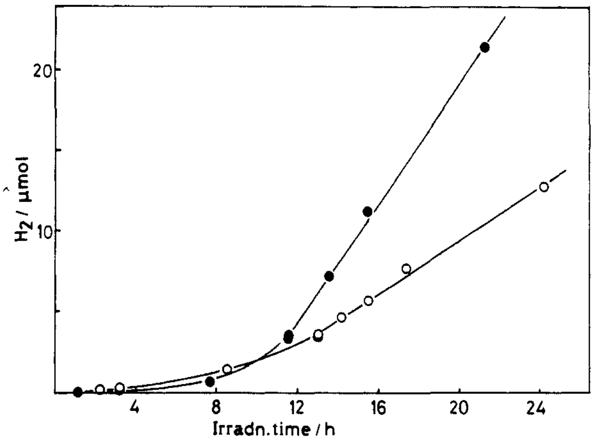

Figure 6. Photogeneration of hydrogen in the ZnS-catalyzed reaction of $MeOH/H_2O$ (10:1 v/v) solution in the presence (○) or absence (●) of *cis*-2-octene (0.05 M). Reaction conditions: identical with those in Figure 5.

on ZnS. In the case of water-soluble 3-hexen-1-ol, moreover, the quantum yield again increased with an increase of water content up to 60% (v/v) as shown in Figure 5. In both cases, the quantum yields have a tendency to level off at higher concentration of water.

It was known that water is an efficient electron acceptor in ZnS-photocatalyzed H_2 generation in the presence of sacrificial electron donors.[3,12,21] Recently, Oosawa and Grätzel reported that BrO_3^- serves as an electron acceptor and enhances a photocatalytic oxygen evolution in aqueous TiO_2 suspensions.[22] In order to carify a role of water as an electron acceptor in the photoisomerization, $NaClO_3$ was added to the *cis*-2-octene/ZnS-2 system in an amount to make a 0.05 M solution. As expected, the quantum yield increased by a factor of 3.3, supporting the idea that electron acceptors like water and $NaOCl_3$ enhance the number and/or the lifetime of active sites on ZnS.[23]

A side reaction in the presence of water was a slow H_2 evolution, and the 2-octene disappeared much more slowly than the photoisomerization. Figure 6 shows a plot of the H_2 evolution against the irradiation time. While the photoisomerization and the disappearance of the octene occurred instantly upon irradiation, the H_2 evolution had a long induction period either in the presence or absence of the octene.

Table IV. ZnS-Photocatalyzed Reactions on *cis*-2-Octene in Aqueous Methanol[a]

catalyst	solvent (v/v)	ϕ_{c-t}	ϕ_{octene}[b]	$\phi_{1/2H_2}$	$\phi_{1/2H_2}$[c]
ZnS-1	MeOH	2.2	$<10^{-3}$	0.007	
ZnS-1	$MeOH/H_2O$ (10:1)	13.5	0.018	0.040	0.086
ZnS-1	$H_2O/MeOH$ (1:10)	10.5	0.056	0.055	0.092
ZnS-2	$MeOH/H_2O$ (10:1)	1.3	0.035	0.015	
ZnS-2	$H_2O/MeOH$ (1:10)	1.5	0.080	0.11	

[a] Reaction conditions: see Table I. [b] Quantum yields for decrease of the octene. [c] Quantum yields for H_2 in the absence of the octene.

Table V. Effect of Solvent Systems on ZnS-Catalyzed Photoisomerization of *cis*-2-Octene to *trans*-2-Octene[a]

solvent system	volume ratio	quantum yield ϕ_{c-t}
MeOH		2.2
$MeOH/CH_3CN$	10:1	2.8
MeOH/THF	10:1	1.4
MeOH/DEA	10:1	0.32
$H_2O/MeOH$	1:9	8.1
$H_2O/MeCN$	1:2	4.3
H_2O/THF	1:2	1.1
H_2O/DEA[b]	1:2	0.03

[a] Reaction conditions: see Table I. [b] Diethylamine.

