Heterogeneous Photocatalysis

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I. Introduction

Heterogeneously dispersed semiconductor surfaces provide both a fixed environment to influence the chemical reactivity of a wide range of adsorbates and a means to initiate light-induced redox reactivity in these weakly associated molecules. Upon photoexcitation of several semiconductors nonhomogeneously suspended in either aqueous or nonaqueous solutions or in gaseous mixtures, simultaneous oxidation and reduction reactions occur. This conversion often accomplishes either a specific, selective oxidation or a complete oxidative degradation of an organic substrate present. Molecular oxygen is often assumed to serve as the oxidizing agent although details about the mode of its involvement have not been unambiguously demonstrated except in a few gas/solid reactions. The incident light that initiates this sequence is in a wavelength region (the visible or low-energy range of the ultraviolet regions of the spectrum) absorbed by the semiconductor rather than by the substrate of interest. These reactions therefore involve photosensitization, i.e., an indirect photoactivation of the heterogeneously dispersed particulate absorber rather than the direct formation of an excited state of the substrate. Furthermore, the suspended semiconductor particle that acts as the photocatalyst is often stable to the photolysis conditions (particularly when a metal oxide is employed) and a large number of oxidative conversions per active site on the catalyst can be attained without significant degradation of the semiconductor's redox catalytic capacity. For these reasons, such semiconductor-mediated redox reactions are often grouped under the rubric of heterogeneous photocatalysis.[1]

Initial interest in these photoinduced redox reactions was prompted by Fujishima and Honda's 1972 discovery that water could be split (simultaneously oxidized and reduced) upon illuminating a TiO_2 single-crystal electrode to which a small electrochemical bias had been applied.[2] This observation prompted extensive work focusing on the production of hydrogen (as a combustible fuel) from water as a means of solar energy conversion. It soon became apparent that novel redox reactions of organic and other inorganic substrates[3-8] could also be induced by band-gap irradiation of a variety of semiconductor particles, of sizes ranging from clusters and colloids to powders and large single crystals. More focused scientific interest in these chemical redox reactions has also developed within the last decade because of the suggested use of photoexcited semiconductor dispersions in environmental protection and amelioration[9-15] and in characterizing interfacial electron transfer.[16,17] The possibility that they might induce selective, synthetically useful redox transformations in specific organic compounds has also become increasingly more attractive.[4,17-19]

It is our intention in this article to briefly summarize the cogent features of the irradiated semiconductor surface which lead to this interesting photocatalytic activity. We shall provide an overview of typical photocatalytic reactions observed on heterogeneous dispersions of semiconductors and describe experiments that help to define the mechanism of the photocatalysis.

II. Survey of Reactivity

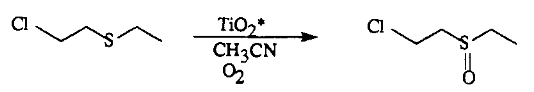
A. Functional Group Transformations

The wide applicability of semiconductor-mediated photocatalysis for functional group transformations of organic compounds has been reviewed previously.[5,19] Because a further compilation of all the relevant literature is both unnecessary and impractical, we provide here only representative examples of some typical conversions in an attempt to represent the versatility of these methods. The reactions accomplished through heterogeneous photocatalysis can be broadly classified as involving oxidations and oxidative cleavages, reductions, geometric and valence isomerizations, substitutions, condensations, and polymerizations.

1. Oxidations and Oxidative Cleavages

Photooxidation is, by far, the most numerous class of the known photocatalytic reactions of organic substrates. It is typical that high (in some cases nearly quantitative) chemical yields of oxidation products are formed, although sometimes with quantum yields of only a few percent or less.[20] (It should be noted that semiconductor surfaces are highly refractory and reflective so that a traditional measurement of quantum efficiency as a ratio of product formed per photon adsorbed is much more difficult on heterogeneous photocatalyst surfaces. Often relative efficiencies are thus reported.) Virtually every organic functional group bearing either a nonbonded lone pair of any π conjugation can be activated toward TiO_2-photocatalyzed oxidative reactivity, either by dehydrogenation, oxygenation, or oxidative cleavage. (In reactions shown in the remainder of the section TiO_2* indicates the excited state formed by band-gap excitation of the suspended photocatalyst.) These processes can be illustrated in the following examples: (1) the gaseous anaerobic photodehydrogenation of ethanol to acetaldehyde over irradiated TiO_2 powder, eq 1,[21] (2) the high yield formation of the corresponding sulfoxide, and successively the sulfone, from β-chlorodiethyl sulfide on TiO_2 powder suspended in aerated aqueous, nonaqueous, or mixed solvents (eq 2),[22] and (3) the nearly quantitative conversion of the C=C double bond of 1,1-diphenylethylene to benzophenone (and formaldehyde) in the irradiation of TiO_2 suspended in oxygenated acetonitrile (eq 3).[23] Even with the organic compounds with the simplest functionality (the alkanes), oxidation products often result when a gaseous stream of substrate passes over an irradiated solid semiconductor film.

$$CH_3CH_2OH \xrightarrow[O_2]{TiO_2^*} CH_3CHO \qquad (1)$$



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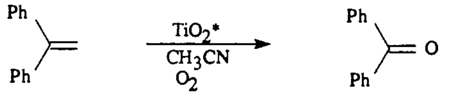
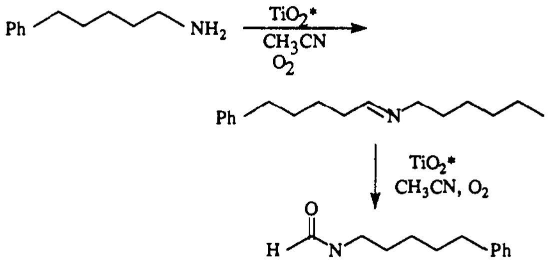


(3)

Metal oxides can sometimes also act as high-temperature thermal oxidation catalysts, but better oxidative selectivity is often observed in the room temperature photocatalytic oxidations. For example, although the oxidation of cyclohexane by O_2 over native or chemically modified TiO_2 is thermodynamically permissible,[24] its rate at room temperature is impossibly slow without photoassistance, and at higher temperatures little oxidative selectivity is observed. In contrast, high oxidative selectivity is attained with TiO_2 photocatalysis, producing 83% cyclohexanone, 5% cyclohexanol, and 12% CO_2. Of particular note are the photo-Kolbe oxidations of carboxylic acids to the corresponding reduced hydrocarbon or hydrocarbon dimer (eq 4).[25,26] Since acetic acid is a common product of biological digestion, this reaction represents a possible means by which heterogeneous photocatalysis could be combined with biological waste treatments to generate combustible fuels.

$$CH_3CO_2H \xrightarrow[H_2O,\ O_2]{TiO_2^*} CH_3CH_3 + CH_4 \qquad (4)$$

More complex sequences are sometimes encountered, with the primary photoproducts themselves being photodegraded or participating in competing thermal pathways. For example, the high yield of ketone formed in the photooxidation of cyclohexane described above results from the faster rate of photooxidation of the primary photoproduct (cyclohexanol) than of cyclohexane.[24] It is also known that in acetonitrile primary alcohols can be oxidized in preference to secondary alcohols[27,28] and that heteroatomic sites (e.g., –OH, –NH, or α-CH-X) are oxidized more efficiently than are the C–C or C–H bonds of hydrocarbons (e.g., arenes, double or triple bonds, benzylic CH, etc.).[5] In a more complicated sequence, aliphatic amines have been photocatalytically oxidized on illuminated TiO_2 powders suspended in acetonitrile to yield the corresponding symmetrical *N*-alkylideneamines via a surface-bound aminium cation radical intermediate (eq 5).[29] Tautomerization to the enamine, followed by C=C oxidative cleavage, produces an oxidatively degraded N-formylated product. Amine reactivity may also be controlled by manipulation of experimental conditions: the identity of the observed product in this photooxidation depends sensitively on the initial concentration of amine. α,ω-Diamines can be similarly oxidized on irradiated semiconductor surfaces through an intramolecular process 17 (eq 6).[30] A similar C–N cleavage occurs in the photocatalytic demethylation of methylene blue and Rhodamine B on an illuminated CdS surface in nonaqueous inert solvents.[31]



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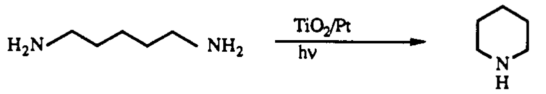
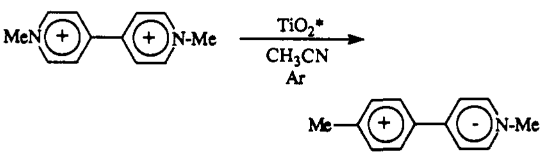


(6)

