or Dewar benzene (and to benzene via a secondary process[4]).

The differences between an intermolecular [2 + 2] cycloaddition (the [2 + 2] reaction of two ethylene molecules[6] that we have studied previously) and the intramolecular [2 + 2] cycloaddition of Dewar benzene to prismane merit some brief comment. The differences ought to be capable of rationalization from behavior of the Coulomb energy Q (i.e., to steric effects that arise from the σ bond framework) since the exchange energy T must have a similar topology in the two systems. While the coulomb energy Q in the [2 + 2] cycloaddition of two ethylene molecules is completely flat (see Figure 4 of ref 6b) and plays almost no role in the determination of the topology of the ground- and excited-state potential energy surfaces, as we have seen, Q plays a crucial role in the mechanism of the transformation of Dewar benzene to prismane. Thus, in contrast to the [2 + 2] cycloaddition of two ethylene molecules, where the lowest energy pathway involves an asynchronous two-step process involving an anti attack, the corresponding thermal pathway for the transformation of Dewar benzene to prismane involving a nonaromatic transoid diradical intermediate is only a "formal" pathway since the diradical intermediate is unreactive and has an energy so high (because of the constraint of the σ frame) that it is of no chemical significance. Rather, the preferred thermal mechanism for transformation of Dewar benzene to prismane corresponds to a two-stage asynchronous process. In the [2 + 2] cycloaddition of two ethylene molecules the "transition state" on this pathway has two imaginary frequencies; however, the constraint of the σ frame turns one of these negative directions positive in the Dewar benzene to prismane transformation. The electronic factors that control the existence of the conical intersection are present in both systems. However the geometry at the conical intersection is so highly strained (large Q) for the transformation of Dewar benzene to prismane that this mechanism may not exist if steric factors are increased consistent with the experimental observation that only the adiabatic photochemical reaction is observed[5] in 1,4-Dewar naphthalene.

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Photoinduced Reduction of Aldehydes on Titanium Dioxide

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Aromatic and aliphatic aldehydes are reduced to their corresponding alcohols using titanium dioxide as a photocatalyst. The reduction proceeds through an electron transfer from the excited state of titanium dioxide to the aldehydes and is followed by a protonation. The electron hole in the valence band of the excited semiconductor causes concomitant oxidation of the alcohol solvent and production of hydrogen. The quantum efficiency for the reduction is directly related to the half-wave potential of the aldehyde, the solvent, the nature of an electron donor, and the presence of a strong acid or base.

Study of light-induced electron-transfer reactions on semiconductors has become one of the most active areas of research in photochemistry. The reactions demonstrate the possibilities of converting solar energy into chemical or electrical energy, providing new synthetic routes, and introducing new ways of photodegradation of industrial wastes.[1] Titanium dioxide is one of the most studied semiconductors due to its ultraviolet–visible absorption band and chemical stability. Irradiation of titanium dioxide promotes one electron from the valence band (VB) to the conduction band (CB). The excited state of TiO_2 can be expressed as $TiO_2(e^-, h^+)$.[2] The electron in the conduction band is readily available for transference (−0.85 eV vs SCE) while the electron hole in the valence band is open for donation (2.4 eV vs SCE).[3] A reactant that receives the electron from TiO_2 would be reduced, while a reactant that donates an electron to TiO_2 would be oxidized. Based on this redox scheme, a variety of organic reactions can be catalyzed by semiconductors. For example, oxidation of protic organic compounds or biomass to produce hydrogen[4] and photodegradation of polychloroaromatic compounds have been explored.[5] Photooxidations of organic compounds such as amines, carboxylic acids, and aromatic olefins[6] on semiconductors also have been fruitfully investigated. However, there are only a few reports on the reduction of organic compounds using a semiconductor as a photocatalyst.[7] Reduction of acet-

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Table I. Photoreduction of Benzaldehyde in TiO_2 Suspension

