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EFFECT OF COSOLVENT ADDITIVES ON RELATIVE RATES OF PHOTOOXIDATION ON SEMICONDUCTOR SURFACES

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ABSTRACT

The effect of solvent additives on the course of TiO_2 photocatalyzed oxygenation of α-methylstyrene has been studied. While the addition of small amounts of nonhalogenated alcohols to TiO_2 powders suspended in acetonitrile was found to decrease the rate of photooxygenation, added halogenated alcohols increase the rate of reaction. In addition, the solvent additives affect the observed product distribution.

INTRODUCTION

Currently, one of the most active areas of research involves the use of semiconductors in the conversion of light into electricity and fuels.[1] In the last several years, a wide range of organic phototransformations at semiconductor surfaces have been discovered and their mechanistic features have been probed. Many organic molecules undergo photooxygenation or photooxidative cleavage when adsorbed on the surface of suspended semiconductor powders.[2]

It is now generally recognized that many of these reactions are initiated by electron transfer between a photogenerated electron–hole pair confined at the surface of the photocatalyst and an adsorbed acceptor or donor. The mechanism for photooxygenation reactions on irradiated titanium dioxide is shown in Scheme 1. Upon band gap excitation, an electron is promoted to

Scheme 1. Mechanism of Semiconductor Photooxygenations

$$TiO_2 \underset{}{\overset{h\nu}{\rightleftarrows}} e^- + h^+ \tag{1}$$

$$h^+ + D \longrightarrow D^{+\cdot} \tag{2}$$

$$e^- + O_2 \longrightarrow O_2^{-\cdot} \tag{3}$$

$$D^{+\cdot} + O_2 \longrightarrow DO_2^{+\cdot} \xrightarrow{e^-} \text{products} \tag{4}$$

$$D^{+\cdot} + O_2^{-\cdot} \longrightarrow DO_2 \longrightarrow \text{products} \tag{5}$$

$$D^{+\cdot} + e^- \longrightarrow D \tag{6}$$

$$O_2^{-\cdot} + h^+ \longrightarrow O_2 \tag{7}$$

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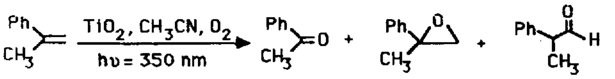
the conduction band ($E_{CB} = -0{\cdot}8$ V vs. SCE in CH_3CN), creating a vacancy in the valence band ($E_{VB} = +2{\cdot}4$ V vs. SCE in CH_3CN).[3] An adsorbed donor, D, then donates an electron to the photogenerated hole at the surface of the TiO_2 particle, forming an adsorbed cation radical (equation (2)). Adsorbed oxygen serves as an electron acceptor for the conduction band electron (equation (3)). In the absence of such an acceptor, the adsorbed cation radical would be rapidly reduced by the photogenerated conduction band electron, thus quenching the photoinduced charge separation. Oxygen serves to inhibit unproductive back electron transfer by interfering with electron–hole recombination at the surface, producing superoxide and allowing observable chemistry to occur.

Oxygenation occurs when the adsorbed cation radical reacts with oxygen or superoxide (equations (4) and (5)). There is ample literature precedent for both reaction pathways in homogeneous media. Investigations by Foote *et al.*,[4] Schaap *et al.*,[5] and Mattes and Farid[6] provide strong evidence for a photooxidation mechanism involving the reaction of superoxide with olefinic cation radicals. On the other hand, Nelsen *et al.*[7] and Clennan[8] have demonstrated that cation radicals of electron rich olefins, generated either chemically or electrochemically, react with ground state oxygen by a radical chain process to form dioxetanes after reduction by another olefin molecule. Barton and others[9–12] have shown that ground state oxygen also reacts with the cation radicals of conjugated dienes, by a similar chain process, to produce endoperoxides. Although no conclusive proof has been presented to distinguish between equations (4) and (5), it seems likely that both mechanisms are operable at the TiO_2 surface.

Two additional surface reactions must be considered. These are the reaction of the adsorbed cation radical (oxidized) donor with the conduction band electron and of superoxide with the valence band hole (Scheme 1, equations (6) and (7)). Both steps are nonproductive and contribute to the inefficiency of these semiconductor catalyzed photochemical oxygenations.