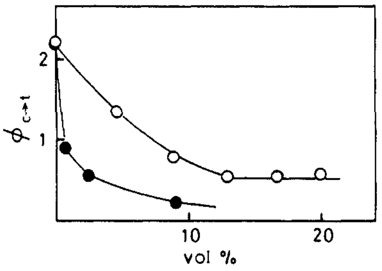

Figure 7. Effect of organic additives on ZnS-catalyzed photoisomerization of *cis*-2-octene: (●) DEA; (○) cyclohexane. Reaction conditions: see Figure 1.

In Table IV, quantum yields for H_2 evolution and for the disappearance of the octene are summarized together with those of the photoisomerization. H_2 evolution should be the consequence of photoreduction of water through concomitant photooxidation of methanol and/or the octene.[25] However, the quantum yields for the photoisomerization are much greater than those for H_2 evolution. Further, ZnS-2 prepared from aqueous solutions was superior in H_2 evolution but inferior in the photoisomerization to ZnS-1.

Effect of Organic Additives on the ZnS-Catalyzed Photoisomerization. In the ZnS-photocatalyzed H_2 generation, either tetrahydrofuran or diethylamine works as a good electron donor.[3b] With this in view, we examined their effects on the photoisomerization of *cis*-2-octene in methanolic and aqueous systems. The effect of acetonitrile on the isomerization was also examined for comparison as an organic additive having a high oxidation potential. The quantum yields were obtained from the initial linear portions of the time-conversion plots under various conditions, which are summarized in Table V. While the effect of acetonitrile is negligible, diethylamine and tetrahydrofuran retard the photoisomerization. In the aqueous systems, H_2 evolved efficiently in their presence as expected.

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(21) (a) Henglein, A.; Gutièrrez, M.; Fischer, Ch.-H. *Berg. Bunsenges. Phys.* **1984**, *88*, 170. (b) Reber, J.-F.; Meier, K. *J. Phys. Chem.* **1984**, *88*, 5903. (c) Zeug, N.; Bücheler, J.; Kisch, H. *J. Am. Chem. Soc.* **1985**, *107*, 1459.

(22) Oosawa, Y.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1629.

(23) The similar increase in quantum yields (by a factor of 2.8) was also observed in the presence of NH_4PF_6 (0.05 M). The salt effect may also include the effect of the increased ionic strength of the medium and/or the ionic interactions of intermediary radical ion species with added salts.[24]

(24) Mizuno, K.; Ichinose, N.; Otsuji, Y. *Chem. Lett.* **1985**, 455.

(25) It has been found that 2-hexenes can serve as electron donors in ZnS-photocatalyzed H_2 evolution in water in a quantum yield of 0.09, which was calculated by assuming that two photons produce one molecule of H_2. This result will be reported elsewhere.

Table VI. Photoisomerization of *cis*-2-Octene Induced by Commercial Sphalerite ZnS in Aqueous Solvent System

solvent (v/v)	$\phi_{c\text{-}t}$[a]	relative rate[b] after the darkening
MeOH	0.061	1
MeOH/H_2O (95:5)	0.16	2.3
MeOH/H_2O (90:10)	0.35	3.4
MeOH/H_2O (80:20)	0.56	5.7
EtOH/H_2O (80:20)	0.14	
EtOH/H_2O (60:40)		3.8
MeCN/H_2O (60:40)		6.6
THF/H_2O (60:40)		4.9

[a] Quantum yields at 313-nm irradiation before the darkening. Concentration of *cis*-2-octene = 0.05 M. ZnS = 40 mg/1 mL. [b] Because of the visible light absorption due to the darkening, the efficiency was evaluated by the relative rate.

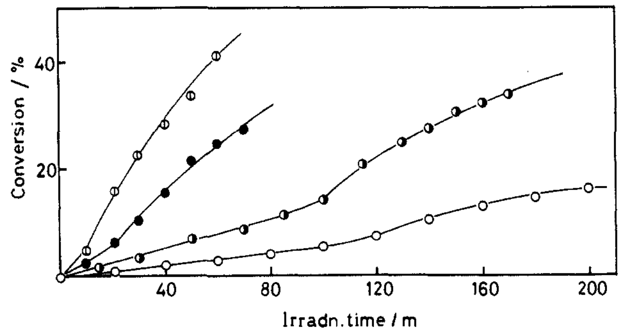


Figure 8. Time–conversion plots for photoisomerization of *cis*-2-octene induced by microcrystalline ZnS (Nakarai) in MeOH/H_2O (v/v) solutions: (◐) 80:20; (●) 90:10; (◐) 95:5; (○) 100:0. Reaction conditions: see Figure 1.

