Semiconductor Photocatalysis:[1] Reaction Mechanisms for the Photoreductive *cis–trans* Isomerization of Electron-Deficient Alkenes Catalyzed by CdS Powder

Tsutomu SHIRAGAMI,† Shinako FUKAMI, Chyongjin PAC, Yuji WADA, and Shozo YANAGIDA*
Chemical Process Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565

(Received February 15, 1993)

Highly pure commercially available CdS powder (99.999%) catalyzes the effective *cis–trans* photoisomerization of electron-deficient alkenes under visible light irradiation using triethylamine (TEA) as an electron donor, accompanying the formation of the dihydro compound as a two-electron reduction product. The photoisomerization does not occur at all in the absence of TEA. Donor effect, solvent effect, deuterium incorporation experiments for photocatalysis, and MOPAC molecular orbital calculation (MNDO/PM3) of the intermediary radical anions from the alkenes were investigated in order to elucidate the mechanism of this photoisomerization. These results reveal that the CdS-catalyzed *cis–trans* photoisomerization should proceed through two pathways involving the photoreduction of alkenes: one through the back electron transfer from the radical anion of the alkene (alkene$^{-\bullet}$) towards the radical cation of TEA (TEA$^{+\bullet}$), both formed by photoexcited conduction band electrons and holes of CdS, respectively. The other is the reoxidation of a radical intermediate (alkyl$^\bullet$), formed by protonation of alkene$^{-\bullet}$, by TEA$^{+\bullet}$.

The photocatalytic *cis–trans* isomerization of alkenes on a semiconductor surface holds much interest since a catalytic site or a photogenerated active species on a semiconductor surface can be investigated. There are many reports of the mechanism for photoisomerization of alkenes in semiconductor particulate systems. For example, it has been suggested that the photoformed O^- and Ti^{3+}–O^- pairs play significant roles as catalytic sites in the photoisomerization of 2-butenes over TiO_2.[2] In addition, for the photocatalytic *cis–trans* isomerization of styrene derivatives by CdS powder in dichlromethane solution, de Mayo et al. have proposed a mechanism via a styrene radical cation intermediate formed by electron transfer from alkenes to valence band holes in the irradiated CdS surface.[3] In a series of our own studies on ZnS photocatalysis, we have found that the photocatalytic *cis–trans* isomerization of simple alkenes in an aqueous methanol solution is very efficient if disulfide ions ($S_2{}^{2-}$) are incorporated into the microcrystallite lattice.[4] From the previous investigation of semiconductor-catalyzed photoisomerizations, two types of mechanisms were proposed. One includes the oxidation of alkenes by electron transfer from the alkene to the semiconductor.[3] The other proceeds through an addition–elimination process between alkenes and photogenerated active species on the surface such as radicals and ions.[2,4,5]

Recently, we have reported that not only nanoscale CdS suspensions but also highly pure commercially available bulk CdS catalyze the effective photoreduction of aromatic ketones and electron-deficient alkenes using triethylamine as a sacrificial electron donor.[6] In this work, we observed that photoreduction by highly pure bulk CdS powder (mean diameter 2.5 μm) was accompanied by a rapid *cis–trans* photoisomerization of electron-deficient alkenes.[6,7] Interestingly, we have also observed that the photoisomerization did not occur at all without TEA. These results demonstrate that this isomerization should proceed through a new mechanism, i.e., the photoreduction of alkenes. The present report, therefore, deals with the detailed mechanism of the *cis–trans* photoisomerization of electron-deficient alkenes catalyzed by highly pure commercially available bulk CdS powder.