Of appreciable interest would be a means for selecting one oxidation pathway over another through heterogeneous photocatalysis, a goal which demands considerable mechanistic insight. Before addressing this question, however, we can inquire empirically whether preferential oxidative selectivity is ever observed in photocatalytic conversions of substrates containing more than one oxidizable site. The product distribution formed from TiO_2-mediated photooxidative degradation of 2-methoxyethanol[32] and 2-ethoxyethanol,[33] which both bear two oxidizable functional groups (an alcoholic hydroxyl (–OH) group and an ethereal (–O–) group), reflects a pronounced proclivity for photooxidation at –OH rather than at the ethereal C–H bond. Dibenzyl thioethers are oxidatively degraded on illuminated TiO_2 in acetonitrile in a pathway involving cleavage of the weakest C–S bond.[34] In contrast, when stronger C–S bonds are present in the substrate as in diaryl sulfides, band-gap irradiation of TiO_2 leads to the sulfoxide and then to the sulfone, with the carbon skeleton remaining intact. As with the C–S bonds, photocatalytic activation of C–M bonds (M = Si, Sn, and Ge)[35] induces cleavage and leads to alkyl radicals in inert solvents.[36,37] When the alkyl group is benzyl, the reaction rate is sensitive to ring substitution, with electron-donating groups enhancing the rate and with electron-withdrawing groups decreasing the rate.[37] In the initial photocatalytic oxidation products, chlorinated thioethers show preferential conversion to the sulfoxide, with subsequent formation of a sulfone after prolonged irradiation (eq 2) rather than oxidative dehalogenation.[22]

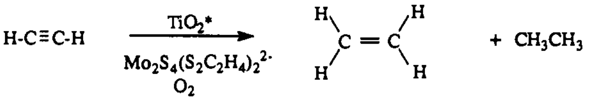
2. Reductions

Photocatalytic reductions are less frequently encountered than are oxidations, presumably because the reducing power of a conduction band electron is significantly lower than the oxidizing power of a valence band hole and because most reducible substrates do not compete kinetically with oxygen in trapping photogenerated conduction band electrons. Methyl viologen dication, a substrate frequently used as an electron trap or as a relay in heterogeneous photocatalysis under deaerated conditions (eq 7) has a much lower reduction potential than most organic substrates by virtue of its double positive charge.[38]



(7)

Many of the known photocatalytic reduction reactions require a cocatalyst like platinum metal. Those cocatalysts which are most effective (Pt, Pd, ZnS, $Mo_2S_4SX_2$, etc.) usually are also active as hydrogenation catalysts, an observation which suggests that surface-bound hydrogen atoms formed by the reduction of protons (H^+) on the cocatalyst surface may in fact be the primary photoproduct, with the hydrogen atom(s) thus formed being transferred in a secondary thermal step to the organic substrate. In fact, the formation of photoreduction products is often accompanied by hydrogen (H_2) evolution, again implicating a competition for surface-bound hydrogen. Although the direct reductions of both CO_2[39] and N_2[40] on irradiated TiO_2 suspensions have been reported, these conversions are extremely inefficient in the utilization of incident photons. The CdS-mediated photoreduction of aqueous solutions of CO_2 with visible light irradiation does yield glyoxylic acid, formic acid, acetic acid, and formaldehyde.[41] The light-conversion efficiency is improved in the presence of hydroquinone, a hole acceptor. The direct photoreduction of pyruvate to lactate on TiO_2 in water appears to be much simpler although lacking in stereospecificity when compared with other photocatalytic carbonyl-reducing systems.[42] Acetylene can be reduced to ethylene or ethane on colloidal aqueous dispersions of TiO_2 suspensions loaded with MoS_4^{2-} or $Mo_2S_4(S_2C_2H_4)_2^{2-}$ (eq 8).[43]



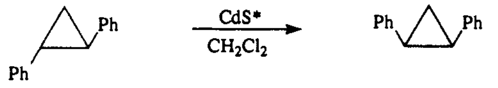
(8)

Primary amines can be converted to secondary amines via two-electron photoreduction of the Schiff bases formed photooxidatively on illuminated ZnS (eq 9).[44]

$$EtNH_2 \xrightarrow{ZnS*} Et_2NH \qquad (9)$$

3. Isomerizations

Geometric and valence isomerizations of unsaturated organic molecules occur on illuminated semiconductor catalysts.[45] For example, the cis–trans isomerization of several simple alkenes proceeds with a light conversion efficiency greater than unity on suspended particles of ZnS,[46] CdS,[46] and vanadium oxides, usually in polar inert solvents,[47] as had been earlier reported for stilbene on TiO_2.[23] As expected for a heterogeneous photocatalyst, the number of isomerizations per surface-active site is high. The semiconductor-mediated geometric interconversion of three 1,2-diarylcyclopropanes in organic solvents is initiated by visible light irradiation of suspended CdS or by near-UV irradiation of ZnO particles (eq 10).[48] The light-conversion efficiency of the valence isomerization of quadricyclene to its ring-opened isomer norbornadiene is influenced by the identity of the photocatalyst (TiO_2, CdS, or ZnO) and the solvent (CH_2Cl_2, CH_3CN, or THF) used,[49] with the chemical yield of ring-closed product decreasing in the following order CdS > TiO_2 ≥ ZnO and CH_2Cl_2 > CH_3CN > THF (eq 11). Although the addition of methyl viologen (an electron scavenger) and diphenylamine (a hole relay) enhanced the chemical yield of norbornadiene, the photocatalytic efficiency was disappointingly low.



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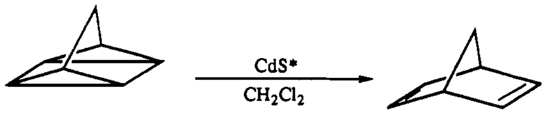
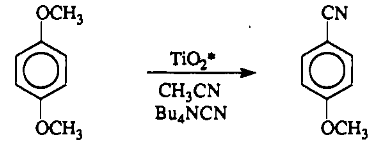


(11)

4. Substitutions

The selective photofluorination of olefins, phosphines, and phosphites on illuminated TiO_2 in the presence of AgF in acetonitrile produces, in most cases, a single fluorinated product (eq 12).[50] The key structural requirement for successful fluorination is the formation by interfacial single electron transfer of a cation radical with sufficient chemical stability to await nucleophilic attack by fluoride in competition with other possible degradation pathways. The concurrent reduction of Ag^+ deposits elemental silver on the semiconductor surface as the fluorination proceeds. In a mechanistically similar process, the cyanation of dimethoxybenzene on illuminated platinized WO_3 or TiO_2 suspensions in aqueous acetonitrile containing tetrabutylammonium cyanide leads to the formation of cyanoanisole as the major product (eq 13).[51] The yield of cyanoanisole was suppressed under anhydrous conditions, and cyanated tributylamine derivatives are formed instead.

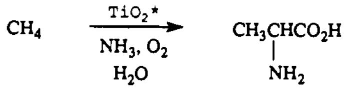
$$(C_6H_5)_3CH \xrightarrow[\substack{AgF \\ CH_3CN}]{TiO_2*} (C_6H_5)_3CF \qquad (12)$$



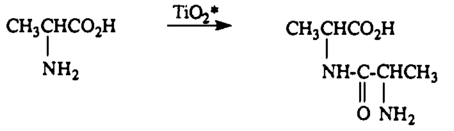
(13)

5. Condensations

Biologically important molecules, such as amino acids[52,53] and nucleic acids,[54] have been assembled in very low yield by semiconductor-mediated photolysis of simpler organic and inorganic components. For example, Bard and co-workers[52] have shown that amino acids are produced upon near-UV irradiation of a platinized TiO_2 photocatalyst in contact with a $KCN/NH_3/H_2O$ mixture (eq 14). Furthermore, the photocatalytic assembly of these units into peptide oligomers has been reported (eq 15).[53]



$$CH_4 \xrightarrow[\substack{NH_3,\ O_2 \\ H_2O}]{TiO_2*} \underset{NH_2}{\underset{|}{CH_3CHCO_2H}} \qquad (14)$$

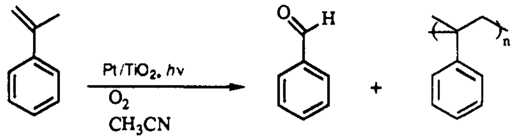


$$\underset{NH_2}{\underset{|}{CH_3CHCO_2H}} \xrightarrow{TiO_2*} \underset{\underset{\substack{\| \quad | \\ O \quad NH_2}}{NH\text{-}C\text{-}CHCH_3}}{\underset{|}{CH_3CHCO_2H}} \qquad (15)$$

Sometimes more complex carbon skeleta are formed from surface-bound intermediates in competition with oxidative degradation. For example, chlorobiphenyls have been detected during the intended oxidative degradation of chlorobenzene[55] and diphenyl ethers are formed in minor amounts during the photocatalytic reaction of chlorophenols on ZnO suspended in water.[56]

6. Polymerizations

Polymerization is usually observed only when oxygen and water are absent from a heterogeneous photocatalysis mixture. Under such conditions, polystyrene is formed when TiO_2 is irradiated in the presence of a nonaqueous solution of styrene,[23] whereas acetophenone is a principal product in aerated aqueous acetonitrile solutions (eq 16).[57] Photoinduced ring-opening polymerization of neat 1,3,5,7-tetramethylcyclotetrasiloxane to form linear poly(methylsiloxane) has been accomplished with TiO_2 photosensitization.[58] The free-radical polymerization of γ-methyl methacrylate[59] and the photoelectrochemical polymerization of pyrrole on semiconductor surfaces suspended in acetonitrile have also been reported.[60,61]



(16)

B. Environmental Decontamination

The need for highly efficient new methods for the treatment of toxic and biologically persistent compounds has led to a compelling interest in semiconductor-mediated photooxidative degradation. The term photodegradation is usually used to refer to complete oxidative mineralization; that is, the conversion of organic compounds to CO_2, H_2O, NO_3^-, or other oxides, halide ion, phosphate, etc. Often degradation begins with partial oxidation, and mechanistic studies relevant to oxidative photodegradation often focus on early stages involving photooxygenation, photooxidative cleavages, or other oxidative conversions (or transformations) taking place through functional group interconversions.