While the basic mechanism of these photooxygenation reactions is known, little information is available concerning solvation of the photogenerated ion radicals.[13] The motivation for understanding solvent effects in photocatalytic oxidation is twofold. Current studies indicate that these reactions suffer low quantum efficiencies.[14] The choice of an appropriate solvent could influence the stability of the surface adsorbed ion radicals and thus could potentially increase reaction efficiency. Furthermore, a study of solvent effects may reveal additional details about the interactions occurring at the solid-liquid interface.

α-Methylstyrene, when photooxidized on TiO_2 powders suspended in CH_3CN, gives three products: acetophenone, 2-methyl-2-phenyloxirane and 2-phenylpropionaldehyde (equation (8)).[15] We have examined the effect of adsorbed cosolvent additives on both the rates of product formation and on the distribution of products. Our studies reveal that while the addition of hydrocarbon alcohols attenuate the rate of α-methylstyrene photooxygenation, halogenated alcohols increase the rate of reaction. In addition, the observed product distribution is affected by the presence of solvent additives.



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1 2 3 4

RESULTS AND DISCUSSION

Solvent effects on relative rates of reaction

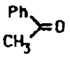
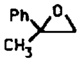
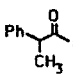
Rather than changing the solvent in each reaction, we added 1 mol % of a cosolvent with acetonitrile, the major solvent component. This method has two major advantages. First, the semiconductor suspensions tend to coagulate in organic solvents, making long term dispersal of small particles difficult, whereas experience has proven acetonitrile to be a very good medium for sustaining a suspension for relatively long periods. Thus, by using acetonitrile as the major solvent, we were able to obtain consistent results. Second, many of the solvent additives are sufficiently expensive to preclude their routine use as reaction media.

For the most part, the solvent additives chosen adsorb more strongly to the surface than does acetonitrile so the reactive species formed at the interface are essentially solvated by these adsorbed solvent additives.[16a] Therefore, the addition of just 1 mol % of the cosolvent can have a significant effect on reactivity.

The effect of nonhalogenated alcohols

The first set of solvent additives considered are hydrocarbon alcohols. In general, the addition of small quantities of alcohol decreases the rate of photooxygenation, Table 1. We attribute these kinetic effects to suppressed substrate adsorption and to competitive hole capture by adsorbed alcohol. Alcohols are generally known to adsorb more strongly to metal oxide surfaces than aromatic hydrocarbons (i.e., **1**), so that the decrease in α-methylstyrene photooxygenation can be attributed to competitive adsorption of the alcohols on the

Table 1. Photooxygenation of α-methylstyrene on TiO_2 with hydrocarbon alcohol additives[a]

added solvent[b] (1 mol %)	rel. rate of reaction	product distribution, %[c]		
				
CH_3CN only	1·00 ± 0·06	78	18	4
MeOH	0·23 ± 0·01	78	19	3
EtOH	0·50 ± 0·02	68	29	3
PrOH	0·65 ± 0·04	57	40	3
BuOH	0·59 ± 0·07	56	41	3
HxOH	0·56 ± 0·04	56	42	2
IPA	0·53 ± 0·04	80	17	3

[a] Irradiation time = 5 h.

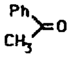
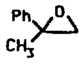
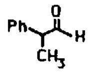
[b] PrOH = *n*-propanol, BuOH = *n*-butanol, HxOH = *n*-hexanol, and IPA = propan-2-ol.

[c] Relative rates of reaction and product yields based on the average of 3 independent runs. These numbers represent chemical yields as well as product distributions. A maximum error of ±2% was calculated for the product distributions.

surface.[16,17] The data in Table 1 also reveal that the relative rate of photooxygenation of **1** in the presence of coadsorbed primary alcohols increases in the order of MeOH < EtOH < PrOH. Adsorption isotherms for these alcohols show that as the length of the carbon chain increases, there is a decrease in the tendency for multilayer formation.[18,19] That is, the amount of adsorbed alcohol decreases in the series MeOH > EtOH > PrOH. Therefore, MeOH is presumably most efficient at suppressing adsorption of **1** on the surface, and consequently, its photooxygenation.