Experimental

Material. Highly pure (99.999%) CdS powder was obtained from Furuuchi (CdS-Furu) or Aldrich (CdS-Ald). Their crystal size was both 2.5 μm as their mean diameter. *p*-Cyanocinnamonitrile (*cis* and *trans* form) and methyl *trans-p*-cyanocinnamate were prepared and purified according to the literature.[8] Methyl *cis-p*-cyanocinnamate was prepared by the photosensitized isomerization of the *trans* form in the presence of benzophenone in benzene and purified by column chromatography on silica gel. Dimethyl maleate and dimethyl fumarate were GR grade (guaranteed reagent grade) of Nacalai Tesque. 1-Benzyl-1,4-dihydronicotinamide (BNAH) was prepared and purified according to the literature.[9] Amines were obtained from the following sources: triethylamine (GR grade), tributylamine (GR grade) and diethylamine (GR grade) from Wako Pure Chemical Industries, *N*,*N*-dimethylaniline (GR grade) from Nacalai Tesque. Liquid amines were purified by fractional distillation before use.

Analysis. Analysis of alkenes and diethylamine was carried out by gas chromatography using a Shimadzu GC-12A apparatus equipped with a flame ionization detector. As column, UCON LB550X (0.5 m×3 mm) for *p*-cyanocinnamonitrile, OV-17 (1 m×3 mm) for methyl *p*-cyanocinnamate, PEG20M (2 m×3 mm) for dimethyl maleate and ASC-L (3 m×3 mm) for diethylamine were used. As internal standards, methyl myristate and methyl benzoate were used.

---

†Present address: Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, 1-1, Minami-Ohsawa, Hachioji, Tokyo 192-03, Japan.

Photocatalytic *cis–trans* Isomerization and Reduction of Alkenes by CdS Powder. A stirred methanol suspension (2 ml) containing CdS powder (70 μmol), alkene (10 mmol dm^{-3}) and triethylamine (1 mol dm^{-3}) was flushed with argon gas and cooled using an ice bath. The container was then closed with a rubber stopper and irradiated by a 300 W tungsten–halogen lamp through an aqueous sodium nitrite solution filter (λ>400 nm).

Deuterium Incorporation Experiments. Deuterium incorporation experiments were performed during photoisomerization and photoreduction of alkenes in some deuterated solvents (CH_3OD, CD_3CN, THF-d_8, etc.) in the same way as mentioned above. When 10—27% of the substrate disappeared, the irradiation was stopped and the deuterium isotope distribution in the substrate and the products were determined by GC-mass spectroscopy.

Semiempirical Molecular Orbital Calculation. MOPAC MO calculation (MNDO/PM3) was carried out with the CAChe system.

Results and Discussion

CdS-Catalyzed *cis–trans* Photoisomerization of Electron-Deficient Alkenes by TEA under Visible Light Irradiation. Figure 1 shows time-conversion plots for CdS-photocatalyzed isomerization and reduction of dimethyl maleate in methanol by using CdS-Furu as a photocatalyst and triethylamine as an electron donor. The photoisomerization of the *cis*-form to the *trans*-form proceeds efficiently at an early stage of the reaction, and a dihydro compound as the two-electron reduction product of the alkene was also produced slowly. The formation of the *trans*-form leveled off and finally decreased, because it is reduced to the dihydro compound. The comparable photoisomerization was also observed when CdS-Furu was replaced by CdS-Ald as highly pure bulk CdS. Accordingly, CdS-Furu was employed for further investigation.

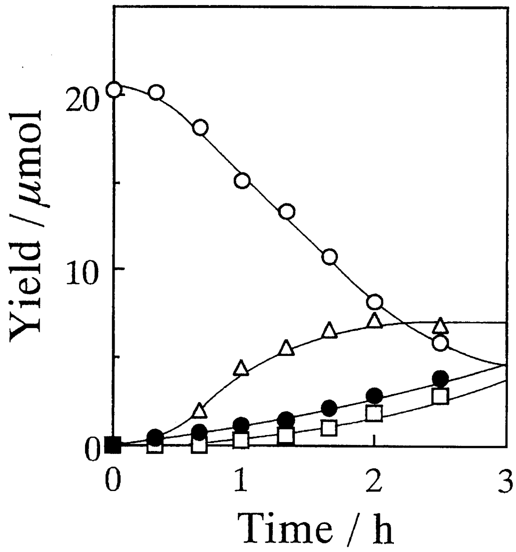


Fig. 1. Time-conversion plots for CdS-photocatalyzed isomerization and reduction of dimethyl maleate by TEA in methanol: (○) dimethyl maleate, (△) dimethyl fumarate, (□) dimethyl succinate, and (●) DEA.