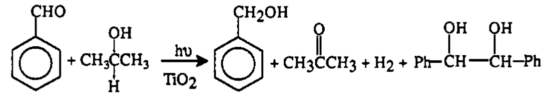
reaction media	photolysis time (h)	yield (%)		
		PhCHO	$PhCH_2OH$	hydrobenzoin
ethanol[a,p]	0	100	0	0
ethanol[a,n]	2	100	0	0
ethanol[a,p]	2	26.0	52.0	7.4
ethanol[a,p]	4	3.0	82.0	6.8
2-propanol[a,p]	2	58.6	17.6	7.4
methanol[a,p]	2	49.2	34.0	5.5
ethanol[b,p,e]	2	100	0	0
ethanol[c,f,g]	2	58.0	11.8	d
ethanol[c,f,g]	18	0	35.0	d
ethanol[c,f,h]	2	62.4	5.8	d
ethanol[c,f,h]	18	20.1	17.8	d
ethanol[p,f,i]	2	0.0	78.4	4.2
ethanol[p,f,j]	2	20.2	54.6	7.2

[a] Purged with nitrogen before photolysis. [b] Purged with oxygen during photolysis. [c] Colloidal TiO_2. [d] Not detected. [e] Trace amount of benzoic acid also detected. [f] Acetal formation makes up the rest of mass balance. [g] 0.001 M HCl is present in solution. [h] 0.1 M HCl is present in solution. [n] No TiO_2 added. [p] Particulate TiO_2, anatase (Degussa, P-25). [i] Diisopropylamine added (0.1 M). [j] *N,N*-Dimethylaniline added (0.1 M).

aldehyde to ethanol in water by illuminated ZnS has been reported. However, when platinized TiO_2 was used under similar conditions, only negligible amounts of ethanol were produced.[8] We report here the photoreduction of aromatic and aliphatic aldehydes to their corresponding alcohols using TiO_2 as a catalyst.

Results

A suspension of titanium dioxide (anatase) in 2-propanol containing benzaldehyde is purged with nitrogen and irradiated with 350-nm light. The photolysis produces benzyl alcohol, acetone, hydrobenzoin, and hydrogen (eq 1). Irradiation of a similar suspension saturated with oxygen gives no benzyl alcohol but yields a trace amount of benzoic acid as the only primary product (Table I). Irradiation of a TiO_2 suspension saturated with oxygen containing benzyl alcohol instead of benzaldehyde does not give any detectable benzoic acid or any other oxidation product from benzyl alcohol. Direct photolysis of benzaldehyde with a 350-nm light in the absence of TiO_2 does not produce any benzyl alcohol. In a control experiment, the suspension is kept in the dark but saturated with hydrogen to simulate the presence of hydrogen during photolysis. The aldehyde is not reduced under this condition. These findings are also true for several other aromatic and aliphatic aldehydes such as *p*-cyanobenzaldehyde, *p*-acetobenzaldehyde, *p*-chlorobenzaldehyde, *p*-bromobenzaldehyde, isonicotinaldehyde, heptanal, and octanal.



(1)

The photoinduced reduction was conducted in three different alcohol media, ethanol, methanol, and 2-propanol.

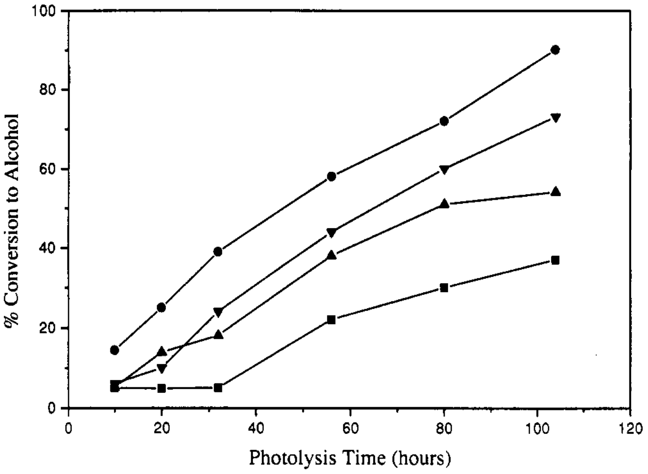


Figure 1. Photocatalytic reduction of heptanal (-●-, DIPA added; -▼-, DIPA and NaOH added; -▲-, NaOH added; -■-, no NaOH or DIPA added).