Extensive work has shown that many organic waste products can be completely mineralized on irradiated TiO_2 suspended in water. Complete oxidative destruction can sometimes also be realized in suspension in inert solvents, but the efficiency of complete conversion is usually lower. Such solvents are more frequently employed for selective oxidations which maintain the organic moiety.[62]

Semiconductor photocatalysis can be more appealing than the more conventional chemical oxidation methods because semiconductors are inexpensive, nontoxic, and capable of extended use without substantial loss of photocatalytic activity. Furthermore, semiconductor particles recovered by filtration or centrifugation or when immobilized in a fluidized bed reactor retain much of their native activity after repeated catalytic cycles.

By far, TiO_2 suspended in aerated water has proven to be the most active photocatalyst for this purpose, with the anatase morphological form showing higher activity than rutile. For example, the complete decomposition of 2-ethoxyethanol,[33,63] a commonly used industrial solvent, can be efficiently carried out on irradiated TiO_2. Under the same conditions, CdS and ZnS are less active, although the same products are ultimately formed. Similarly, methyl vinyl ketone, an industrial pollutant found in waste water, has been photooxidized on suspended TiO_2 and over TiO_2 immobilized on glass surfaces.[64] The photocatalytic degradation of phenol has been extensively studied because of its high toxicity and ubiquity.[65,66,130] With phenols and halophenols, such as 2-chlorophenol, photodegradation over TiO_2 leads to rapid mineralization to CO_2 and HCl. Again, anatase showed a high photoactivity than rutile. ZnO is also an efficient catalyst for the photodecomposition of phenol,[67] but unlike TiO_2, ZnO shows appreciable instability during irradiation. Thus, phenol oxidation must compete with the photocorrosion of the photocatalyst.

Halogenated substrates[68] have been decomposed successfully on irradiated semiconductor suspensions. When fluoroalkenes[69] or fluoroaromatics[70] were exposed to an irradiated, air-saturated, aqueous suspension of anatase TiO_2 with UV light at room temperature, CO_2 and HF were formed. The irradiation of an O_2-purged solution of chlorobenzene over TiO_2 similarly leads to complete mineralization to CO_2, H_2O, and HCl.[71] Extensive studies of the photocatalytic degradation of organochlorine compounds have been undertaken because of their known carcinogenicity and because they are formed during water purification by chlorination. Perchloroethylenes, chloroethanes, chlorinated acetic acids, and chlorobenzenes, for example, are all readily mineralized on irradiated TiO_2 suspensions, as are chloroform and carbon tetrachloride, other common contaminants of municipal water supplies.[72] Photodegradation of chlorodioxins (e.g., 2,7-dichlorobenzodioxin) over TiO_2 requires very long irradiation times.[73] With atrazine (2,4-diamino-6-chloro-N-ethyl-N′-(1-methylethyl)-1,3,5-triazine), an herbicide, the photodegradation is rapid, but formation of cyanuric acid, the final product, is comparatively slow.[73] DDT is also degraded on TiO_2 excited by simulated sunlight.[74] Brominated alkanes are completely mineralized upon photocatalytic degradation.[75,76]

Surfactants, such as the anionic sodium dodecylbenzenesulfonate, the cationic benzyldodecyldimethylammonium chloride, and nonionic *p*-nonylphenyl poly(oxyethylene) have been photocatalytically degraded over TiO_2 particles suspended in water and exposed to ambient solar irradiation.[77,78] Those moieties bearing aromatic rings are more easily decomposed than those surfactants containing only alkyl and/or alkoxylate groups.

Toxic phosphorus-containing substrates[79] are amenable to photocatalyzed decomposition, ultimately to completely mineralized products, over illuminated semiconductor suspensions. Organophosphorus insecticides, dimethyl 2,2-dichlorovinyl phosphate and dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphate are efficiently degraded on suspended aqueous TiO_2.[80] Pt loading of the TiO_2 photocatalyst and the addition of H_2O_2 enhanced the observed degradation rates. The final degradation products are Cl^-, PO_4^{3-}, H^+, and CO_2. Complete mineralization of 4-nitrophenyl diethyl phosphate on Nb-doped TiO_2 has been demonstrated.[81] Degradation of organophosphonic acids through C–P bond cleavage is catalyzed by irradiated TiO_2 suspensions in aqueous media.[82]

III. Mechanism of Photocatalysis

With this brief survey of typical photocatalytic reactions in hand, we are now ready to consider evidence bearing on the mechanistic details that govern such conversions. Both theory and experiments are discussed, with appropriate abbreviation where other existing reviews adequately cover a topic elsewhere.

A. Photoelectrochemistry

The primary photochemical processes occurring upon irradiation of a semiconductor are now well established.[3,83–85] By definition, a semiconductor has band structure, roughly characterized as a series of energetically closed spaced energy levels associated with covalent bonding between atoms composing the crystallite (the valence band) and a second series of spatially diffuse, energetically similar levels lying at higher energy and associated with conduction in the macromolecular crystallite (the conduction band). The magnitude of the fixed energy gap between the electronically populated valence band and the largely vacant conduction band governs the extent of thermal population of the conduction band (and hence the magnitude of the electrical conductivity of the particle) in its intrinsic (undoped) state.[86] The band gap also defines the wavelength sensitivity of the semiconductor to irradiation.

Photoexcitation with light of an energy greater than the band gap promotes an electron from the valence

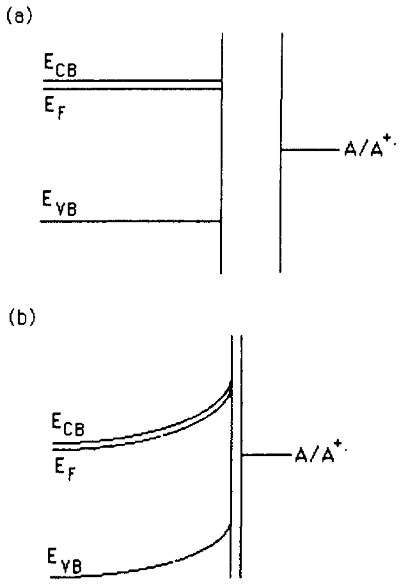


Figure 1. Band structure in a semiconductor: (a) before contact with an electrolyte and (b) in contract with an electrolyte.

band to the conduction band, creating an electronic vacancy or "hole" (h^+) at the valence band edge. The classical picture of a hole is that of a highly localized electron vacancy in the lattice of the irradiated semiconductor particle. This hole can also be identified as a chemical entity: for example, a bound $O^{\bullet-}$ lattice radical or a surface-associated OH radical in a metal oxide or an $S^{\bullet-}$ or $^{\bullet}SH$ radical in the substructure or surface of metal chalcogenide. This hole can initiate further interfacial electron transfer or other chemical reactions to an adsorbate or, with the surface-bound OH radical, can itself diffuse into the solvent bulk. Since the carrier trapping is so fast, it is often the reaction of the hole with a substrate, rather than the carrier trapping itself, that often constitutes the rate determining step of a given sequence.

The photogenerated electron (e^-) usually relaxes thermally to the conduction band edge (and the hole to the valence band edge), but further deactivation is more difficult because of energetic mismatching of the energies of the electron and hole. Only in special cases can nonthermalized "hot electrons" be transferred across the semiconductor interface at a rate competitive with internal relaxation.[87] Conduction band electrons generated within TiO_2 clusters by pulse radiolysis or by flash excitation of the suspended semiconductor exhibit characteristic chemical reactivity patterns which can be monitored by microwave conductivity measurements.[88] The electrons, which have a mobility of at least 1×10^4 m^2/V, are rapidly trapped through equilibrium localization at a trap, followed by eventual recombination with a photogenerated hole at the semiconductor surface. Appreciable negative charge can be built up on a particle in the absence of an appropriate acceptor.[89]

Unlike metals, semiconductors lack a continuum of interband states to assist the recombination of the electron–hole pair. This assures an electron–hole pair lifetime sufficiently long to allow these species to participate in interfacial electron transfer.[90] Thus, the act of photoexcitation usually generates an electron–hole pair poised respectively at the conduction band and valence edges (eq 17). The components of this activated pair, when transferred across the interface, are capable, respectively, of reducing and oxidizing a surface-adsorbed substrate, forming on a common surface a singly oxidized electron donor and singly reduced electron acceptor (eqs 18 and 19).

$$\text{semiconductor} \xrightarrow{h\nu} (e^-,h^+) \qquad (17)$$

$$h^+ + D \rightarrow D^{\bullet+} \qquad (18)$$

$$e^- + A \rightarrow A^{\bullet-} \qquad (19)$$

When the semiconductor is in contact with an electrolyte containing a redox couple, the Fermi level of the semiconductor moves to equilibrate with the potential of the redox couple. Contact between the semiconductor and the electrolyte establishes a Schottky barrier. The electric field of this Schottky barrier induces spatial separation between e^- and h^+ by driving the photogenerated e^- and h^+ in opposite directions, causing the bands to bend at the solid–liquid interface. The Fermi level of the semiconductor then moves to equilibrate with the potential of the redox couple. Charge carriers are driven to surface trapping sites either by diffusion or by migration induced by the space–charge gradient.