A similar tendency was also observed in the photolysis of *cis*-*p*-cyanocinnamonitrile by CdS-Furu in methanol as shown in Fig. 2. On the other hand, when the photocatalysis was started from dimethyl fumarate (*trans*-form), the isomerization to the *cis*-form did not proceed at all, only the reduction to the dihydro compound occurs. However, in the case of *trans*-*p*-cyanocinnamonitrile, the isomerization to the *cis*-form was confirmed. Table 1 shows the results of the isomerization and reduction of *cis*-*p*-cyanocinnamonitrile catalyzed by CdS-Furu powder in various solvents. In polar solvents such as methanol, acetonitrile and DMF, both isomerization and reduction occurred efficiently, whereas the nonpolar solvents such as methylene chloride and benzene were not effective for the photocatalysis by CdS powder. This result is consistant with the involvement of an electron-transfer process to alkene in

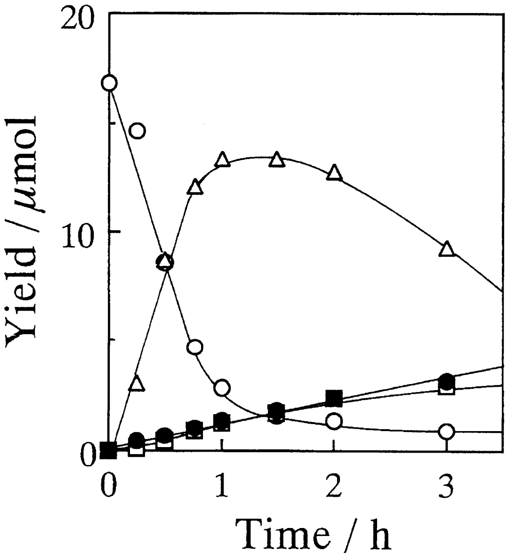


Fig. 2. Time-conversion plots for CdS-photocatalyzed isomerization and reduction of *cis*-*p*-cyanocinnamonitrile by TEA in methanol: (○) *cis*-form, (△) *trans*-form, (□) dihydro compound, and (●) DEA.

Table 1. CdS-Photocatalyzed Isomerization and Reduction of *cis*-*p*-Cyanocinnamonitrile with TEA

Solvent	Initial rate/μmol h^{-1}		Yield/%[a)]
	trans	Dihydro product	Dihydro product
MeOH	25.5	1.1	85.0
MeCN[b)]	35.2	2.4	80.4
DMF[b)]	22.4	1.2	44.8
THF[b)]	17.2	0.3	15.2
CH_2Cl_2[b)]	6.8	0.2	13.1
Benzene[b)]	3.4	0.2	16.2

a) Yields are based on the substrate converted. b) Containing H_2O (0.28 M).

Table 2. CdS-Photocatalyzed Isomerization and Reduction of Olefins in MeOH

Electron donor	*cis-p*-Cyanocinnamonitrile			Dimethyl maleate		
	Initial rate/μmol h^{-1}		Yield/%$^{a)}$	Initial rate/μmol h^{-1}		Yield/%$^{a)}$
	trans	Dihydro prod.	Dihydro prod.	*trans*	Dihydro prod.	Dihydro prod.
TEA (1 M)	25.5	1.1	85.0	8.0	0.4	20.4
TBA (1 M)	11.9	0.7	68.9	9.3	2.4	35.5
BNAH$^{b)}$ (0.1 M)	0.4	1.0	62.1	0.0	1.9	37.8
DMA$^{c)}$ (1 M)	0.0	0.0	0.0	0.0	0.0	0.0
$H_2PO_2^-$ (0.35 M)	0.0	0.0	0.0	0.0	0.0	0.0

a) Yields are based on the substrate converted. b) 1-Benzyl-1,4-dihydronicotinamide. c) *N*,*N*-dimethylaniline.

this system.