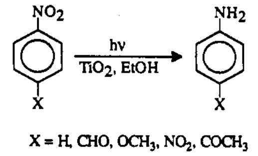
Table II. Photoreduction of Heptanal in TiO_2 Suspensions

$[H^+]$ or $[OH^-]$ added	pH before photolysis	heptanol yield (%) (30 h)	pH after photolysis (30 h)
$[H^+] = 10^{-3}$	3.66	5	3.65
$[H^+] = 10^{-4}$	6.03	12	5.70
$[H^+] = 10^{-5}$	6.20	15	5.92
$[H^+] = 10^{-6}$	6.04	18	6.18
water	6.00	19	6.35
water[a]	6.00	20	5.45
$[OH^-] = 10^{-6}$	6.24	19	6.00
$[OH^-] = 10^{-5}$	6.28	24	6.43
$[OH^-] = 10^{-4}$	6.38	26	5.77
$[OH^-] = 10^{-3}$	7.00	26	6.54
$[OH^-] = 10^{-2}$	10.28	0	9.14

[a] No aldehyde is added in this run.

In the cases of ethanol and methanol, the solvents were oxidized to acetaldehyde and formaldehyde, respectively. The comparison shows that the photoinduced reduction is most efficient when ethanol is employed as the solvent. Methanol offers slightly higher quantum efficiency than 2-propanol (Table I). The analyses based on the UV–vis absorption spectra of aldehyde solutions and TiO_2 suspensions indicate that the photoredox reaction is halted when the aldehyde becomes predominant in light absorption; i.e., there is a higher limit in aldehyde concentration for the reduction. The quantum efficiencies also depend on the electronic nature of the aldehydes. Photoreductions of electron-deficient *p*-acetobenzaldehyde and *p*-halobenzaldehydes in the suspensions of TiO_2 are at least 20 times more efficient than that of anisaldehyde and aliphatic aldehydes (Figure 1, Table I).

The photoreduction is selective for several multifunctional compounds. The aldehyde group is reduced in *p*-cyanobenzaldehyde and *p*-acetobenzaldehyde while the cyano and aceto groups are retained. The nitro group, however, is reduced more readily than the aldehyde group when *p*-nitrobenzaldehyde is employed as a substrate. Selective photoreduction of the nitro group in bifunctional compounds on semiconductors (eq 2) will be the focus of a forthcoming paper.[9]



(2)

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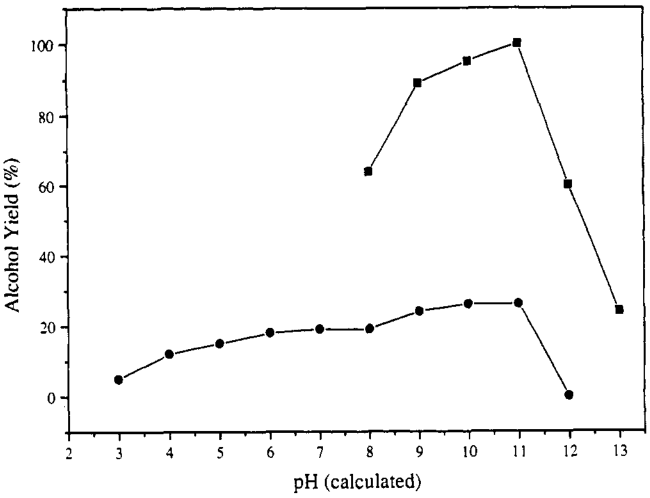
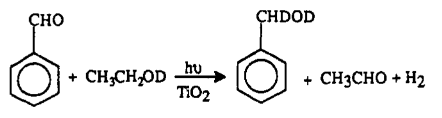


Figure 2. Photoinduced reduction of benzaldehyde and heptanal in the presence of NaOH and HCl (-■-, benzaldehyde; -●-, heptanal).