It is well known that alcohols are oxidized on TiO_2 surfaces.[20] In addition to competing for adsorption sites, the alcohols also scavenge valence band holes, thus decreasing the efficiency of α-methylstyrene oxidation. It was found that ketones, aldehydes and carboxylic acids were formed from the alcohols in these reactions, indicating that the alcohols do compete with **1** for holes.

Table 2. Photooxygenation of α-methylstyrene on TiO_2 with halogenated alcohol additives[a]

added solvent[b] (1 mol %)	rel. rate of reaction	product distribution, %[c]		
				
CH_3CN only	1·00 ± 0·06	78	18	4
TFE	1·25 ± 0·07	72	10	3
TFP	1·16 ± 0·04	76	12	1
HFP	1·70 ± 0·06	79	12	1
TCE	2·33 ± 0·02	56	0	5
CH_2Cl_2 only	2·35 ± 0·02	39	0	6

[a] Irradiation time = 5 h.

[b] TFE = 2,2,2-trifluorethanol, TFP = 1,1,1-trifluoropropan-2-ol, HFP = 1,1,1,3,3,3-hexafluoropropan-2-ol, TCE = 2,2,2-trichloroethanol.

[c] Relative rates of reaction and product yields based on the average of 3 independent runs. These numbers represent chemical yields as well as product distributions. A maximum error of ±2% was calculated for the product distributions.

The effect of halogenated alcohols

Table 2 reveals that the addition of 1 mol % of halogenated alcohols results in an increase in the rate of α-methylstyrene photooxygenation. This effect is particularly striking when compared to the significant rate suppression observed with the nonhalogenated alcohols. A strict comparison between these two groups of additives is not valid, as their adsorption behaviors and reactivities are different.

While preadsorption of the alcohols is necessary for observation of a solvent effect, there is evidence which indicates that the halogenated alcohols adsorb to the surface less strongly than the nonhalogenated alcohols. Adsorption isotherm studies on TiO_2 by Rossi *et al.* have shown that the amount of reversibly adsorbed HFP (1,1,1,3,3,3-hexafluoropropan-2-ol) is less than that for propan-2-ol (IPA).[21] Although detailed adsorption equilibria are sensitive to surface hydration and Rossi's system was rigorously dehydrated, their results for reversible adsorption should be similar to ours.* The adsorption of smaller quantities of halogenated alcohols also results from reduced self-association of these alcohols compared with the nonhalogenated alcohols.[22] Thus, strong multilayer adsorption does not occur. This is particularly important for trifluoroethanol (TFE) and trichloroethanol (TCE) since ethanol does show strong multilayer adsorption.[17,18]

Attempts to obtain electrochemical oxidation potentials for these alcohols under conditions similar to the reaction conditions (1 mol % in CH_3CN) failed. However, when the pure alcohol and electrolyte were scanned anodically, the onset of oxidation was found to occur at +2·3 V vs. SCE for HFP and TCE, and +2·0 V vs. SCE for TFE. TFP was not tested since it is presumably easier to oxidize than HFP. These extreme conditions (high alcohol concentration vs. 1 mol %) admittedly do not reflect experimental conditions, however, they indicate that competition of these alcohols for holes is a possibility.

The observed rate increase may be explained as follows. When halogenated additives are adsorbed at the particle surface, primarily through hydrogen bonding,[23] approximately a monolayer of alcohol exists. Thus, there will be a high local concentration of trihalomethyl groups near the surface. Also adsorbed on the surface is superoxide, formed from reaction of oxygen with the conduction band electron. If superoxide interacts favorably with the trihalo groups, through charge transfer-type interaction,[24a] stabilization of superoxide will ensue, thus decreasing the driving force for back electron transfer from the superoxide to the valence band hole. By decreasing the efficiency of equation 7 (Scheme 1) the number of holes available for reaction with the substrate will increase (equation (2)).