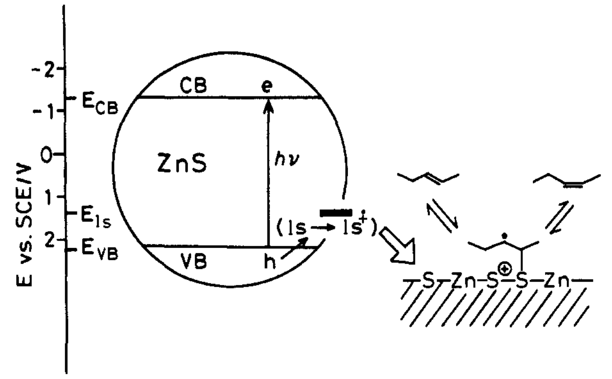
The effects of diethylamine as an electron donor and that of cyclohexane as the additive which may compete for the active sites without any photochemical quenching were compared by changing additive concentrations as shown in Figure 7. A small quantity of diethylamine quenches the isomerization effectively, which suggests that the photoisomerization should closely relate with photoformation of holes on irradiated ZnS. With cyclohexane, the photoisomerization was gradually retarded with increase in its concentration and, at the concentration more than 12%, no change in quantum yields was observed. These observations argue in favor of a surface reaction wherein the olefins should be strongly adsorbed as discussed with Figure 3.

Photoisomerization with Commercially Available Semiconductor Powders. Previously we demonstrated that highly pure microcrystalline ZnS, which is commercially available, shows effective photocatalysis for H_2 evolution in sacrificial systems while ZnS for electroluminescence is inactive.[3c] Reber and Meier also reported comparable results for some crystalline ZnS.[21b]

It has been found that the case is true for the cis–trans photoisomerization; the above-mentioned highly pure microcrystalline ZnS (Nakarai) works as a catalyst, but the ZnS for electroluminescence does not at all. The quantum yields in aqueous solvent are summarized in Table VI. The commercial active ZnS has a narrow surface area (<1 m^2/g) due to its microcrystalline structure (sphalerite) as reported.[3c] Therefore, it was quite unexpected that it showed the high efficiency comparable with ZnS sols whose surface area was more than 100 times as large as the commercial ZnS when powdered. It should be noted, however, that other semiconductor powders, i.e., ZnO, SnO_2, TiO_2, and ZnSe, did not induce the photoisomerization of *cis*-2-octene under irradiation of 313-nm light.

As observed for ZnS sols, the presence of water also enhanced the photoisomerization in the commercial ZnS systems (Figure 8). After the slow isomerization step at the early stage of the irradiation, the more efficient isomerization occurred concomitantly with the darkening of ZnS microcrystals in the presence of water (Table VI).

Scheme I



With commercial CdS, photoisomerization was also observed under irradiation at 313 nm. However, activities depend on the source of CdS; the Aldrich CdS showed the comparable efficiency as the Nakarai ZnS but the Nakarai CdS did not. Further investigation is in progress and will be reported elsewhere.

Mechanism. With regard to mechanisms of cis–trans photoisomerization of olefins in either homogeneous or heterogeneous solution, there have been proposed several mechanisms, i.e., triplet energy transfer mechanism,[26] exciplex mechanism,[26] electron-transfer mechanism,[8c,10] chain cation radical mechanism,[27] and radical-mediated mechanism (hot ground-state mechanism).[28] The quantum yields which exceed largely over unity exclude energy-transfer mechanism including the quantum chain mechanism proposed by Tokumaru et al.[28] for the present photoisomerization.