If a photogenerated hole reaches the surface of the semiconductor, it can react with an adsorbed substrate by interfacial electron transfer, assuming that the adsorbate possesses a redox potential appropriate for a thermodynamically allowed reaction. Thus, an adsorbed electron donor can be oxidized by transferring an electron to a photogenerated hole on the surface, and an adsorbed acceptor can be reduced by accepting an electron from the surface. Hole trapping generates a cation radical, $D^{\bullet+}$ (eq 18), and electron trapping generates an anion radical, $A^{\bullet-}$ (eq 19).

These radical ions can participate in several pathways: (1) They may react chemically with themselves or other adsorbates. (2) They may recombine by back electron transfer to form the excited state of one of the reactants or to waste the excitation energy by a nonradiative pathway. (3) They may diffuse from the semiconductor surface and participate in chemical reaction in the bulk solution. If the rate of formation of $D^{\bullet+}$ is kinetically competitive with the rate of back electron transfer, photoinduced oxidation will occur for any molecule with an oxidation potential less positive than the semiconductor valence band edge, since under these conditions interfacial electron transfer at the illuminated interface is thermodynamically allowed. By similar considerations, the photoinduced reduction can occur, barring kinetic restraints, to any molecule possessing a reduction potential less negative than the conduction band edge.

B. Carrier Trapping

In order for photocatalysis to be productive chemically, electron–hole pair recombination must be suppressed. This can be accomplished by trapping either the photogenerated electron, the photogenerated hole, or both. Photoreflectance spectroscopy using an intensity-modulated argon ion laser has shown that charge is trapped at the surface of an irradiated CdS single-crystal electrodes.[91] Electrolyte electroreflectance spectroscopy (EER) has been used similarly to demonstrate interfacial h^+ transfer. The formation and decay of spectra assigned to trapped conduction band electrons on the surface of TiO_2 colloids have been monitored by picosecond flash photolysis.[92] The trapped charge carriers are formed within a 20-ps pulse, but have lifetimes in the nanosecond range.[93] Trapping of photogenerated electrons at Ti^{3+} sites within the semiconductor bulk has been confirmed by EPR experiments.[94]

Since the recombination of a photogenerated electron–hole pair in TiO_2 occurs within a fraction of a nanosecond, the rate of interfacial carrier trapping must be very rapid if efficient conversion of the absorbed photon to a chemically stored redox equivalent is to be achieved. The required rate for carrier trapping is faster than diffusion, so that the species acting as the carrier trap must be preassociated with the photocatalyst surface before the arrival of the activating photon.

We have seen in the previous sections that virtually any organic species bearing nonbonded electrons or a delocalized π system like that in a conjugated molecule can be photocatalytically degraded, although with varying quantum efficiency. This is as would be expected if interfacial hole trapping by the organic substrate were to occur in a critical mechanistic step. Hole trapping is usually achieved by the use of degradable adsorbates or a sacrificial reagent. For example, triethylamine and hydroquinone have been used successfully as sacrificial electron donors in CdS-mediated photoreductions,[95] functioning as hole traps so that the conduction band electron can be transferred more slowly without significant electron–hole recombination. Hole trapping occurs with sufficient efficiency that enough charge is built up on a particle that it can migrate as an ion in an electrophoretic field.[96] Time-resolved microwave conductivity measurements on Degussa P-25 produced an increased lifetime for the electron (the mobile charge carrier) in the presence of 2-propanol, presumably because of hole (surface $OH^•$ radical) scavenging.[88]

One should also note that many solvents can themselves meet these broad criteria for photoactivity and should be able to compete effectively with a dissolved substrate for the photogenerated hole. In particular, when water is the solvent, oxidative hole trapping gives $H–OH^{•+}$ which fragments rapidly to a surface-bound hydroxy radical and an adsorbed proton. Kinetic evidence indicates that in water even a polar solute like 3-hydroxybenzoic acid occupies only a fraction of the surface–solution monolayer, with solvent occupying the remainder of the monolayer. Greatly enhanced adsorption is observed when this same solute is in contact with acetonitrile.[97] At high-solute concentrations, multilayer adsorption is also possible. As we shall see below, the involvement of the surface-bound hydroxy radical in heterogeneous photocatalytic conversions conducted in contact with an aqueous solution, particularly at high pH, must be considered as probable in any realistic mechanistic scheme.[98] Even in acidic water, the surface-bound OH radical is usually mechanistically significant.

Electron trapping similarly suppresses electron–hole recombination. Because the conduction band of TiO_2 is nearly isoenergetic with the reduction potential of oxygen in inert solvents, adsorbed oxygen serves as a trap for the photogenerated conduction band electron in many heterogeneous photocatalytic reactions.[23] It is often found that photocatalytic activity is nearly completely suppressed in the absence of oxygen, possibly because of back interfacial electron transfer from active species present on the photocatalyst surface, and the steady-state concentration of oxygen has a profound effect on the relative rate of photocatalyzed decontamination occurring under ambient conditions.[99] The resulting species, superoxide O_2^-, is highly active and can attack either organic molecules or adsorbed intermediates or, after protonation, can provide another source for surface-bound hydroxy radicals. Its precise role has yet to be established unambiguously.

Even after the charge carriers have been transferred to adsorbates, reverse electron transfer can quench the observed photoreactivity. Direct transfer to some substrates, e.g., a halophenol, would be irreversible, however, since electron capture and fragmentation of the intermediate radical anion is known to be extremely fast.[100]

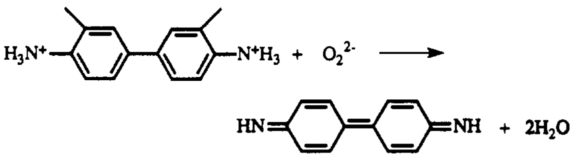
C. Inhibition of Electron–Hole Recombination by Oxygen

The rates and efficiencies of photoassisted degradation of organic substrates are significantly improved in the presence of oxygen or by the addition of several inorganic oxidizing species, such as peroxydisulfate, periodate, and peroxides. The effect of molecular oxygen is primarily as an efficient conduction band electron trap, suppressing electron–hole recombination as described above. Oxygen concentration dependence has been explained as involving O_2 adsorption and depletion, both in the dark and during illumination, at the photocatalyst surface. That rutile possesses much lower photoactivity than anatase (despite the fact that both forms of TiO_2 are thermodynamically capable of reducing O_2) has been explained by the higher rate of electron–hole recombination on rutile because of its lower capacity to adsorb O_2.[101]

The superoxide ($O_2^{•-}$) thus formed is an effective oxygenation agent, attacking both neutral substrates and surface-adsorbed radicals and/or radical ions.[102] This attack occurs before desorption from the surface since the presence of dissolved superoxide traps in solution does not inhibit photocatalytic oxidative reactivity.[22] Alternatively, a protonation–reduction–protonation sequence generates hydrogen peroxide, which can be decomposed on the photocatalyst surface to form hydroxy radical, which can also initiate oxidative functional group interconversions.

The effect of H_2O_2 on the efficiency of photocatalytic degradation of organic substrates on irradiated TiO_2 particles suspended in water has been ambiguous and contradictory data regarding its effects are available in the literature. The treatment of polycrystalline TiO_2 powder with H_2O_2 produces a paramagnetic species identified by ESR spectroscopy as superoxide ($O_2^{•-}$) formed from the decomposition of H_2O_2.[103] An identical species is formed when MgO is treated with H_2O_2 although the observed *g* values differed slightly from those obtained for TiO_2/H_2O_2. These peroxo species were similar to those generated by the reaction of $TiCl_4$ with H_2O_2. The peroxo species thus becomes stabilized against photodecomposition by incorporation into TiO_2.[25]

A method using *o*-tolidine[104] as a redox indicator has been developed to study peroxide adsorbed at the semiconductor surface, presumably in the form of a titanium peroxo complex. This colorimetric method has shown that H_2O_2 is produced when H_2 is evolved during the TiO_2^- mediated photooxidation of water. *o*-Tolidine undergoes a two-electron oxidation with H_2O_2, forming a colorimetrically detectable diimine (eq 20). When Pt is deposited onto TiO_2, peroxide formation in aerated water occurs over a wide pH range. The structure of the surface-bound peroxo species formed remains ambiguous, but the μ-peroxo species[24] formed by hole trapping at the surface seems a likely candidate. Peroxo species are also implicated by the lack of O_2 evolution observed on irradiated metal-loaded TiO_2 powders or colloids in contact with water, even after prolonged irradiation.[105]


(20)

The possibility that back electron transfer from adsorbed superoxide to a surface-bound hole generates singlet oxygen as a primary oxidant in these photocatalytic reactions appears to be unlikely.[106] Although the products of singlet oxygenation are occasionally observed in these photocatalytic schemes, these same products can also be formed by other routes. In addition, the detection of products consistent with singlet oxygenation is the exception rather than the rule, and many examples are available in which the observed oxidation products differ from those expected from pathways involving singlet oxygen. Furthermore, the inclusion of traps specific for homogeneously dispersed singlet oxygen fail to significantly alter the course of photocatalytic oxidative cleavage reactions.

Because adsorbed oxygen exchanges with surface oxides in many metal oxides, the form from which oxygen atoms appearing in oxygenated products are transferred to the surface-bound intermediate is difficult to establish. Isotopically labeled O_2 appears in oxygenated products, but this does not preclude exchange onto the semiconductor surface.