Solvolysis[25] and conductance[26] studies have similarly shown that these halogenated alcohols strongly solvate anions and are good proton donors. Thus, favorable solvation of superoxide by halogenated alcohols not directly adsorbed to the surface (or weakly adsorbed) can occur.

Evidence which supports this role for the halogenated alcohols is the similarity in the physical properties of TFE and TCE. NMR studies[27] have shown that the trifluoroethyl and trichloroethyl alcohols have similar pK_a values, hydrogen bonding and self association properties; therefore, their interaction with the TiO_2 surface should be similar. However, charge transfer interaction with superoxide would be more favorable with TCE since the chlorine atoms are more polarizable and better able to accommodate the excess negative charge. It has been shown that superoxide reacts with TCE,[24a] so in fact, TCE traps superoxide rather than just stabilizing it, resulting in a more effective charge separation and a greater conversion of starting material.

Another consideration was that the halogenated alcohols may be accepting the conduction band electron. Electroreduction of the alcohols (1 mol % in CH_3CN) was not observed to occur at potentials positive of the conduction band edge; therefore, it is unlikely that they are being directly reduced by the semiconductor.

A third alternative which might explain the increased reactivity of α-methylstyrene with the addition of halogenated alcohols is the intervention of singlet oxygen. Singlet oxygen ($^1\Delta_g$) may be formed by back electron transfer from superoxide to the conduction band hole or to the oxidized substrate and its role in TiO_2 photooxygenations has long been of interest. A study by Gohre and Miller demonstrated that singlet oxygen could not be trapped by gas phase substrates on illuminated TiO_2.[28] Yet, the lifetime of singlet oxygen is known to increase in halogenated solvents,[29] thus its role in our reactions was investigated. 1,2-Dimethylcyclohexene was chosen as the substrate since it reacts efficiently with singlet oxygen

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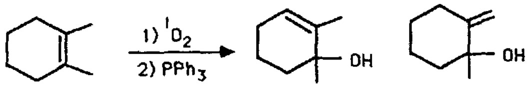
*See Experimental section: solvents and reagents for TiO_2 drying.

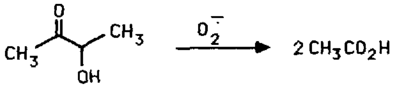
to give ene products (equation (9)).[28] When added to suspensions of TiO_2 in CH_3CN, trace amounts (< 2%) of **5** and **6** were observed. The same reaction run with 1% HFP did not affect the yield of these alcohols. Therefore, singlet oxygen cannot be implicated in the increased reactivity observed with the addition of the halogenated alcohols.



5 **6**

(9)

If hole scavenging by superoxide (equation (7)) is indeed a major source of inefficiency in these reactions, then a similar increase in reactivity should be observed if superoxide is efficiently trapped by a reagent other than TCE. San Filippo has shown that α-hydroxy ketones are good superoxide scavengers.[30] We chose acetoin as a superoxide quencher, equation (10). Cyclic voltammograms of acetoin were run to insure that it would not be directly reduced by the conduction band electron. Since the reduction potentials of α-hydroxy ketones are pH dependent,[31] and TiO_2 is known to have acidic protons,[17] we chose to use polycrystalline TiO_2 electrodes for these experiments since they would mimic the TiO_2 suspension reactions better than a platinum or carbon electrode. No reduction peak was observed in the range from −0·9 to −2·3 V (vs. SCE) for acetoin when scanned negative of the flat band potential. The same experiment was performed on benzoin, which should be easier to reduce.[32] Its reduction potential was found to be −2·1 V vs. SCE, well above the conduction band edge. Thus, acetoin would not be reduced by a photogenerated electron at the TiO_2 surface, and would behave only as a superoxide quencher.



