

Organic Heterogeneous Photocatalysis: Chemical Conversions Sensitized by Irradiated Semiconductors

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One of the most active areas of photochemical research involves the light-induced generation of fuels from abundant, inexpensive materials. Prominent among such studies is the production of hydrogen gas by catalytic splitting of water. A pioneering approach to this problem was described in 1972 by Fujishima and Honda¹ who reported the sustained oxidation of water at illuminated TiO₂ in a photoelectrochemical cell. Although the related reduction to produce hydrogen could not be effected without applying a 0.2-V external bias, their paper unleashed a worldwide effort at discovering new, alternate catalyzed routes for photoredox reactions occurring on illuminated semiconductors. Specifically, the possibility of using the semiconductor/liquid junction as a site for light-stimulated redox reactions² has provided a simple conceptual framework for extensive progress toward efficient hydrogen generation by water splitting³⁻⁵ or by other important conversions such as the water gas shift reaction.⁶

Given the rapid progress toward understanding photocatalytic, heterogeneous redox reactions of water and other simple inorganic molecules, the virtual absence of analogous studies for organic systems is perplexing. It is the aim of this Account to outline possible applications of the principles of photoelectrochemistry to sensitized organic phototransformations. This area is important not only because of its potential for uncovering new techniques for functional group modification but also because of its relationship to general problems involving heterogeneous photocatalysis and radical ion intermediates.

Principles

Any mechanistic description of a photoreaction begins with the absorption of a photon. In heterogeneous systems, either the solid or the contacting liquid may be initially excited. Specifically, for reactions occurring at the semiconductor/liquid interface, either the semiconductor itself or the adsorbent may function as the chromophore. In the former case, net chemical change results via direct production of an excited state, whereas in the latter case, sensitization via either electron or energy transfer initiates reactions.

When stable, robust, solid semiconductors (in single crystal, polycrystalline, or powdered form) are used as sensitizers, the stimulation of solution-phase reactivity by initial excitation of the solid-phase semiconductor has been termed photocatalysis, since the photosensitive solid can be recovered unchanged after many turnovers

of the redox system. Any net redox reaction requires concomitant operation of both an oxidation and a reduction. The reductant and oxidant can each be described by characteristic electrochemical potentials, which relate the ease of electron donation or acceptance to a common energetic scale. The energy difference between these potentials defines a free energy of reaction. If the electron transfer of interest is thermodynamically permissible, but kinetically slow in the ground state, and if photostimulation opens an alternate, kinetically favorable route for the interaction, then such a sensitization can be termed photocatalytic or photoelectrocatalytic.⁷ If, on the other hand, the electron exchange is endothermic, the sensitization can be called photosynthetic or photoelectrosynthetic.⁷ Typical energetic orderings for these two cases are shown in Figure 1 and specific examples of these conversions are given below.

Band Theory: Semiconductor Redox Sensitization

Semiconductor sensitization of either organic or inorganic redox reactions involves the absorption of light and the induction of electron transfer across the semiconductor/liquid interface. Both experimental and theoretical descriptions of the principles governing these events are available elsewhere,⁸⁻¹³ and only a brief summary of their operation is given here.

The energetics for the critical interfacial electron transfer can be obtained from the working model proposed originally for photoelectrochemical cells by Gerischer.¹³ As shown schematically in Figure 2, a semiconductor is characterized by band structure, i.e., a filled valence band (VB) separated by an energy gap (E_g) from a vacant conduction band (CB). When a semiconductor is immersed in a liquid electrolyte solution containing a redox couple, charge transfer occurs across the interface to equilibrate the potentials of the

(1) Fujishima, A.; Honda, K. *Nature (London)* 1972, 37, 238.

(2) Nozik, A. J. "Photoeffects at Semiconductor-Electrolyte Interfaces"; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 146.

(3) Leygraf, C.; Hendewerk, M.; Somorjai, G. A. *Proc. Natl. Acad. Sci. U.S.A.* 1982, 79, 5739 and references therein.