When a small amount of a strong base, e.g., NaOH, is added into a TiO_2 suspension, the photoreduction efficiency is increased (Figure 1, Table II).[10] But, the pH of the suspension does not increase significantly. The pH of the suspension increases only when excess base is added. The increase in pH is accompanied with a sharp decrease in the photoreduction efficiency. Therefore, there is generally an optimum for the added OH^- concentration. For most aldehydes this concentration is ca. 10^{-3} M (Figure 2). Addition of a strong acid, HCl, to the suspension of TiO_2 does not decrease the pH until the added [HCl] reaches 10^{-3} M (Table II). The decrease in pH is also accompanied by a sharp decrease in the reduction efficiency. Photoreduction of benzaldehyde was also carried out in colloidal TiO_2 containing 0.001 or 0.1 M HCl. The acidic condition is required to stabilize the colloids. Compared to the suspensions with large particles, these colloids are much more transparent and therefore expected to have higher redox quantum efficiencies. On the contrary, our results (Table I) indicate that the reduction rates for these systems are at least 50% slower than those of the reactions carried out in large TiO_2 particle suspensions (Degussa P25).

Addition of diisopropylamine (DIPA) accelerates the photoreduction of aldehydes. However, addition of *N,N*-dimethylaniline (DMA) does not increase the reduction efficiency noticeably (Table I). A suspension that contains diisopropylamine (0.1 M) and its optimal [OH^-] has a higher reduction efficiency compared to the suspension containing optimal [OH^-] only. A suspension that contains only diisopropyl amine (0.1 M) has the highest efficiency for the reduction (Figure 1).

Irradiation of TiO_2–benzaldehyde in O-deuterated ethanol (C_2H_5OD) gives a product labeled with two deuterium atoms (eq 3). irradiations of various TiO_2 suspensions in dry acetonitrile containing aldehydes do not give any photoreduction products. Irradiation of a suspension of TiO_2 in dry acetonitrile containing *p*-bromobenzaldehyde gives benzaldehyde, a debromination product (eq 4). Addition of ethyl alcohol changes the reaction toward reduction of the carbonyl group and production of bromobenzyl alcohol. Irradiations of suspensions containing bromobenzene or chlorobenzaldehyde, however, do not give any dehalogenation products.



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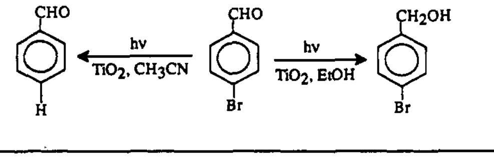
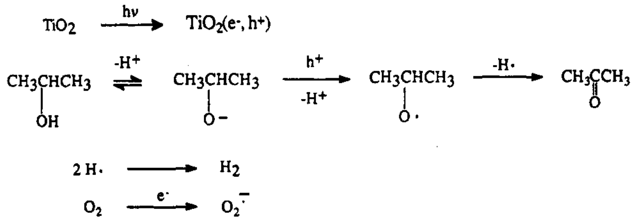
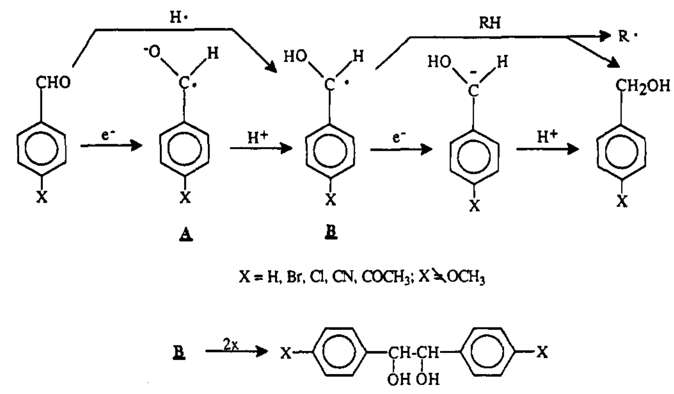


(4)

Scheme I. Oxidation of Alcohols Using TiO_2 as a Photocatalyst



Scheme II. Photoreduction of Aldehydes Using TiO_2 as a Catalyst



Discussion

It is known that alcohols can be oxidized to aldehydes or ketones on TiO_2 upon irradiation accompained by a production of hydrogen (Scheme I).[4] In the absence of oxygen or other electron acceptor, this oxidation proceeds until enough electrons are accumulated in the conduction band so that the electrons efficiently compete with alcohol for electron hole quenching. In the presence of oxygen, the electrons in the conduction band of the excited TiO_2 are captured by oxygen to give a series of oxidative species such as hydrogen peroxide and atomic oxygen. These species are capable of oxidizing the adsorbed aldehyde to a carboxylic acid.[11] Our control experiments clearly demonstrate that the photoreduction of an aldehyde is initiated by the excitation of the semiconductor rather than by the excitation of the aldehyde in a Norrish type II reaction or by a direct hydrogenation.