With respect to the valence band potentials (E_{VB}) of powder and colloidal systems, Bard et al. recently reported that apparent flat band positions of CdS systems are more positive by about 0.7 V than that of the single crystals due to the presence of a number of surface states.[29] If this is the case, the E_{VB} in sols of CdS[30] and ZnS[31] should shift to 1.62 and 2.29 V vs. SCE (pH 7), respectively. Since the oxidation potentials of simple alkenes are >2.2 V vs. SCE,[32] electron transfer may occur only with irradiated ZnS sols but not for irradiated ZnS microcrystals[33] and CdS sols. The following observations, however, suggest that the participation of alkene cation radicals is negligible in the ZnS-catalyzed photoisomerization: (1) the 2-hexenes underwent photooxidation in the ZnS aqueous sol system,[25] but the resulting H_2 evolution occurred much more slowly and less efficiently than the photoisomerization. (2) The activity of ZnS sols in photoisomerization is not parallel to that in H_2 evolution. (3) Neither positional isomerization nor consumption of the starting alkenes was observed.[34] (4) Neither O_2 acceleration nor oxidative cleavage of

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[26] (a) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197. (b) Yang, N. C.; Cohen, J. I.; Shani, A. *J. Am. Chem. Soc.* **1968**, *90*, 3264. (c) Inoue, Y.; Takamuku, S.; Kunitomi, Y.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1672. (d) Snyder, J. J.; Tise, F. P.; Davis, R. D.; Kropp, D. J. *J. Org. Chem.* **1981**, *46*, 3609 and references cited therein.

[27] (a) Majima, T.; Pac, C.; Sakurai, H. *Chem. Lett.* **1979**, 1133. (b) Lewis, F. L.; Petisce, J. R.; Oxman, J. D.; Nepras, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 203.

[28] Arai, T.; Karatsu, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1983**, 2873.

[29] Finlayson, M. F.; Wheeler, B. L.; Kakuta, N.; Park, K.-H.; Bard, A. J.; Campion, A. *J. Phys. Chem.*, in press.

[30] V_b of CdS crystals was determined as 1.62 V vs. SCE (pH 7) (Negative shift, 55 mV per pH unit increase was taken into account): Kohl P. A.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 7531.

[31] V_b of ZnS crystals was determined as 2.29 V vs. SCE (pH 7): Fan, F.-R. F.; Leempoel, P.; Bard, A. J. *J. Electrochem. Soc.* **1983**, *130*, 1866.

[32] Fleischmann M.; Pletcher, D. *Tetrahedron Lett.* **1968**, 6255.

[33] As for the V_b of ZnS, the numbers 2.7 and 2.3 V vs. NHE (pH 7) are cited in the literatures.[21a,c] The former is based on the estimated value, 3.00 V vs. NHE (pH 2.5), and the latter on the estimated difference in potentials between CdS and ZnS. The value 3.00 V seems to be too positive to quote: Tributsch, H.; Bennett, J. C. *J. Chem. Technol. Biotechnol.* **1981**, *31*, 565.

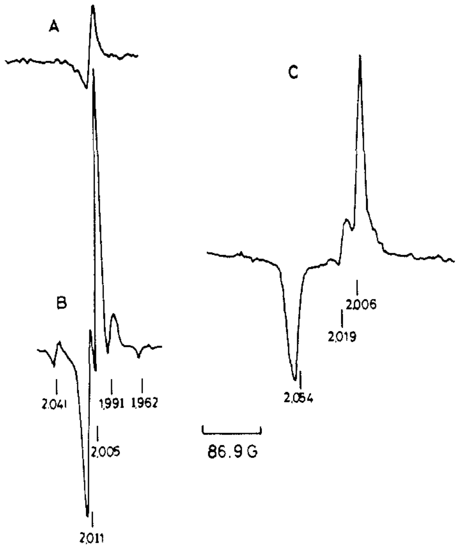

Figure 9. ESR spectra observed in UV irradiated ZnS in mehanol: (A) ZnS-1 sols after irradiation at >294 nm at room temperature; (B) ZnS-1 sols after irradiation at 254 nm at liquid nitrogen temperature; (C) ZnS sols prepared in water after irradiation at 254 nm at liquid nitrogen temperature.

alkenes was observed under irradiation in the O_2-saturated system. (5) Platinized TiO_2 (5 wt% Pt on Anatase, Merk) which was efficient in the H_2 generation in aqueous methanol induced the photoisomerization of *cis*-2-octene only in very low efficiency, accompanied by consumption of the octene.