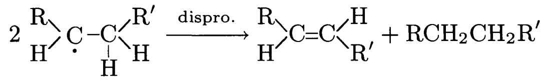
Analysis of the oxidation products from TEA revealed that only diethylamine (DEA) was formed during the photocatalysis. It was confirmed that both the dimer of TEA and the adducts of TEA and alkenes were not detected at all.$^{10)}$ As reported, the formation of DEA can be explained by the hydrolysis of the iminium intermediate $[(Et)_2N\text{–}CHCH_3]^+$ formed through a two-electron oxidation process.$^{11)}$ As shown in Figs. 1 and 2, the formation of DEA was observed concomitantly with that of the dihydro compound. Interestingly, the electron balance was not discrepant between the formation of dihydro compound and that of DEA. These results suggest that TEA apparently should not be consumed for the *cis–trans* photoisomerization, although TEA should be necessary to induce the effective isomerization. This may be an important result to consider for the mechanism of the photoisomerization (described in a later section).

Effect of Electron Donor on *cis–trans* Photoisomerization by CdS Powder. In Table 2 are summarized the results for the CdS-catalyzed photoisomerization of *cis-p*-cyanocinnamonitrile and dimethyl maleate using various electron donor in methanol. When tributylamine (TBA) was employed as electron donor, the time-course plots for the isomerization was similar to that with TEA. TBA also works fairly well as a sacrificial electron donor for CdS-catalyzed reduction and isomerization. Interestingly, however, the use of 1-benzyl-1,4-dihydronicotinamide (BNAH) as an electron donor induced only the formation of the dihydro compounds, and the *cis–trans* photoisomerization did not occur at all in this case, although BNAH was the effective electron donor for the CdS-catalyzed reaction system. Furthermore, *N*,*N*-dimethylaniline (DMA) and $H_2PO_2^-$ were not effective at all.

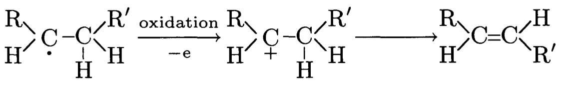
These results indicate that the photoisomerization is well dependent on a kind of electron donor and that the aliphatic tertiary amine such as TEA and TBA plays an important role for *cis–trans* photoisomerization in the CdS-catalyzed system.

Deuterium Incorporation Experiments. In order to elucidate the mechanism of isomerization in detail, deuterium incorporation experiments for the photolysis of the various alkenes were carried out in methanol-d and acetonitrile-d_3 containing D_2O (0.25 M, M = mol dm^{-3}). Table 3 shows all deuterium isotope distributions incorporated in the recovered alkenes and dihydro compound, which were analyzed by GC-mass spectroscopy at an early stage of the photoreaction (about 15% conversion of the starting alkenes). As shown in Table 3, the monodeuterated *trans*-form was observed for the photoisomerization of the *cis*-form, and the amount of the monodeuterated *trans*-form increased when methanol-d was used. Furthermore, when the isomerization was started from *trans-p*-cyanocinnamonitrile, the *cis*-form was also monodeuterated.

These results strongly suggest that the alkyl radical formed by the protonation of the alkene radical anion (alkene$^{-\bullet}$) exists as an intermediate during the CdS-catalyzed photoisomerization. There may be two possible pathways leading to the *trans*-form of the alkene: (1) through the disproportionation of the alkyl radical (Eq. 1), and (2) through the reoxidation of the alkyl radical (Eq. 2).