(10)

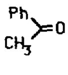
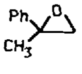
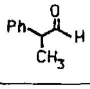
When 1 equivalent of acetoin was added to the standard reaction mixture, a 42% increase in the rate of photooxygenation of **1** was observed. Thus, trapping of superoxide (presumably inhibiting hole trapping by this species) reduces a major source of inefficiency in these reactions. A chemical filter with a cutoff at 355 nm was used to insure no light adsorption by acetoin. Control experiments showed that Bartlett-type epoxidation did not occur in the absence of TiO_2.[33]

Although an increase in the rate of reaction is observed with the addition of halogenated alcohols, several different products are formed. This is most significant with TCE in which approximately 40% of the starting material was converted to these other products. When this same reaction was run with CH_2Cl_2 as the solvent, the reaction rates and the product distributions observed were similar to those obtained with 1% TCE in CH_3CN. It is well known that superoxide reacts with both TCE and CH_2Cl_2.[34] Thus it is likely that intermediates formed from reaction of superoxide with these chlorinated solvents are reacting with **2**–**4** to form the unidentified products. It was found that **1** was inert to a reaction mixture containing superoxide and TCE; therefore, the rapid consumption of starting material is a result of oxidation of **1**, and not its reaction with other species in solution. The best results appear to come from addition of HFP, which gives nearly a 2-fold rate enhancement with only 8% side reaction.

The effect of nonalcoholic additives

The necessity for strong additive–surface interaction is demonstrated by the addition of cosolvents which adsorb by different mechanisms. The relative rates and photooxygenation yields upon addition of 1 mol % of benzene, hexane, and their perfluorinated analogs in CH_3CN are shown in Table 3.

Table 3. Photooxygenation of α-methylstyrene on TiO_2 with nonalcoholic solvent additives[a]

added solvent (1 mol %)	rel. rate of reaction	product distribution, %[b]		
				
CH_3CN only	1·00 ± 0·06	78	18	4
C_6H_6	0·45 ± 0·01	67	30	3
C_6F_6	1·01 ± 0·05	76	19	5
C_6H_{14}	0·97 ± 0·04	75	20	5
C_6F_{14}	0·98 ± 0·04	77	19	4

[a] Irradiation time = 5 h.

[b] Relative rates of reaction and product yields based on the average of 3 independent runs. These numbers represent chemical yields as well as product distributions. A maximum error of ±2% was calculated for the product distributions.

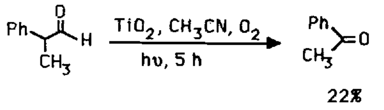
Benzene is generally thought to act as a weak π base on TiO_2, interacting primarily with hydroxyl groups on the surface.[16a,33] **1** should adsorb at the same sites. The addition of 1% benzene to the solvent cuts the rate of product formation from **1** to half its value in CH_3CN. Since it is likely that the equilibrium constants for adsorption of benzene and **1** are similar and since there is roughly ten times more benzene than **1** in the reaction mixture under typical conditions, this result is consistent with competitive adsorption of benzene at photoactive sites on the TiO_2 surface.

Similar concentrations of hexafluorobenzene, however, permit a rate of product formation similar to that observed in neat acetonitrile. It has been reported that the equilibrium constant describing the interaction of hexafluorobenzene with porous vycor glass surfaces is significantly less than that for benzene, reflecting the fact that it is a poor proton acceptor.[35] Thus, we propose that the difference in reactivity induced by benzene and hexafluorobenzene is caused by a difference in their competitive adsorption with α-methylstyrene at active sites on the irradiated surface. Consistent with this proposition is the observation that the product distribution is not changed by the addition of 1 mol % hexafluorobenzene.

Hexane interaction with oxide surfaces is nonspecific and is primarily due to dispersive forces.[16a] These interactions are much weaker than those for aromatic hydrocarbons, and no change in the rate of product formation in the photooxygenation of **1** with the addition of 1 mol % hexane is observed. Likewise, perfluorohexane has no influence on the rate of reaction or product distribution, as it would interact very weakly, if at all, with the surface.

Solvent effects on product distribution

Under the reaction conditions, two of the products, **3** and **4**, undergo secondary photoinduced reactions. The aldehyde is further oxidized to acetophenone in a 22% yield after 5 h of irradiation in CH_3CN (equation (11)). When exposed to the same reaction conditions, **3** is converted to **2** in 5% and **4** in 23% (equation (12)).