If nonoxygenated products deriving from the ion radicals formed by interfacial electron transfer are desired, an electron trap to serve the role of adsorbed oxygen is needed. Thus, an electron acceptor whose reduced form is chemically inert would be beneficial. Methyl viologen can sometimes fill this role, although the efficiency for electron trapping appears to be lower than with oxygen. For example, in the photocatalyzed Diels–Alder reaction of 2,4-dimethyl-1,3-pentadiene on light-activated TiO_2 suspensions, methyl viologen can be used as an electron acceptor.[38] This use of MV^{2+} obviates the need for oxygen saturation, thus circumventing the formation of oxygenated products.[107] Minimal acid-catalyzed dimerization occurs under these conditions. Xylene and xylylene-bridged viologen radicals[108] are also effective electron-transfer relays, able to undergo efficient two-electron transfer because of their relatively long lifetimes and with no strikingly adverse effect on the activity of the catalyst.

D. Involvement of the Hydroxy Radical

Many isolated intermediates encountered en route to complete mineralization of organic substrates on aqueous TiO_2 suspensions are hydroxylated.[65c,109] Such products could be formed, in principle, either by homolytic attack by a hydroxyl radical on a π system or by hydration of a singly oxidized intermediate. Numerous studies have assumed competing roles for the photogenerated OH radical[110-113] and for the trapped hole[94] in photocatalysis. For example, it has been suggested that in dilute aqueous solutions, phenol is preferentially oxidized by homogeneous reaction with hydroxyl radicals, whereas in concentrated solutions, the oxidation is initiated by hole trapping.[67] An increase in the phenol decomposition rate in the presence of CN^- suggests that $OH^{\bullet}$ radical attack is the favored mode of attack in dilute solutions. CN^- is converted to cyanogen by direct hole oxidation, assuming that phenol does not compete with CN^- for a hole.

The reaction of OH radical with a TiO_2 particle has been probed by pulse radiolysis.[114] Trapping of the OH radical on the TiO_2 surface occurs with a rate of about $6 \times 10^{11}\ M^{-1}\ s^{-1}$ and is unaffected by O_2. Upon collapse of two trapped holes on the same particle to yield an intermediate peroxide, a TiO_2–OH radical complex that decays according to first order kinetics is formed. In the oxidation of SCN^- to $(SCN)_2^-$, surface photooxidation occurs primarily through trapped holes, although a surface-trapped hole and a surface-bound OH radical are spectroscopically indistinguishable. Hydroxyl radicals have been observed upon irradiation of aqueous suspensions of TiO_2 in the presence of spin traps such as 5,5-dimethyl-1-pyrroline *N*-oxide.[63]

Both electron-spin resonance detection of a spin-trapped OH adduct[115] and indirect kinetic evidence[116] point to the formation of the hydroxy radical on illuminated TiO_2 in contact with water. Spectra of other transient intermediates formed from organic or inorganic adsorbates on the surface of the illuminated semiconductor after hole trapping can be detected by diffuse reflectance spectroscopy.[117] On irradiated TiO_2 powders in contact with strongly adsorbed substrates, however, time-resolved diffuse reflectance spectroscopy was used to assign the observed transients as single electron oxidized intermediates (formed by hole trapping) rather than to hydroxy radical adducts.[117a]

Note that a surface-bound OH radical is chemically equivalent to a surface-trapped hole and that many investigators use these terms interchangeably. The diffuse reflectance experiments show only that the activated surface presumes a surface-bound hydroxyl radical since many semiconductors retain an associated water of hydration at the surface even when dispersed in a nonaqueous medium. The detection of singly oxidized transients indicates merely that the surface-bound OH can act as a hole trap, rather than merely diffusing to solution and initiating secondary hydroxylations. It is likely, in other words, that the principal charge trapping event is formation of a surface OH group, which can initiate primary oxidation chemistry of substrates bound at the surface before diffusing into the bulk solution.

A surface-bound intermediate is implicated as well by differences in redox transient lifetimes observed in heterogeneous photocatalysis[114,118] from the same intermediate formed by pulse radiolysis in homogeneous solution.[119] Furthermore, HCO_3^-, a known scavenger of hydroxy radicals, has no effect on the rate of photocatalytic degradation of 3-chlorophenol, implying that any reaction mediated by hydroxy radicals must occur at the surface of the photocatalyst rather than by free diffusion into the homogeneous phase.[120] A surface-adsorbed reactant was also invoked to explain the nonlinear dependence of the oxidation product yield as a function of photon flux.[121] The two-electron process induced by alcohol oxidation on irradiated semiconductor electrodes (current doubling)[122] requires a singly oxidized intermediate to remain associated with the electrode surface for a period long enough to undergo the second oxidation.

On the other hand, the inhibitory effect of 2-propanol on the oxidation of furfuryl alcohol in photooxidation on ZnO has been interpreted as suggestive of a homogeneous phase trapping of the hydroxy radical.[123] Kinetic arguments have been made that, at low substrate coverages by phenol, the photogenerated hydroxy radical diffuses to solution where it effects photooxidation, while it reacts at the surface when the substrate is present at higher coverages. Contrasting studies in the literature claim that a free hydroxy radical can diffuse several hundred angstroms from the photocatalyst surface into the bulk solution,[116] or no more than a few atomic distances at best.[124] The suppression of photocatalytic reactivity when a substrate is bound tightly to an insulating surface during the illumination of a metal oxide semiconductor when both are suspended in a common aqueous solvent demonstrates that active oxidant cannot migrate far from the active site on which it is formed on TiO_2.[125] Nozik has recently reported that when a slurry photoelectrochemical reactor was used to study organic photocatalytic decompositions, an initial cathodic photocurrent rapidly becomes anodic under continuing irradiation, implying the formation of a surface-generated electroactive intermediate which must diffuse through the solution to the counter electrode to generate the observed photocurrent.[126]

If a freely diffusing hydroxy radical were the sole oxidant in photocatalysis, one might expect that addition of a redox-active precursor, e.g., hydrogen peroxide, would increase uniformly the photocatalytic efficiency of a given oxidative conversion. It would also be expected that as higher concentrations of hydrogen peroxide were formed during the photocatalysis that the oxidative degradation rate might be proportionately enhanced. For example, H_2O_2 can be competitively reduced by a conduction band electron (or by a reagent formed by electron trapping) to give a hydroxyl radical and a hydroxide ion. In fact, however, the effect of added quantities of hydrogen peroxide on the photocatalyzed oxidation of chloroethylenes and of chloral hydrates on TiO_2 shows no evidence of enhancement at concentrations below 10^{-4} or above 10^{-1} M[127] and a negative (or no) effect on the photocatalysis was observed in the degradation of chloroacetic acids,[128] atrazine,[129] or chlorinated solvents[128] or when the photocatalyst was changed to ZnO.[127] Nonetheless, an enhancement upon adding hydrogen peroxide was observed in the photocatalytic decomposition of phenol,[130] organophosphorus derivatives,[131] and dioxins.[129] It is possible that hydrogen peroxide or the hydroperoxy radical may in fact function as a hydroxy radical scavenger.

The role of surface OH groups present on TiO_2 powders can also be probed by chemically blocking them by attachment to silicon oxides.[132] With this surface modification, the photocatalytic activity of Pt-loaded TiO_2 declines, as is evidenced by a decrease in the H_2 evolution rate from an aqueous methanol solution and a marked decrease in the oxygen isotope exchange between TiO_2 and $^{18}O_2$.

E. Adsorption Effects

Because recombination of the photogenerated electron and hole is so rapid (occurring on a picosecond timescale), interfacial electron transfer is kinetically competitive only when the relevant donor or acceptor is preadsorbed before photolysis. Indeed, it has been suggested that preliminary adsorption is a prerequisite for highly efficient detoxification.[133] Surely in aqueous metal oxide suspensions, dangling hydroxy groups or water molecules can serve the role of surface-bound traps for the photogenerated hole, forming a surface-adsorbed hydroxy radical. Temperature-programmed desorption[140] and X-ray photoelectron spectroscopy[134-136] indicate strong adsorption of acetone and 2-propanol on ZnO. Metal oxide surfaces have a surface density of about 4–5 hydroxyl groups/nm^2. These can be grouped into sets of surface hydroxyl groups with varying acidities,[21,137,138] as has been shown with a Freundlich isotherm requiring a continuous distribution of adsorption energies.[139]

There is also firm evidence that many organic substrates can themselves act as adsorbed traps for the photogenerated hole, either directly or through the intermediacy of a surface hydroxyl radical. For example, radical ions are detected directly in the flash excitation of an optically transparent colloidal suspension of TiO_2 in acetonitrile.[140] Furthermore, a clear correlation is observed in the dependence of photocatalytic efficiency on both the substrate oxidation potential and σ^+ in a series of para-substituted diphenyl ethylenes.[141] Regioselectivity in oxidative ring cleavage in fused aromatic ring compounds also follows the order predicted from ESR charge and spin densities in the corresponding cation radical.[142]