However, there are still two alternative pathways for the generation of the α-hydroxyl radical (B) as shown in Scheme II. It could be formed from either the addition of a hydrogen atom (Scheme I) to the aldehyde or by a single electron transfer from the excited state of TiO_2 to the aldehyde followed by a protonation. If the first pathway is followed, all aldehydes should react regardless of their electronic nature. Our results, however, show that the reduction occurs only to the electron-deficient aldehydes. The quantum efficiency for the reduction strongly depends on the reduction potentials of the aldehydes. For example, the reduction potentials for the electron-deficient

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aldehydes, including benzaldehydes, are near the conduction band energy of TiO_2 (−0.85 eV vs SCE). These aldehydes can be easily reduced on the semiconductor particles. The reduction potentials for the anisaldehyde and the aliphatic aldehydes are significantly lower (from −1.48 to −1.90 eV vs SCE).[12] These electron-rich aldehydes are much less reducible because of their lesser abilities to accept a single electron from TiO_2. In the cases of heptanal and octanal, the radical anions A (X = hexanyl and heptanyl) would be particularly unstable due to the lack of resonance compared to aromatic aldehydes. The demonstrated competition between the aldehydes and molecular oxygen also indicates that the reduction is initiated by an electron transfer from TiO_2 to the aldehyde.

There are also two possible pathways for the formation of alcohol product from radical B. The radical may be reduced to give the same final product either by a second electron transfer from TiO_2 followed by a protonation or by a hydrogen abstraction from the solvent. Irradiation of TiO_2–benzaldehyde in the presence of O-deuterated ethanol (C_2H_5OD) gives a product labeled with two deuterium atoms (eq 3). This indicates that the reduction occurs through two stages of electron transfer and protonation. If hydrogen abstraction occurs instead of electron transfer and protonation, the hydrogen source would most likely be the secondary hydrogen on ethanol. The product, then, would be labeled with only one deuterium.

According to the reaction mechanisms illustrated in Schemes I and II, the oxidation of an alcoholic solvent and the reduction of the aldehyde substrate are logically coupled. The protons produced from the oxidation are completely consumed in the reduction. The proton concentration, therefore, remains essentially the same during the photolysis (Table II). Assuming no side reaction is involved, a balanced equation can be written for a two-photon event (eqs 5–7).

$$\mathrm{PhCHO} + 2e^- + 2H^+ \rightarrow \mathrm{PhCH_2OH} \quad (5)$$

$$2\mathrm{CH_3CH_2OH} + 2h^+ \rightarrow 2\mathrm{CH_3CHO} + 2H^+ + H_2 \quad (6)$$

$$\mathrm{PhCHO} + 2\mathrm{CH_3CH_2OH} \xrightarrow{2h\nu} 2\mathrm{CH_3CHO} + H_2 \quad (7)$$

This equation is consistent with our observation that the reduction of an aldehyde is enhanced by the oxidation of solvent. When the suspension is irradiated without an aldehyde, the reduction that consumes the protons (eq 6) is absent. The proton concentration is increased during the photolysis (Table II).

The most important event that reduces the quantum efficiency of a photoredox reaction on a semiconductor is the fast recombination of the electron in the conduction band and the electron hole in the valence band.[13] For photoreduction, a sacrificial donor can be added to quench the electron hole and prevent the recombination. An amine can be considered a better electron donor than an alcohol. The fact that addition of *N,N*-dimethylaniline does not significantly affect the reduction may be due to the fact that it is a weaker electron donor than DIPA.

When a small amount of strong base, NaOH, is added to a TiO_2 suspension containing heptanal, the photoreduction efficiency of the aldehyde increases (Figure 1, Table II). However, the pH of the suspension does not increase because the hydroxy groups on the surface of TiO_2 consume most of the added base; i.e., the hydroxide ions are completely absorbed onto the surface.[14] When an excess amount of the base is added, the hydroxide ion concentration exceeds the number of the absorption sites on the surface of the semiconductor. The excess hydroxide ions remain in the suspension and cause an increase in pH and shortage of protons. The shortage of protons translates to a less effective protonation which slows down the reduction process. The balancing of the need for a proton in reduction and the need for a hydroxide to prevent fast electron–electron hole recombination results in an optimal OH^- concentration (ca. 10^{-3} M).