Quantum yields larger than unity and the oxygen quenching effect led us to conclude that the photoisomerization should be mediated by photoformed radical species derived from semiconductors. It is said that in the forbidden zone, there are several energy levels (surface states) attributable to the surface defects (vacancies, lattice imperfections, and interstitial impurity). Recent studies on photoluminescence of ZnS and CdS revealed that such surface defects act as acceptors or donors to produce various surface states on semiconductors.[35,36] Recently, Nakato et al.[37] proposed the concept of surface-trapped holes to understand the electroluminescence of n-type semiconductor in redox solution, in which the holes are formed in contact with oxidants in solution.

With these in view, we now porpose that photoformed radicals which originate from surface states should be the active sites for the cis–trans photoisomerization and that surface defects like interstitial sulfur (I_S) and/or Zn vacancies (V_{Zn}) play important roles in their formation. If I_S or the three sulfur ions next to V_{Zn} donate electron to the photoformed hole at the valence band before the recombination, a trapped hole should be produced as was proposed for the color center[38] and the photoluminescence.[35,36] The trapped holes arising from I_S and/or V_{Zn} can be regarded as sulfur radicals as exemplified for I_{S^+}. in Scheme I. Addition and elimination reactions of alkens should occur to sulfur radicals on the surface of catalysts, leading to the catalytic cis–trans isomerization. The cis–trans ratios at the photostationary state which are comparable with those achieved by phenylthio radical strongly suggest the participation of radicals derived from sulfur.[39]

The formation of sulfur radicals in the active ZnS by band-gap irradiation was supported by ESR spectrometry. Figure 9 shows the ESR spectra obtained by irradiating ZnS-1 sols in methanol at >290 nm for 30 min (A) and at 254 nm for 10 min (B). The signals at $g = 2.005$ and 2.011 were assigned to paramagnetic species from the ZnS sols, since the signals ($g = 2.041$, 1.991, 1.962) in B were observed in a blank measurement and ascribed to paramagnetic species arising from photolysis of methanol. The signal ($g = 2.005$) was singly observed under irradiation at >290 nm at room temperature (A) and increased under irradiation at 254 nm (B). The g value was almost identical with that reported by Schneider and Räuber[40] and ascribed to singly positively charged sulfur vacancy, i.e., the F center in ZnS. In addition to the F-center signal, Shono recently reported some signals attributable to hole traps in electron-irradiated crystalline ZnS.[41] On the basis of this fact and the comparison with the g values attributed to such trapped holes, the signal ($g = 2.011$) may be interpreted as due to a hole localized on the lattice sulfur ion, i.e., sulfur radical. In addition, the g value of the S_4 radical obtained in the deep blue solution of NaS_4 was reported to be 2.024.[42]

The comparable signals were also observable for the irradiated microcrystalline ZnS (Nakarai). Interestingly, the signal ($g = 2.015$) ascribed to the trapped hole was observed before irradiation and increased on irradiation. On the other hand, irradiated ZnS sols prepared in the aqueous system gave unsymmetrical ESR signals (C) in Figure 9. In addition to the signals ascribed to the F center (2.006) and the trapped hole (2.019), another signal was observed at $g = 2.054$, which may be explained as due to another trapped hole as reported.[41]

The oxygen effect can be explained as scavenging of sulfur radicals. It is also understandable that ZnS sols containing polysulfide anions show the high efficiency in the photoisomerization; polysulfide anions can serve as interstitial sulfur, i.e., good sources of trapped holes under band-gap irradiation.