(1)



(2)

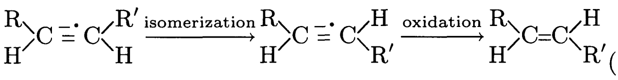
If path (1) is dominant for isomerization, the deuterium isotope distribution in the dihydro compound which is a product formed by disproportionation should be $d_1 : d_2 = 1 : 1$. It was, however, observed that the dihydro compound consists almost entirely of the dideuterated product, as shown in Table 3. These results indicate that the formation of the dihydro compound should proceed through sequential two-electron transfer (ECE process), not through the disproportionation of the intermediary alkyl radical. Accordingly, path (2) may prevail in this photolysis. On the other hand, we also observed the nondeuterated isomer during the photolysis. The formation of the nondeuterated form could be explained as follows: The *cis*-alkene$^{-\bullet}$ is formed by photoexcited conduction band electrons of CdS and isomerize to the *trans*-alkene$^{-\bullet}$, leading to *trans*-alkene by

Table 3. Deuterium Isotope Distribution in Products Formed by CdS-Photocatalyzed Isomerization and Reduction of Olefins

Substrate RCH=CHR′ R	R′		Solvent	Convn. %	Yield/%[a)] *cis* d_0	d_1	d_2	*trans* d_0	d_1	d_2	Dihydro product d_0	d_1	d_2	d_3	d_4
p-CNPh	CN	*cis*	MeOD	15	97	3	0	36	63	1	0	9	91	0	0
p-CNPh	CN	*cis*	MeCN-d_3[b)]	17	98	1	1	88	12	0					
p-CNPh	CN	*trans*	MeOD	10	23	77	0	60	40	0					
p-CNPh	CN	*trans*	MeCN-d_3[b)]	16	79	21	0	79	21	0					
p-CNPh	CO_2Me	*cis*	MeOD	27	100	0	0	58	41	1	17	13	64	6	0
p-CNPh	CO_2Me	*cis*	MeCN-d_3[b)]	24	100	0	0	86	13	1					
CO_2Me	CO_2Me	*cis*	MeOD	10	100	0	0	59	37	4	5	15	59	21	0

a) Determined by GC-MS analysis. b) Containing D_2O (0.25 M).

a back electron-transfer process (described in detail below).



$$\underset{H}{\overset{R}{>}}C\overset{-\bullet}{=}C\underset{H}{\overset{R'}{<}} \xrightarrow{\text{isomerization}} \underset{H}{\overset{R}{>}}C\overset{-\bullet}{=}C\underset{R'}{\overset{H}{<}} \xrightarrow{\text{oxidation}} \underset{H}{\overset{R}{>}}C=C\underset{R'}{\overset{H}{<}} \quad (3)$$

In acetonitrile-d_3, the relative amount of the nondeuterated isomer is larger than that in methanol-*d*, although a large amount of D_2O is contained in the reaction system. This result shows that the mechanism of Eq. 3 may be more dominant for the photoisomerization in acetonitrile.

Table 4 shows the deuterium isotope distribution in products from the CdS-catalyzed system using the various deuterated solvents. In DMF-d_7, THF-d_8, dichloromethane-d_2, and benzene-d_6, deuterium atoms were scarcely incorporated into the *trans*-form during the photolysis. This fact clearly indicates that it is not necessary to assume hydrogen atom transfer such as $H^\bullet$ abstraction from the solvents as a mechanism of the photoisomerization catalyzed by CdS powder.

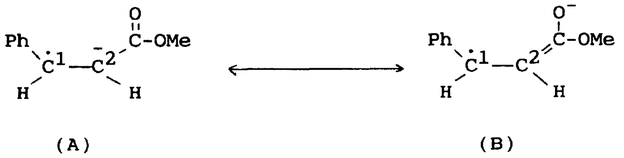
Mechanism. Figure 3 shows a plausible mechanism for the photoisomerization and photoreduction catalyzed by CdS powder in the presence of TEA. As for the photoisomerization, the deuterium incorporation experiments reveal that there are two possible mechanisms through which the electron-transfer process from alkene$^{-\bullet}$ and the reoxidation of the alkyl radical can proceed.