Addition of an amine to a suspension containing optimal $[OH^-]$ does not produce any additional anionic sites on the surface of semiconductor but gives higher reduction efficiency compared to the suspension containing optimal $[OH^-]$ only. This clearly indicates that the amine does not rely on adsorption onto the surface or the deprotonation of the hydroxy centers on the surface to increase the reduction efficiency; it donates an electron to the electron hole directly. Unlike strong base, a higher amine concentration can be used without decreasing the proton availability significantly. As a result, the highest efficiency for the reduction can be obtained in a suspension that contains only diisopropylamine (Figure 1).

Similar analysis can be made for the acidic TiO_2 suspensions. The low quantum efficiency in these low pH suspension perhaps due to the fact that a higher proton concentration converts more TiO_2 particles to positively charged species.[15] The recombination of an electron and an electron hole on a positively charged TiO_2 particle is much faster than on a neutral one. The quantum efficiency for reduction or oxidation is, therefore, reduced in a more acidic solution. The buffer effect on the absorption sites on the TiO_2 surface retards the impact of the added strong acid on the pH of the suspension.

The differences among the three alcohols can also be explained by a similar analogy considering their proton-donating and electron hole-quenching capabilities. For isopropyl alcohol, having the highest pK_a, the lowest concentrations of protons and alkoxy anions are available for the protonation and the electron hole quenching. Although methanol has the smallest pK_a and provides more protons than the other alchohols, the methoxy radical is kinetically much less stable. Ethanol provides the best combination of both aspects. Therefore, the photoreduction carried out in ethanol is most efficient.

When irradiation of a semiconductor suspension is carried out in an aprotic solvent such as acetonitrile, there is neither a proton nor an electron hole quencher available. In the absence of an electron hole quencher, the electron and electron hole recombination on the semiconductor will be so rapid that the competitive electron transfer to an organic substrate would be almost impossible. In the absence of a proton source, even if electron transfer from a semiconductor to an organic substrate occurs, the radical anion of the substrate would return to its neutral state very quickly via back-electron transfer. The reduction is, therefore, stopped. Irradiation of bromobenzaldehyde in acetonitrile containing titanium dioxide gives a radical anion A (X = Br) as illustrated in Scheme II. In the absence of a proton source, the radical anion debrominates to give a radical. The radical then abstracts a hydrogen from the solvent to give benzaldehyde. Irradiation of a

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similar suspension containing bromobenzene instead of bromobenzaldehyde does not give debromination product. This indicates that an electron-deficient functional group such as an aldehyde is required to accept an electron initially. Then the electron is transferred from the aldehyde group to bromine. Bromobenzene has a reduction potential at −1.9 eV (vs SCE) and cannot effectively accept an electron from the conduction band of TiO_2. Although the reduction potential of *p*-chlorobenzaldehyde is high enough (−1.1 eV vs SCE)[12] to undergo electron-transfer reaction with the semiconductor, the chloride atom is not a good enough leaving group. The dechlorination process, therefore, is much less efficient.

Conclusion

The most fundamental yet difficult issue in semiconductor-mediated photochemical transformations is how to logically and practically couple the reductive and the oxidative aspects of the catalyst together in one system, so that an electron can be completely recycled. In our experiments, the reduction of organic functional groups is logically coupled with the oxidation of an alcoholic solvent. There are at least two advantages of using alcohols as the solvents: (1) compared to water, alcohols offer better solubility for an organic substrate and a better suspension for TiO_2 particles by providing closer interaction between aldehydes and the TiO_2 surface, and (2) compared to acetonitrile, alcohols are better proton donors. Deprotonation of alcohols generates alkoxy anions that are excellent electron hole quenchers which prevents recombination between electron holes and electrons on the surface of the photocatalyst.