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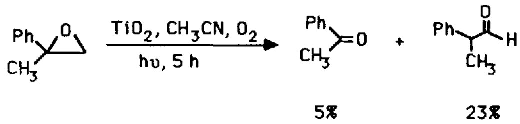

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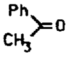
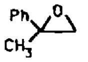
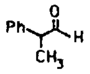
Table 4. The effect of alcohol branching on product distribution[a]

added solvent (1 mol %)	product distribution, %[b]		
			
n-BuOH	64	35	1
s-BuOH	70	27	3
t-BuOH	81	16	3

[a] Irradiation time = 4 h.

[b] Product yields based on the average of 3 independent runs. These numbers represent chemical yields as well as product distributions. A maximum error of ±2% was calculated for the product distributions.

Table 1 reveals that the addition of 1 mol % primary hydrocarbon alcohols results in a higher yield of oxirane, compared with neat CH_3CN or secondary alcohols. The trend is more apparent in Table 4, where the product distributions observed in the presence of isometric butanols (1-BuOH, 2-BuOH and *t*-BuOH) are reported. Here, a clear shift toward more acetophenone with increased alcohol branching is observed. Control experiments in which **3** was exposed to the standard reaction conditions have shown that this shift in product distribution is caused mostly, if not completely by accelerated cleavage (with increased alcohol branching) of **3** to **2** and **4**. Thus, the alcohol structure appears to have a significant effect on adsorption of the oxirane onto the TiO_2 surface. This phenomenon is apparently not related solely to the amount of alcohol adsorbed to the surface, since IPA suppresses the overall rate of reaction more than PrOH (Table 1); however, the overall yield of oxirane is greater with IPA.

No significant change in product distribution was observed upon addition of 1% of the fluorinated alcohols, except with TCE, where no oxirane was observed. When **3** was exposed to irradiated TiO_2 suspensions containing 1% TCE, it was converted to some of the unidentified products observed in the photooxygenation of **1**. Thus, we propose that oxirane is formed, but it is rapidly converted to other products.

In conclusion, we have determined that solvent additives which appreciably adsorb to the TiO_2 surface can have a significant effect on the rate of photooxygenation reactions. While hydrocarbon alcohols cause a decrease in the rate of olefin photooxygenation, the structure of the alcohol appears to have a significant influence on the observed product distribution. Halogenated alcohol additives cause an increase in the rate of photooxygenation, probably by decreasing the rate of back electron transfer from superoxide to the valence band hole. Addition of a superoxide quencher also enhances reactivity. Optimal efficiency in photoinduced oxygenation of **1** was observed with 1% HFP.

EXPERIMENTAL

Instrumentation

Gas chromatography mass spectrometry (GC/MS) analyses were performed on a Finnigan Model 4023 automated GCMS with INCOS data system using a 50 meter DB-1 capillary column. Gas–liquid chromatographic (GLC) analyses were obtained with a Hewlett-Packard 5890A instrument equipped with a flame ionization detector and a 0·53 mm × 15 meter DB-5 column.

Irradiation of the semiconductor suspensions were conducted in a Rayonet photochemical reactor (Southern New England Ultraviolet Company) equipped with a cooling fan and lamps emitting maximally at 350 nm. Dye sensitized singlet oxygen formation was achieved using a 450 W medium pressure mercury lamp immersed in a pyrex reaction vessel, cooled by circulation of chilled water.

Electrochemical measurements were performed with a Bioanalytical Systems BAS-100 electrochemical analyzer equipped with a Houston Instruments DMP-40 digital plotter.

Solvents and reagents

Titanium dioxide (Degussa P25, surface area measured as 57 m^2/g by N_2 adsorption) was dried for 7–14 days at 125 °C before use. This drying procedure was adopted to obtain samples with fairly consistent hydroxyl content, as surface water has a significant effect on the reaction rates. The exact hydroxyl content of our samples is unknown, however, some dehydration had occurred since the TiO_2 powders used were slightly yellow in color, indicative of dehydration. The drying procedure was not sufficiently rigorous to introduce Lewis acid sites.[36,37]

Acetonitrile (Aldrich, 99%) was stored over 3 Å molecular sieves for 1 week prior to use. HPLC grade acetonitrile was used for electrochemical studies. α-Methylstyrene, 2-phenylpropionaldehyde, acetophenone, rose bengal, potassium superoxide, dibenzo-18-crown-6 (Aldrich), and 1,2-dimethylcyclohexene (ICN-KNK Pharmaceuticals) were used without further purification. Acetyl methyl carbinol dimer (Lancaster) was dried under vacuum for several hours prior to use. All of the solvent additives were stored over 3 Å or 4 Å sieves.