The effect of electron donors can be rationalized as due to the disappearance of trapped holes by electron injection. The potential of the trapped hole can be estimated to be located between 2.29 and ca. 1.0 V vs. SCE from the valence band edge and the oxidation potential of diethylamine[43] which quenchs the isomerization almost completely. The presence of an electron acceptor like water allows the capture of the electrons associated with the F centers: an evolution of hydrogen resulting from this redox reaction was observed. The remarkable effect of water originates from the elongation of the lifetime of the trapped hole due to depression of the recombination between the photoformed electron and the trapped hole. In fact, no ESR signal was observed in the irradiated ZnS sols at 77 K in the presence of both electron acceptor (water) and donor (THF). This fact is consistent with the decreased rate of the isomerization in this system and well explains the important roles of surface states in the isomerization.

The enhanced activity of the crystalline ZnS by darkening may be reasonably interpreted by assuming the accumulation of the trapped holes. In the darkened ZnS in the presence of water, the signals attributable to trapped holes were observable with the signal of the F center.

Conclusion

It has been demonstrated that ZnS and CdS particles are efficient photocatalysts for the cis–trans isomerizations of simple

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[34] Alkene cation radicals would undergo deprotonation and further oxidation,[3d] yielding alkene radicals and alkene cations which lead to positional isomerization and consumption of the starting alkenes.

[35] Becker, W. G.; Bard, A. J. *J. Phys. Chem.* **1983**, *87*, 4888.

[36] Ramsden J. J.; Grätzel, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 919.

[37] (a) Nakato, Y.; Tsumura, A.; Tsubomura, H. *J. Electrochem. Soc.* **1980**, 127, 1502. (b) Nakato, Y.; Tsumura, A.; Tsubomura, H., *Ibid.* **1981**, 128, 1300. (c) Nakato, Y.; Tsumura, A.; Tsubomura, H., *Chem. Lett.* **1981**, 127. (d) Nakato, Y.; Tsumura, A.; Tsubomura, H. *Ibid.* **1981**, 383.

[38] Kettle, C. "Introduction to Solid State Physics"; John Wiley & Sons: New York, 1976.

[39] In the case of CdS/3-hexene derivatives and methyl oleate, the equilibria deviated from the thermodynamic ones. On the basis of these facts, a referee pointed out that CdS and ZnS are not following the same surface mechanism and ZnS may be oxidizing and proceeding at least in part by a chain mechanism leading to thermodynamic equilibria. The authors appreciate this suggestion. Considering the surface reactions and the deviation obtained for ZnS/3-hexene, it seems that the difference in adsorption equilibria between semiconductors and cis or trans isomers, and/or the rotational barrier to trans isomers at isomerization sites may also explain the anomalous equilibria.

[40] Schneider, J.; Räuber, A. *Solid State Commun.* **1967**, *5*, 779.

[41] (a) Shono, Y. *J. Phys. Soc. Jpn.* **1979**, *47*, 590. (b) Shono, Y. *Ibid.* **1981**, *50*, 2344.

[42] Giggenbach, W. *J. Inorg. Nucl. Chem.* **1968**, *30*, 3189.

[43] Bard, A. J. "Encyclopedia of Electrochemistry of the Elements"; Mercel Deeker, Inc.: New York, 1980; Vol. 15.

alkenes. Trapped hole levels (I_{S^+}. and/or V_{Zn} center) on their surface have been proposed to play an essential role in the photoisomerization. To our knowledge, this is the first example that reveals a crucial role of the surface states of the semiconductor. Further investigations on reactions related with surface states are in progress.

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Bonded vs. Nonbonded Electron Transfers in Molten Salts: Characterization and Rates of Formation of the Radical Cations and Dications of Phenoxazine and Phenothiazine and Behavior of the M(2,2′-bipyridine)$_3{}^{2+/3+}$ (M = Fe, Ru, Os) Complexes in SbCl$_3$-Rich Media

D. M. Chapman,[1] A. C. Buchanan, III, G. P. Smith,* and G. Mamantov[1]

Contribution from the Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831. *Received July 2, 1985*