More spectroscopically distinct transient spectra and kinetically different rates are observed in the photocatalytic oxidation of a range of organic and inorganic substrates on TiO_2 powders suspended in water than in those of these same intermediates when homogeneously dispersed.[118] In the presence of electron donors with less positive oxidation potentials than the 1,2-diarylcyclopropanes, the geometric isomerization described earlier is quenched, implying that the more easily oxidized substrate is interfering with an interfacial electron transfer.[48] The latter process forms an adsorbed cation radical in which the ring C–C bond can be opened and closed to the isomeric product. A structurally labile cation radical was also suggested as critical for the valence isomerization of quadricyclane to its more stable isomer norbornadiene.[49]

Fragmentation reactions observed during photocatalytic oxidative cleavage are also consistent with the intermediacy of a surface-bound radical cation. Thus, the alkyl thioether cleavages described above produce exactly the fragments (a thioalkyl radical and an alkyl cation) expected from an intermediate cation radical.[34] In addition, the relative rates of sulfoxidation and sulfonation of the aryl thioethers in aqueous acetonitrile exhibit a linear dependence on σ^+, as is consistent with the localization of positive charge on sulfur in the critical step. The resulting radical cation can then be trapped either by adsorbed oxygen or by superoxide, in the latter case forming a zwitterion which is a known precursor to the observed sulfoxide and sulfone products.[143] Similarly, the mechanism for the photomediated oxidation of primary amines in nonaqueous solvents can be rationalized by formation of an intermediate immonium cation formed by two sequential one-electron oxidations. The stability of the Schiff base formed in a second stage under these conditions dictates the observed distribution of products.[29]

Although mechanistic information of the photomediated substitutions is sparse, the photocatalytic fluorinations of the organic substrates studied so far most likely occur by attack of fluoride ion on a surface-adsorbed cation or cation radical.[50] The mechanism of photocatalyzed nucleophilic cyanation also involves the intermediacy of a dimethoxybenzene cation radical, as has been confirmed by laser flash photolysis studies of colloidal semiconductor solutions.[51] The steady-state concentration of the dimethoxybenzene cation radical decreased in the presence of CN^- ions because of competitive oxidation (hole trapping) by the hydrocarbon and CN^-. ESR spectroscopy provides evidence for the formation of the singly oxidized $CN^{\bullet}$ radical on the surface of illuminated semiconductors.

Infrared spectroscopic studies reveal that alcohols are chemisorbed onto TiO_2 through their OH moieties, forming a surface ester-like species.[33,63] With ethanol, for example, this primary product is further converted upon prolonged irradiation to acetaldehyde. Two mechanisms can be envisioned for the formation of these products: (1) direct hole oxidation to produce an aldehyde and (2) dehydration of the alcohol to an alkene followed by oxidation at the C=C double bond to form CO_2 and an aldehyde with fewer carbon atoms than the original alcohol.

Adsorption of both substrates and oxygen on metal oxides are sometimes enhanced during photolysis, with hydrogen peroxide concentrations at the surface increasing with longer irradication periods.[144] Photoadsorption can thus dramatically perturb adsorption isotherms measured in the dark.

F. Langmuir–Hinshelwood Kinetics

The importance of substrate preadsorption on a given photocatalyst can be probed by the use of a Langmuir–Hinshelwood (LH) kinetic model[116,144–146] modified to accommodate reactions occurring at a solid–liquid interface. This model assumes that (1) at equilibrium, the number of surface adsorption sites is fixed; (2) only one substrate may bind at each surface site; (3) the heat of adsorption by the substrate is identical for each site and is independent of surface coverage; (4) there is no interaction between adjacent adsorbed molecules; (5) the rate of surface adsorption of the substrate is greater than the rate of any subsequent chemical reactions; and (6) no irreversible blocking of active sites by binding to product occurs. With these assumptions, the surface coverage Θ is related to the initial concentration of the substrate C and to the apparent adsorption equilibrium constant K_1 (eq 21). The rate of product

$$\Theta = KC/(1 + KC) \qquad (21)$$

formation can then be written as a single-component LH kinetic rate expression (eq 22) where k is the

$$r_{LH} = -dC/dt = kKC/(1 + KC) \qquad (22)$$

apparent reaction rate constant occurring at the active site on the photocatalyst surface. The linearity of a plot of $1/r_{LH}$ versus $1/C$ tests the validity of the LH model, where $1/k$ is the y intercept and $1/kK$ is the slope. Many photocatalytic reactions show good linearity in such plots,[65d,119,146–148] the early work on the photocatalytic mineralization of alkyl halides[149] being representative. Unfortunately, this fit cannot be taken as a solid proof of preadsorption since an identical analytical formulation of the rate law is obtained even for reactions occurring entirely within a homogeneous phase.[116] The initial phase of the oxidation of methyl vinyl ketone is also described by Langmuir–Hinshelwood kinetics, indicating once again the importance of preadsorption.[64] This linearity has led to the inference that the photocatalytic decomposition occurs completely on the catalyst surface,[148] although this interpretation has been criticized.[116] In fact, this study argued that analytically identical rate expressions would be obtained if the reaction between substrate and photogenerated oxidant were to occur while both species were adsorbed, with an adsorbed substrate and a free oxidant, with a bound oxidant and a free substrate, or with both the oxidant and substrate freely dissolved. The processes in which a surface-generated catalytic species diffuses to the bulk solution where the primary catalytic conversion occurs are described by an Eley–Rideal pathway, whose potential applicability to photocatalysis has been specifically discussed elsewhere.[150] Unfortunately an experimental distinction between these pathways, based on kinetics alone, is not possible because of the kinetic ambiguities discussed above.

Although the LH approach avoids the necessity for a complex mathematical formulation of surface binding, and hence the need for several experimentally undeterminable parameters, it still possesses inherent limitations.[97,150,151] The following expression has been suggested to account for reactions involving competition between two or more species for a single adsorption site:

$$r_{LH} = kKC/(1 + KC + \textstyle\sum_i K_i C_i) \qquad (23)$$

where i is a competitively adsorbed species.[126] For example, the effect of HCl on the initial photomineralization rate of organic substrates in aqueous acid can be described by[72b]

$$r_{LH} = kKC/(1 + KC + K_{HCl}C_{HCl}) \quad (24)$$

$$1/r_{LH} = K_{app}/KC + 1/k \quad (25)$$

where $K_{app} = K/(1 + K_{HCl}C_{HCl})$. This model, however, does not seem ideally in accord with the near independence of surface concentration of Cl^- on bulk concentration as predicted from electrostatic model.[152] Furthermore, a direct competition by a neutral, nonpolar organic adsorbate and a highly solvated small ion for a common site is somewhat chemically counterintuitive.

Nonetheless, examples exist which imply that this coadsorption may be reasonably general. For example, the dye methylene blue, when completely mineralized over thin films of near-UV illuminated TiO_2, followed LH kinetics,[146a] but the decomposition of an intermediate product as a precursor to CO_2 was indicated by the slower rate of CO_2 formation (ca. 4 times) than the rate of dye degradation.

Because a basic assumption of the LH kinetic model is the requirement for surface preadsorption, a broad range of reaction rates might reasonably be expected from differences in adsorptive affinity of different substrates on a given semiconductor surface. However, the observed rates k are surprisingly similar in different reactions that have been studied.[116]

G. pH Effects

A common feature of photocatalytic reactions occurring on metal oxide or metal chalcogenide semiconductor powders suspended in aqueous solution is the weak dependence of the reaction rate on solution pH.[20,53,153–155] The particle size, surface charge, and band edge positions of TiO_2 are strongly influenced by pH.[156] The isoelectric point for TiO_2 in water is about pH = 6,[157] and positive surface charge is expected at lower pH and negative surface charge is predicted at higher pH values. Nonetheless, changes in rate of photocatalytic activity from one end of the pH range to the other are usually small, often less than 1 order of magnitude. Despite clear evidence for the importance of surface charge on substrate adsorptivity, evidence for higher reaction rates for various photocatalytic conversions at both low pH or at high pH can be found in the literature.

With TiO_2 powders (anatase and rutile) suspended in aqueous silver nitrate solution, the rate of photoproduction of O_2 and elemental Ag was affected by the solution pH.[158] The observed pH dependence was attributed to surface-charge dependence of Ag^+ adsorption: a decrease in pH led to protonation of either thermal or bridging surface O^- and OH groups which inhibited Ag^+ adsorption to the surface. pH effects have also been shown to be significant factors in governing photoreduction (and deposition) of metals.

H. Temperature Effects

Like most photoreactions, photocatalytic reactions are not dramatically sensitive to minor variations in temperature. The rate of photoassisted decomposition of aliphatic alcohols was insensitive to temperature variation.[159,160] Thus, the potentially temperature-dependent steps, such as adsorption, desorption, surface migration, and rearrangement do not appear to be rate determining in this case. Arrhenius behavior was observed in the photodetoxification of phenol[161] and salicylic acid,[10] although a linear dependence of reaction rate on temperature was reported in the photocatalyzed decomposition of chloroform.[162]

I. Sensitization

Charge carriers can also be formed in semiconductor particles by excitation of a dye attached by chemisorption or physisorption to the surface of the photocatalyst. The excited state can inject either a hole, or more commonly, an electron to the particle. High efficiencies for charge injection are observed when monolayer coverages of dyes are dispersed on high surface area photocatalysts. This sensitization permits expansion of the wavelength response of the photocatalyst, a goal which is particularly important when the photocatalysts are to be illuminated with natural sunlight since the chemically stable metal oxides are wide band gap semiconductors whose absorption onsets typically occur in the low energy end of the ultraviolet spectrum. Photosensitization of semiconductors by various dyes, monitored by nanosecond and picosecond flash photolysis,[92] has provided valuable information on the mechanism of interfacial electron transfer on the semiconductor surface. Upon pulsed excitation of a dye-sensitized semiconductor, a shift in the flat-band potential caused by localization of electric charge on the semiconductor surface also occurs.[88] Furthermore, very highly efficient sensitization of high area metal oxides has been attained with transition metal cyanides (presumably by surface precomplexation)[163] or electrostatic association with metal complexes bearing carboxylate groups.[164]

Laser flash photolysis studies demonstrate that electronic excitation in the visible absorption band of phenylfluorone (2,6,7-trihydroxy-9-phenylisoxanthen-3-one, PF) greatly accelerates the electron transfer from the conduction band to solution acceptors such as methyl viologen.[165] A structure of the surface chelate formed by the interaction of PF with the surface of TiO_2 has been proposed on the basis of changes in the infrared vibrational modes for C=O, OH, and C=C. PF functions as a h^+ trap, greatly facilitating efficient electron transfer of conduction band electrons to MV^{2+} molecules coadsorbed on the surface.