Tetra-*n*-butylammonium perchlorate (Southwestern Analytical Chemicals, electrometric grade) was recrystallized three times from ethyl acetate: hexane and was dried 24 h prior to use.

2-Methyl-2-phenyloxirane was prepared according to a literature procedure.[38]

General procedure for semiconductor-mediated photooxygenations

To a 0·01 M solution of α-methylstyrene or 1,2-dimethylcyclohexene in acetonitrile was added 1 mg of TiO_2 per 10 ml of solution. These mixtures were sonicated in an ultrasonic bath while bubbling with oxygen for 10 min. The suspensions were then irradiated while stirring for 5 h at 350 nm without further oxygenation. Sample analysis was accomplished by vacuum filtration of the catalyst and direct analysis of the reaction mixture by GC. Products were identified by isolation[15] and comparison with authentic samples. Product yields were determined by standardization using pentamethylbenzene as the internal standard. The relative rates of reaction were determined from the loss of starting material after 5 h of irradiation.

In experiments involving acetoin, a chemical filter which cuts off at 360 nm was used. The filter solution was prepared by dissolving 6 g bismuth acetate in 3 l of H_2O and 350 ml conc. HCl.

Reaction of superoxide and TCE with α-methylstyrene

0·4 mmol of KO_2, 0·2 mmol of dibenzo-18-crown-6 and 0·2 mmol of α-methylstyrene was added to 20 ml of dry CH_3CN. The solution was magnetically stirred until the crown ether dissolved. Then, 2 mmol of TCE was added to the stirring solution. The superoxide was consumed after 20 min. and the formation of a solid precipitate of KCl was observed. GC analysis of the reaction mixture showed **1** to be unaffected by this procedure.

Preparation of *5* and *6*

A 50 ml methanol solution containing 1·5 mmol 1,2-dimethylcyclohexene and 5×10^{-5} mol rose bengal was prepared and irradiated for 4 h using a 450 W medium pressure Hanovia lamp with a pyrex filter. The solution was bubbled with oxygen during the photolysis. Diethyl ether was then added to the reaction mixture and then extracted twice with a saturated sodium bicarbonate solution and once with water. The ethereal solution was then stirred over excess triphenylphosphine for 30 min. GCMS analysis of the reaction mixture showed that two products, **5** and **6** were formed.[39]

Polycrystalline TiO_2 electrode

The polycrystalline TiO_2 electrodes were prepared by thermal oxidation of Ti foil in air at 650 °C for 2 hours. The edges and back side of the electrode were coated with five minute epoxy, and then covered with Ring® epoxy (Ring Chem. Co.). Contact to the titanium foil was made with silver paint. The electrodes were mounted onto hollow glass tubes using five minute epoxy. The electrodes were dried in the oven at 125 °C overnight prior to use.

Electrochemical experiments

All electrochemical experiments were performed using 0·1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte. The solutions were deaerated and kept under a positive pressure of nitrogen during each run. Silver–silver nitrate (0·1 M in CH_3CN) served as the reference electrode. A platinum wire coil was used as the counter electrode. A polycrystalline TiO_2 electrode was used in the acetoin and benzoin reduction experiments.

The supporting electrolyte-acetonitrile solutions were scanned over the solvent window prior to addition of substrate to ensure the absence of electroactive impurities.

In the acetoin reduction experiments, the TiO_2 electrode was scanned negative of the flatband, from −0·9 V to −2·3 V vs SCE. Some evidence indicates that acetoin is reduced just negative of this range, outside the solvent window. Benzoin, a more easily reduced analog, reduces at −2·25 V. On a Pt working electrode, acetoin was not reduced within the solvent window of either CH_3CN or CH_3CN/MeOH.

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