Abstract: The electrochemical and homogeneous oxidations of phenoxazine (POZ) and phenothiazine (PTZ) to their highly persistent radical cations, POZ$^{+\cdot}$ and PTZ$^{+\cdot}$, and dications, POZ^{2+} and PTZ^{2+}, were studied in anhydrous SbCl$_3$–AlCl$_3$–BPCl (BPCl = *N*-(1-butyl)pyridinium chloride) mixtures with formal compositions close to neutral, i.e., 60–20–20 m/o at 23–27 °C. The progress of these oxidations was followed by fast optical spectroscopy. The cations and dications were found to be persistent (no loss of nitrogenic protons) up to 150 °C. ESR spectra of the radical cations were exceptionally well-resolved and allowed the first determination of all of the hyperfine constants. ^{1}H NMR spectra of the dications, measured in SbCl$_3$–AlCl$_3$ melts, are the first to be reported. The M(bpy)$_3{}^{\nu+}$ (bpy = 2,2′-bipyridine; M = Ru, Fe, Os; ν = 2, 3) complex ions, used as homogeneous single electron transfer (SET) agents, were found to be robust and their SETs were facile in these media. In basic media (AlCl$_3$/BPCl < 1), the electrochemical oxidations of POZ and PTZ were nernstian SET processes, and homogeneous oxidations by Os(bpy)$_3{}^{3+}$ and Sb(V) were fast nonbonded (outer-sphere) SET processes. In acidic media (AlCl$_3$/BPCl > 1), the oxidizing potential of solvent Sb(III) is greatly enhanced and these media spontaneously oxidize POZ, PTZ, and Os(bpy)$_3{}^{2+}$ The oxidation of Os(bpy)$_3{}^{2+}$ by Sb(III) proved to be very slow, and this was attributed to the formation of a reactive intermediate containing mononuclear Sb(II). This factor probably also contributed to the very slow rates at which Sb(III) was found to oxidize POZ and PTZ. However, the presence of another rate inhibiting factor was demonstrated by the slow rates at which Ru(bpy)$_3{}^{3+}$ oxidized POZ and PTZ in acidic melts. This was attributed to the formation of heteroaromatic–solvent complexes with N–Sb bonds. Thus, oxidations of heteroaromatics by Sb(III) were bonded (inner-sphere) processes. In acidic media the homogeneous oxidations of POZ$^{+\cdot}$ and PTZ$^{+\cdot}$ to POZ^{2+} and PTZ^{2+} by Sb(V) were slow reactions whose rates were inhibited by radical cation–solvent complexation involving the formation of chalcogen–Sb bonds.

Molten, anhydrous SbCl$_3$ (mp 73 °C) is an associated molecular liquid[2] that has proven to be an especially effective hydrogen transfer catalyst for dissolved arenes.[3] When AlCl$_3$ is added to SbCl$_3$, the weak oxidizing power of Sb(III) is substantially enhanced and hydrogen transfer may be accompanied by oxidation leading to some unusual types of reactions such as the following:[4]

$$4\mathrm{ArH} + {}^{2}\!/_{3}\mathrm{Sb}^{\mathrm{III}} \rightarrow 2\mathrm{ArH}_2^+ + \mathrm{Ar{-}Ar} + {}^{2}\!/_{3}[\mathrm{Sb}] \qquad (1a)$$

$$3\mathrm{ArH}_3 + {}^{2}\!/_{3}\mathrm{Sb}^{\mathrm{III}} \rightarrow 2\mathrm{ArH}_2^+ + \mathrm{ArH}_5 + {}^{2}\!/_{3}[\mathrm{Sb}] \qquad (1b)$$

where ArH is an arene, ArH$_3$ and ArH$_5$ are hydroarenes, Ar–Ar is a condensed arene, ArH$_2{}^+$ is an arenium ion, and [Sb] represents soluble lower oxidation state species of antimony.[5,6] The stability of the arenium ion in these otherwise aprotic media is noteworthy. The added AlCl$_3$ enhances the oxidizing power of Sb(III) by acting indirectly as an acceptor for chloride ions released during reduction as described below.[7,8]

It has been proposed that a key step in many of the above reactions is single electron transfer (SET) from an oxidizable substrate to Sb(III)[3,4] and the present investigation provides a closer look at such reactions. In most of the measurements re-

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