Table 4. Deuterium Isotopic Distribution of Products Formed by CdS-Photocatalyzed Isomerization of *cis*-*p*-Cynocinnamonitrile

Solvent	Convn. %	Yield/%[a)] *cis* d_0	d_1	d_2	*trans* d_0	d_1	d_2
MeOD	15	97	3	0	36	63	1
MeCN-d_3[b)]	17	98	1	1	88	12	0
DMF-d_7[b)]	15	98	2	0	90	9	1
THF-d_8[b)]	16	99	1	0	91	9	0
CD_2Cl_2[b)]	17	99	1	0	98	2	0
C_6D_6[b)]	14	99	1	0	97	3	0

a) Determined by GC-MS analysis. b) Containing D_2O (0.25 M).

The intermediary radical anions from alkenes were evaluated by the semiempirical molecular orbital calculation (MOPAC, MNDO/PM3). The bond length of the olefinic bond and the distributions of spin density and a negative charge for the radical anions were obtained for methyl *trans*-cinnamate, methyl *trans*-*p*-cyanocinnamate, and *trans*-*p*-cyanocinnamonitrile (Table 5). The C^1–C^2 bond lengthens and becomes easy to rotate for isomerization. Further, the spin density is mainly distributed on the C^1 carbon atom and the phenyl ring, while the negative charge is localized on the C^2 carbon and the electron-withdrawing group ($-C^3N^4$) or –COOMe) linked to the C^2, as depicted by the following resonance structures for methyl *cis*-cinnamate.[8)]



(4)

The bond order character of the C_1–C_2 bond should contribute to the efficient isomerization of the intermediary radical anion.

Another question is what chemical species acts as an oxidant of the alkene anion radical or the alkyl radical. We can consider two possibilities for this system: the oxidation (1) by $TEA^{+\bullet}$ and (2) by holes from CdS. We suggest that the oxidant may be $TEA^{+\bullet}$ for the following reasons: (1) TEA was apparently not consumed during the photoisomerization, although TEA is necessary as an electron donor to the isomerization (See Figs. 1 and 2). (2) BNAH, which enables an efficient electron donor for the photoreduction by CdS powder, did not lead to the isomerization at all. If the oxidant are holes of CdS, the isomerization should not depend on the kind of electron donor (See Table 2). (3) The