Experimental Section

General. GC–MS measurements were carried out on a Hewlett-Packard Model 5890 series II GC with a Model 5971A mass spectrometer. Yields were determined on a Perkin-Elmer Sigma-2000 GC with an FID detector and a Hewlett-Packard 1050 series HPLC. Photolyses were carried out in a Rayonet photochemical reactor equipped with 350-nm bulbs. pH measurements were preformed with a Chemtrix type 60A pH meter equipped with an SCE electrode. Benzaldehyde (reagent grade), 1,2,3,4-tetrahydronaphthalene (practical), *p*-chlorobenzaldehyde, and *p*-anisaldehyde (reagent grade) were obtained from Eastman-Kodak Co. Diisopropylamine and isonicotinaldehyde were obtained form Lancaster Synthesis Ltd. Benzyl alcohol (reagent) and *N,N*-dimethylaniline (reagent) were obtained from Baker. *p*-Nitrobenzaldehyde (reagent), heptanal, octanal, and *O*-ethanol-*d* (C_2H_3OD) were obtained from Aldrich. Titanium dioxide (P-25 anatase) was obtained from Degussa Corp. All reagents were used without further purification except *p*-chlorobenzaldehyde which was recrystallized twice from ethyl alcohol.

General Procedure for Photolysis with Particulate TiO_2. In a 5-mL shell vial equipped with a magnetic stir bar were mixed 2 mL of aldehyde solution in 95% ethanol (1.0×10^{-3} M) and 2 mL of TiO_2 suspension in 95% ethanol (10.0 g/L). The vial was sealed with a rubber septum and purged with nitrogen for five min. The mixture was irradiated and filtered with an 0.2-μm HPLC syringe filter to remove the TiO_2 particles. Two mL of the reaction mixture were mixed with 2 mL of a 0.02 M solution of tetralin (an internal standard) and analyzed with GC–MS and HPLC. All alcohol products were identified by their GC–MS spectra and confirmed by comparison with authentic samples obtained commercially or prepared according to literature procedures.[16]

Percent Yield Determination. Six solutions of known concentrations of an aldehyde or its alcohol ranging from 5×10^{-4} to 5×10^{-3} M with 0.0097 M tetralin were analyzed using the GC or HPLC. Area ratios of the alcohol to tetralin or the aldehyde to tetralin were then determined. Using these data, a standard curve of area ratio vs alcohol or aldehyde concentration was constructed. From these graphs, concentrations of reactant and product could be determined after photolysis.

Photolysis Using Colloidal TiO_2.[17] To a 250-mL volumetric flask were added 25 mL of 100% ethanol and efficient HCl to achieve desired proton concentration. Titanium(IV) isopropoxide (4.61 g, 16.2 mmol) was then added to the solution dropwise while stirring. The solution was then diluted to 250 mL with 95% ethanol and stored at room temperature for 3 days for complete hydrolysis. The general procedure for photolysis described above was followed except that the suspension of TiO_2 in ethyl alcohol was substituted by a TiO_2 solution. After the photolysis, TiO_2 was precipitated with the addition of 5 mL of water. The products were extracted with ethyl ether (3 × 3 mL). The ether solution was then analyzed with GC or GC–MS.

Photolysis with Deuterated Solvent. TiO_2 suspensions containing 5×10^{-3} M of benzaldehyde were irradiated as described in the general procedure except C_2H_5OD was used as the solvent. The mixture was photolyzed and analyzed. The GC–MS spectrum showed a molecular ion of 110 for the benzyl alcohol, indicating the structure of PhCHDOD. The reduction was also carried out in C_2H_5OD using tri-*n*-butyltin hydride as the reducing agent. GC–MS analysis revealed a molecular ion of 109 for the benzyl alcohol, indicating the structure $PhCH_2OD$.

Detection of Hydrogen Formation. The formation of hydrogen from the photolysis of a TiO_2 suspension was analyzed with a hydrogenation experiment. The suspension is continuously purged with nitrogen while it is irradiated, and the nitrogen stream coming out of the suspension is introduced into a round-bottom flask containing hexane, cinnamaldehyde, and Pt/C. The hexane solution was analyzed before and after photolysis. After the photolysis, the aldehyde is partially reduced to 3-phenylpropanal and 3-phenylpropanol. When a similar setup is used for a control experiment, without photolysis, cinnamaldehyde is not reduced.

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