It has also been suggested that inclusion of transition metal ion dopants might alter the e^-/h^+ pair recombination rate and enhance the photoresponsiveness of the semiconductor.[166–168] For some dopants, enhanced reactivity is observed but, unfortunately, homogeneous doping of TiO_2 with tri- and pentavalent heterocations, such as Ga^{3+}, Cr^{3+}, Sb^{5+}, and V^{5+} proved to reduce, rather than enhance, photocatalytic activity, as is discussed in more detail below.

IV. Semiconductor Pretreatment and Dispersion

A. Photocatalytically Active Semiconductors

Because of their resistance to photocorrosion, wide band-gap metal oxides have found greatest utility in heterogeneous photocatalysis. Metal chalcogenides such as CdS and CdSe have narrower band gaps, making them sensitive to incident light in the visible spectrum. With these semiconductors, however, photocorrosion is significant and can only be partly suppressed by the addition of sulfide and sulfite to the contacting solution. Hematite (α-Fe_2O_3), for example, is absorptive in the visible region (absorption onset = 560 nm), but shows much lower photocatalytic activity than does TiO_2 or ZnO, probably because of corrosion or the formation of short-lived metal-to-ligand or ligand-to-metal charge transfer states.[169,170] The most commonly studied photocatalysts are TiO_2, ZnO, and CdS. Because of its high photocatalytic activity, titanium dioxide has become the benchmark photocatalyst against which photocatalytic activity is measured. Of the three crystalline forms of TiO_2 (anatase, rutile, and brookite), anatase is most commonly used. In_2O_3 and $SrTiO_3$,[93] as well as SnO_2 and WO_3,[62] typically demonstrate much lower levels of photoactivity, and SiO_2 and MgO,[171] as insulators, are not active photocatalysts.

Although cadmium sulfide is not as photoactive as TiO_2, it has been extensively studied because of its good spectral response to wavelengths of the solar spectrum. Like ZnO, CdS suffers from photocorrosion induced by self-oxidation[172] (eqs 26 and 27). These competing

$$CdS + 2h^+ \rightarrow Cd^{2+} + S \tag{26}$$

$$ZnO + 2h^+ \rightarrow Zn^{2+} + {}^1/_2O_2 \tag{27}$$

reactions lead to depressed photoactivity and the release of sometimes dangerous metal ions (e.g., Cd^{2+}) into solution.

B. Photocatalyst Preparation[167]

Most commercial semiconductor samples exhibit photocatalytic activities that can vary from batch to batch[47,65b,156,173] because surface characteristics are influenced by physicochemical features determined by the catalyst's origin and preparation. Among the variables which alter photocatalytic activity are surface area (roughness), the state of surface hydration and hydroxylation, surface crystallinity, surface charge caused by an excess of cations or anions on the surface, annealing pretreatment, and the presence of dopants and impurities. Because of difficulties in quantitatively reproducing photocatalyst activities from one laboratory to another, Matthews has suggested, following consensus suggestions made at several international meetings, that the photodegradation of phenol on Degusa P-25 TiO_2, used without further treatment, might provide a basis for future comparative photocatalytic reactor performance evaluations.[174] This commercially available TiO_2 powder is mostly anatase in crystalline form and has a surface area of about 50 m^2/g and a primary particle size of 30 nm.

Heating samples of amorphous TiO_2 prepared by precipitation of titanium isopropoxide at 350 °C for a few hours results in increased photoactivity for the photocatalytic decomposition of water, acetic acid, and 2-propanol.[175] Presumably, this annealing produces anatase from amorphous TiO_2. Annealing in air at an even higher temperature (1300 K) renders the semiconductor more photocatalytically active for the otherwise difficult photoreduction of N_2,[112] possibly by introducing defect states within the semiconductor's band gap. However, the photocatalytic behavior of annealed TiO_2 toward N_2 photoreduction is sustained for only several hours before the surface becomes catalytically inactive.

The photocatalytic activity of ZnS has not received as much attention as TiO_2 or CdS because of its generally poorer catalytic efficiency and photoinstability, without appreciably improved wavelength response. However, photostable, freshly prepared ZnS suspensions without noble metal surface modification have been reported recently.[176] ZnS is efficient in the photocatalysis of one- or two-electron photoreductions.[176b,177]

Rapid mixing of Cd^{2+} and SH^- solutions produces very small particles (diameters to 1–3 nm) with very narrow size distributions. The differences in the morphology of these freshly-prepared quantized-sized CdS samples and commercially available CdS powders caused improved quantum efficiency and selectivity in visible light-induced two electron-transfer photoreductions on the small CdS particles.[178] Fast-flow chromatography employing high-pressure size exclusion was used for the fractionation and size determination of the CdS sols.[179]

C. Surface Perturbation

1. Surface Chelation and Covalent Attachment

Photocatalytic activity can also be influenced by surface derivatization. Further improvements on interfacial electron transfer have been achieved by surface chelation of metal oxide semiconductor particles. Sulfur-containing compounds, OH anions, EDTA, and other chelating agents are known to influence the band-edge positions of some semiconductors, shifting the conduction band to a more negative potential.[180]

Derivatization of semiconductor surfaces has a profound effect on the interfacial electron-transfer rate. Chelated cobalt(II) tetrasulfophthalocyanine ($Co^{II}TSP$) is an efficient electron relay for promoting photoassisted redox reactions on TiO_2.[181] Specifically, $Co^{II}TSP$ covalently linked to a TiO_2 surface channel photogenerated conduction band electrons to $Co^{II}TSP$ to form $O_2^{\bullet -}$. The photoefficiency of *n*-octyl-derivatized TiO_2 in the oxidation of α-methylstyrene to acetophenone in nonaqueous solution showed a 2.3-fold increase over that observed on Pt/TiO_2.[57] This increase in photoefficiency has been attributed to the enhanced surface adsorption of the hole trap, α-methylstyrene. Alkanethiols with long aliphatic hydrocarbon chains can be covalently attached to colloidal CdS when present in solution during the precipitation of a CdS colloid.[182] The hydrocarbon chain on the thiolate-stabilized CdS renders the colloids soluble in organic media without too adversely influencing photoactivity.

2. Salts

The effects of common inorganic anions on the rates of photooxidation of organic compounds on irradiated TiO_2 has been examined by monitoring the rate of CO_2 evolution from salicyclic acid, aniline, and ethanol.[183] Perchlorate and nitrate had very little effect on the photooxidation rates, but sulfate, chloride, and phosphate are rapidly adsorbed by the catalyst and reduce the observed oxidation rate by 20–70%. These observations suggest that inorganic anions may compete with the organic substrate for surface active sites or can form a highly polar environment near the particle surface, thus blocking the diffusion or organics to the active site.

The efficiency of oxalate dianion as a hole scavenger was determined by measuring the rate of oxalate photooxidation.[164] At pH 8, oxalate is irreversibly oxidized with high efficiency. Scavenging of photogenerated H_2O_2 by Ba^{2+} ions to form insoluble barium peroxide leads to a striking improvement in water cleavage in aqueous Pt/TiO_2 dispersions.[185]

3. Codeposition of Metals

The codeposition of noble metal islands on TiO_2 has been shown to be useful in improving the efficiency of photoredox transformations, particularly when gas evolution is expected. Metallic platinum can be deposited on TiO_2 powder by photocatalytic reduction of an aqueous suspension containing chloroplatinic acid, sodium chloroplatinate, hexahydroxyplatinic acid, or platinum dinitrodiammine.[186] Formation of large agglomerates of small Pt particles results from platinum's proclivity to act as an electron accumulation center,[187] producing a high metal loading while the semiconductor surface remains accessible to photons and adsorbates. ^{195}Pt NMR has been used to investigate the strong metal-support interaction in Pt/TiO2 and Pt/SiO2 catalysts.[188] Other noble metals can be comparably deposited, often leading to similar photoactivity effects.