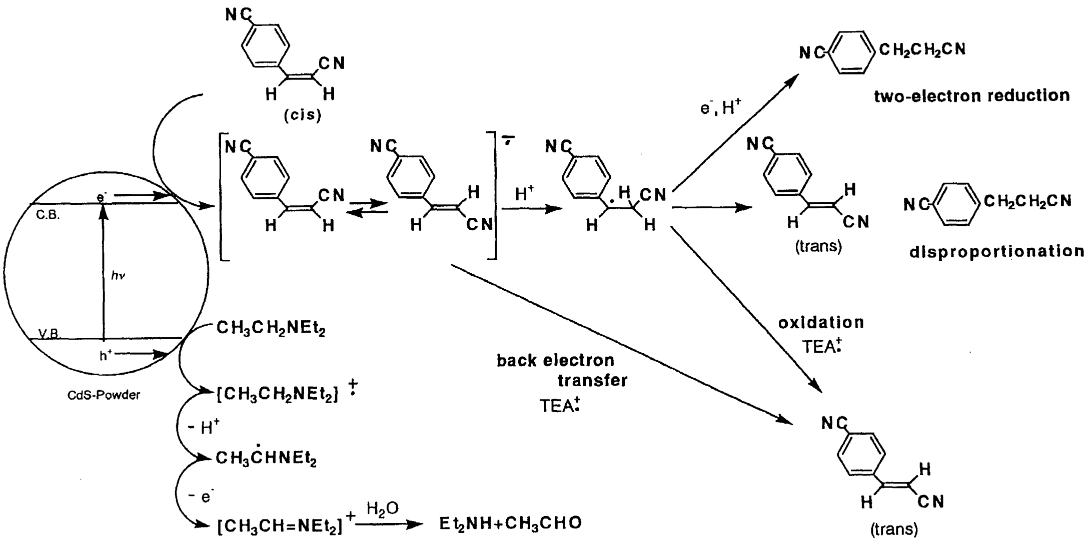
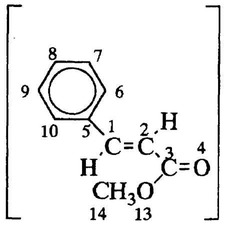
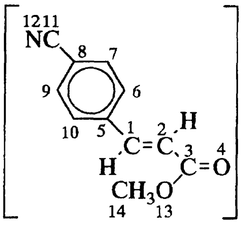
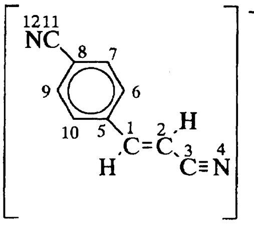


Fig. 3. Plausible mechanism for the photoisomerization and photoreduction of electron-deficient alkenes catalyzed by CdS powder in the presence of TEA.

Table 5. Computer-Assisted Calculation of Radical Anions of Methyl *trans*-Cinnamate, Methyl *trans*-*p*-Cyanocinnamate, and *trans*-*p*-Cyanocinnamonitrile

						
			C^{1}–C^{2} Bond length (ground state)/Å			
	1.390 (1.340)		1.382 (1.340)		1.381 (1.342)	
			C^{1}–C^{2} Bond order (ground state)			
	1.390 (1.856)		1.458 (1.862)		1.462 (1.850)	
			Distribution of spin density and negative charge			
	spin density	charge density	spin density	charge density	spin density	charge density
C^{1}	0.2042	−0.0835	0.1342	−0.0249	0.1206	−0.0505
C^{2}	0.1844	−0.3822	0.1717	−0.3795	0.1964	−0.2711
C^{3}	0.0651	+0.3978	0.0420	+0.4146	0.0174	−0.0263
O^{4}	0.0599	−0.5086	0.0432	−0.4836	—	—
N^{4}	—	—	—	—	0.0630	−0.2638
C^{5}	0.1055	−0.0709	0.1433	−0.1110	0.1500	−0.1080
C^{6}	0.0998	−0.1709	0.0779	−0.1418	0.0756	−0.1407
C^{7}	0.0113	−0.0860	0.0339	−0.0629	0.0347	−0.0613
C^{8}	0.1515	−0.2689	0.1685	−0.1585	0.1669	−0.1630
C^{9}	0.0146	−0.0872	0.0377	−0.0638	0.0385	−0.0599
C^{10}	0.0937	−0.1610	0.0756	−0.1370	0.0723	−0.1466
C^{11}	—	—	0.0150	−0.0194	0.0151	−0.0188
N^{12}	—	—	0.0150	−0.0194	0.0151	−0.0188
C^{13}	0.0093	−0.3035	0.0070	−0.2951	—	—
C^{14}	0.0000	+0.0884	0.0000	+0.0850	—	—

adduct of the anion radical or the alkyl radical with the $[(Et)_2NCHCH_3]^\bullet$ radical formed by the deprotonation of $TEA^{+\bullet}$ could not be detected. (4) Since it is expected that the oxidation of TEA and the reduction of $TEA^{+\bullet}$ may always proceed on the irradiated CdS surface, the steady-state concentration of $TEA^{+\bullet}$ may be very high on the CdS surface upon irradiation.

On the other hand, the dihydro compound is formed by a second electron-transfer process to the intermediary alkyl radical (sequential two-electron-transfer process).

Conclusion. As shown in Fig. 3, it has been clarified that CdS powder catalyzes the effective *cis–trans* photoisomerization of electron-deficient alkenes in the presence of TEA as an electron donor, and that the photoisomerization proceeds spontaneously through two different mechanisms: (1) through the back electron-transfer process between the alkene anion radical and $TEA^{+\bullet}$, (2) through the reoxidation of the alkyl radical resulting from the alkene anion radical by $TEA^{+\bullet}$. To our knowledge, this photoisomerization is the first example via the photoreductive process of alkenes on a semiconductor surface.

We thank Professor Haruo Inoue (Tokyo Metropolitan University) and Dr. Dieter Meissner (ISFH, Germany) for their helpful discussions. This work was supported by a Grant-in-aid for Scientific Research Nos. 61550617, 62213021, and 02203119 from the Ministry of Education, Science and Culture.

References

1) Semiconductor Photocatalysis. Part 15: T. Shiragami, S. Fukami, C. Pac, and S. Yanagida, *J. Chem. Soc., Faraday Trans.*, **89**, 1857 (1993).

2) a) M. Anpo and Y. Kubokawa, *J. Phys. Chem.*, **88**, 5556 (1984); b) S. Kodama, M. Yabuta, M. Anpo, and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, **58**, 2307 (1985); c) M. Anpo, M. Yabuta, S. Kodama, and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, **59**, 3765 (1986); d) S. Kodama, A. Matsumoto, Y. Kubokawa, and M. Anpo, *Bull. Chem. Soc. Jpn.*, **59**, 259 (1986); e) S. Kodama and S. Yagi, *J. Phys. Chem.*, **93**, 4556 (1989).

3) a) H. Al-Ekabi and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, **1984**, 1231; b) H. Al-Ekabi and P. de Mayo, *J. Phys. Chem.*, **89**, 5815 (1985); c) T. Hasegawa and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, **1985**, 1534; d) T. Hasegawa and P. de Mayo, *Langmuir*, **2**, 362 (1986).

4) S. Yanagida, K. Mizumoto, and C. Pac, *J. Am. Chem. Soc.*, **108**, 647 (1986).

5) G. M. Bancroft, A. M. Draper, M. M. Hyland, and P. de Mayo, *New. J. Chem.*, **14**, 5 (1990).

6) T. Shiragami, H. Ankyu, S. Fukami, C. Pac, S. Yanagida, H. Mori, and H. Fujita, *J. Chem. Soc., Faraday Trans.*, **88**, 1055 (1992).

7) T. Shiragami, C. Pac, and S. Yanagida, *J. Phys. Chem.*, **94**, 504 (1980).

8) C. Pac, Y. Miyauchi, O. Ishitani, M. Ihama, M. Yasuda, and H. Sakurai, *J. Org. Chem.*, **49**, 26 (1984).

9) Y. Ohnishi and M. Kitami, *Bull. Chem. Soc. Jpn.*, **52**, 2674 (1979).

10) Neither H_2 due to the reduction of water nor ethanol due to the reduction of the photoformed acetaldehyde[10c)] were detected. Ethylene which may be formed by the decomposition of the intermediary iminium salt and its reduction product, ethane, were not detected during the photolysis.

11) a) S. Yanagida, T. Azuma, H. Kawakami, H. Kizumoto, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, **1984**, 21; b) O. Ishitani, I. Namura, S. Yanagida, and C. Pac, *J. Chem. Soc., Chem. Commun.*, **1987**, 1153; c) T. Shibata, A. Kabumoto, T. Shiragami, O. Ishitani, C. Pac, and S. Yanagida, *J. Phys. Chem.*, **94**, 2068 (1990).