On the other hand, platinization of TiO_2 was found to be detrimental to its catalytic activity in the photodegradation of hydrocarbons such as cyclohexane. The loading level was important in governing the net effect of metallation, with heavy metal loading inducing faster electron-hole recombination.[187]

Numerous studies[159,189-191] have been performed to clarify the role of photodeposited metallic Pt in the surface redox reactions. At low Pt loadings (0.1-1 wt %) of the TiO_2 surface, enhancement of photoactivity probably results from an optimal attraction of free electrons of titania by Pt crystallites. Transmission electron microscopy indicates that the perturbed reactivity is not caused by any surface area or roughness alterations introduced during platinization. In H_2 evolution from alcohols, the Pt crystallites are believed to assist in the formation and desorption of H_2 molecules. Also, faster electron exchange can occur between Pt crystallites and TiO_2, leading to modification of the catalytic properties of the semiconductor. The efficiency of Pt as a one- or two-electron channel has been illustrated in the high specificity for photocatalysis of halothanes on Pt/TiO_2.[72c] Efficient channeling of electrons from the conduction band through the Pt relay is thought to be responsible. Silver[192] and gold[193] deposits similarly influence photocatalytic activity. Because of the expense of noble metal cocatalysts, metal chalcogenides have sometimes been deposited as hydrogen evolution catalysts on metal oxide or metal chalcogenide photocatalysts.[177]

Semiconductor surface metalation offers a method for metal (Au, Pt, Pd, Rh, and Ag) recovery from industrial wastes or dilute solutions. The potential use of semiconductor photocatalysis to the recovery of Au from an alloy containing Au, Cu, Ni, or Zn has been demonstrated on either UV-irradiated TiO_2 in HCl/HNO_3 mixtures (pH 3-6) or visible-irradiated WO_3.[194] The photoreduction of Au(III), however, proved to be difficult in the presence of CN^-, which is present in conventional effluents from mining and electroplating. Under these conditions, $Au(CN)_4^-$ was formed, and the driving force for its photoreduction was small. Cyanide is itself photocatalytically degraded under these conditions.[195-196] Another study focused on the oxidation reactions of CN^- and $Au(III)CN^-$ ions in solution in the presence of H_2O_2 and $S_2O_8^{2-}$, where removal of CN^- prior to the photoreduction of Au(III) proved to be advantageous.[197]

4. Dopants

Transition metal doping can expand to the responsiveness of suspended metal oxide particles to the visible.[198-205] On such doped materials, enhanced photocatalytic activity for the reduction of CO_2[204] and N_2[40,206] have been reported. Enhancement in the rate of photoreduction upon metal ion loading of the semiconductor can produce a photocatalyst with an improved trapping-to-recombination rate ratio.[112] This effect seems to be sensitive to dopant level, however, for although Fe^{3+} doping increases carrier lifetimes in TiO_2[207] and Fe^{3+} doping at below 0.5% improves MV^{2+} reduction, it sharply reduces the efficiency at higher levels.[208] Therefore, significantly decreased activity has also been described as resulting from doping,[209] and the effects of transition metal ion dopants are understandably somewhat difficult to generalize for all systems.

Some transition metal dopants, such as Fe^{3+} [110] and V^{4+},[210] inhibit e^-/h^+ pair recombination, while others such as Cr^{3+} are detrimental to the photocatalytic efficiency of the semiconductor, the inhibitory action of Cr^{3+} on the photoreduction of N_2 to NH_3 being illustrative.[211] Improved results for sustained water photocleavage in the visible region with Cr^{3+}-doped colloidal TiO_2 have been reported, although subsequent reproducibility of these experiments has been difficult.[212] In Fe^{3+}- and V^{4+}-doped TiO_2, an increase in intensity of the ESR Ti^{3+} signal[110b] indicates that there is an accumulation of trapped conduction band electrons as Ti^{3+}.

In phenol degradation, the photoactivity of TiO_2 is not affected by Cr^{3+} or Fe^{3+} ions. The difference in reactivity between the photoreduction of N_2 and the photooxidation of phenol has been attributed to inherent differences in the gas-liquid and liquid-solid interfaces, rather than to differences induced by metal-doping at the semiconductor surfaces.[67]

From a chemical point of view, TiO_2 doping is equivalent to the introduction of defect sites, such as Ti^{3+}, into the semiconductor lattice where the oxidation of Ti^{3+} species is kinetically fast. The differences in photoactivity between Fe^{3+}/TiO_2 and Cr^{3+}/TiO_2 derive from the differences of the diffusion lengths of the minority carriers: the diffusion length is 1 μm for pure TiO_2, 0.2 μm for Cr^{3+}/TiO_2, and 2 μm for Fe^{3+}/TiO_2.[199] On this basis, e^-/h^+ recombination for Cr^{3+}/TiO_2 is more efficient than with Fe^{3+}/TiO_2.

For optimal e^-/h^+ separation, the magnitude of the potential drop across the space-charge layer should not fall below about 0.2 V.[213] The dopant content therefore directly influences the rate of e^-/h^+ recombination as reflected in

$$W = (2\epsilon\epsilon_0 V_s/eN_d) \tag{28}$$

where W is the thickness of the space-charge layer, ϵ is the static dielectric constant of the semiconductor, ϵ_0 is the static dielectric constant of vacuum, V_s is the surface potential, N_d is the number of dopant donor atoms, and e is the electron charge. When W approximates the penetration depth of light into the solid ($l = 1/a$, where a is the light absorption coefficient at a given wavelength), all of the photons adsorbed generate e^-/h^+ pairs that are efficiently separated.

Polyvalent heterocations, such as vanadium,[24,214] molybdenum,[215] Ga^{3+},[24] Cr^{3+},[24] and Sb^{5+},[24] also negatively affect the photoactivity of TiO_2. It is postulated that the electrons in the d orbitals of vanadium and molybdenum act as donors to quench the photogenerated holes by indirect recombination before they can diffuse to the surface. Likewise, homogeneous doping of TiO_2 with Ga^{3+}, Cr^{3+}, and Sb^{5+} creates acceptor and donor centers that behave as recombination centers for the photogenerated charge carriers.

In aqueous semiconductor dispersions of metal-doped semiconductors, metal ions contribute to increase semiconductor photoactivity through their interaction with peroxo species produced on the catalyst surface as well as in solution. The photodegradation of phenol in aqueous polycrystalline TiO_2 (anatase and rutile) has been used to probe the influence of Fe^{3+}, Fe^{2+}, and Ag^+ on the rate of carrier recombination.[215] Fe^{3+} and Fe^{2+} behaved similarly under the same reaction conditions. Negligible phenol photooxidation was observed in the absence of O_2 or other efficient electron scavengers. The Ag^+/Ag redox couple may play a similar role to that of Fe^{3+}/Fe^{2+} in the decomposition of H_2O_2. With Fe^{3+}/Fe^{2+} and Ag^+/Ag couples, there is indirect evidence for the photoreduction of O_2 on anatase TiO_2 with the production of H_2O_2, with both couples enhancing the photooxidation rate of phenol in aerated water on anatase.

Surface-adsorbed Ag^+ ions enhance water oxidation by photogenerated holes through efficient trapping of the photogenerated conduction band electron.[158]

V. Conclusions

Heterogeneous photocatalysis involves electron-hole pair formation initiated by band-gap excitation of a semiconductor particle. Photocatalysis, a widely applicable method for activating adsorbed organic molecules, is promising as a route to selective synthetic transformations or as an advanced oxidation process for environmental cleanup. In oxidatively inert solvents (like acetonitrile), single-electron oxidation to capture a photogenerated hole by interfacial electron transfer is the primary activation step for many organic molecules, and secondary chemical reactions of these adsorbed cation radicals can effect a range of interesting conversions. In water, hole trapping by solvent (to form a surface-bound hydroxy radical) is probably the dominant primary step, although direct hole trapping (by a surface oxide or bound hydroxy radical) followed by interfacial electron transfer from a coadsorbate may be at least partially kinetically competitive for very strongly adsorbed substrates. Thus, the surface-bound hydroxy radical can effect either direct hydroxylation or can act as a strong electron-transfer oxidant.

The photogenerated electron is usually trapped by oxygen or (in the absence of air) by adsorbed protons. In the former case, oxidative cleavage and/or oxygenation products result, in some cases proceeding to complete mineralization of the organic substrate. In the latter case, hydrogenation and/or chemical reduction products are formed. With a noble metal cocatalyst present on the surface of the dispersed semiconductor, hydrogen gas evolution can sometimes also be observed.

The surface-bound hydroxy radical (hole trap) generated by photocatalysis exhibits kinetically different reactivity from that observed for a free hydroxy radical completely solvated in homogeneous bulk solution. This is suggestive of at least a significant portion of the net oxidative conversions in aerated water occurring on the surface of the photocatalyst before desorption of the reactive intermediate into the bulk of the contacting solution. A continuing challenge in photocatalysis research is to provide unambiguous evidence for the site of the secondary reactions that determines the course of these redox transformations. Suggestive evidence exists that photocatalytic reactions frequently occur at the surface of the photocatalyst and, more ambiguously and less generally, in the bulk of the contacting solution.

The photocatalytic activity of a given semiconductor as a photocatalyst can be influenced by the choice of semiconductor, with metal oxides (particularly TiO_2) showing best photostability and hence highest sustained photocatalytic activity. Photocatalytic efficiency, being controlled often by the effectiveness of suppression of electron–hole recombination, is also affected by reaction conditions, the inclusion of dopants or sensitizers during photocatalyst preparation, and surface treatments by ions, coadsorbates, or metallic cocatalysts. A detailed investigation of these effects requires a range of interdisciplinary chemical talents: such problems provide continued intellectual rationale for seeking to understand the basic science which governs interfacial electron transfer.

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VI. References

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