(4) Kalyanasundaram, K.; Borgello, E.; Duonghong, D.; Graetzel, M. *Angew. Chem., Int. Ed. Engl.* 1981, 20, 987.

(5) Sato, S.; White, J. M. *Chem. Phys. Lett.* 1980, 72, 83; *J. Phys. Chem.* 1981, 85, 336, 592.

(6) Sato, S.; White, J. M. *J. Am. Chem. Soc.* 1980, 102, 7206.

(7) Bard, A. J. *J. Photochem.* 1979, 10, 50.

(8) Bard, A. J. *Science* 1980, 207, 139.

(9) Bard, A. J. *J. Phys. Chem.* 1982, 86, 172.

(10) Nozik, A. J. *Ann. Rev. Phys. Chem.* 1978, 29, 189.

(11) Memming, R. In "Electroanalytical Chemistry"; Bard, A. J., Ed.; Marcel Dekker: New York, 1979; p 1.

(12) Wrighton, M. S. *Acc. Chem. Res.* 1979, 12, 303.

(13) Gerischer, H.; Willig, F. *Top. Curr. Chem.* 1976, 61, 33.

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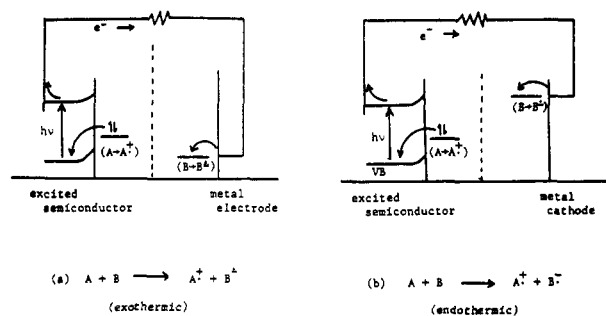


Figure 1. Energy orderings in photoelectrochemical cells: (a) photocatalytic, (b) photosynthetic.

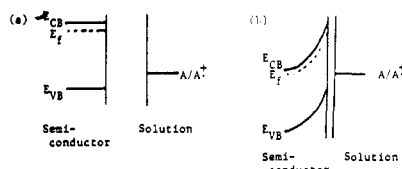


Figure 2. Band structure in a semiconductor: (a) before contact with an electrolyte, (b) after contact with an electrolyte.¹³

two phases, an electric field is formed at the surface of the semiconductor, and the bands bend as the field forms from the bulk of the semiconductor toward the interface.

Photoexcitation of the semiconductor promotes an electron from the valence band to the conduction band, leaving an electron deficiency or hole in the valence band. In a n-type semiconductor, one rendered electron rich by doping with effective electron donors, band bending provides a method for electron-hole pair separation, i.e., for inhibition of collapse of the photoelectron into the photogenerated hole. Thus, when this pair forms in the space charge region of the semiconductor by virtue of absorption of a photon, the electron will move away from the interface to the bulk of the semiconductor as the hole migrates toward the interface where oxidation can occur. The interface energetics will be governed by the potentials of these photogenerated holes and electrons, the hole potential being defined by the energy of the valence band (E_{VB}) and the electron potential being defined by the energy of the conduction band (E_{CB}).

As the oxidation of the adsorbate occurs, charge accumulation in the bulk of the semiconductor is discharged at the connected cathode in a photoelectrochemical cell. In powders, sufficient charge can build up to render the particle electrophoretically mobile.¹⁴ Ultimately, such a charged aggregate can act as a reducing center and effect solution-phase reductions.

Mechanism of Photosensitized Oxidations

A general scheme operative in photoinduced oxidation of adsorbed organics is shown in Figure 3. Here, absorption of a photon by the semiconductor effects electron-hole (e^-h^+) pair formation. After migration of these charge centers to the surface of the irradiated semiconductor, capture of either the photogenerated electron by a reducible, adsorbed species and/or the photogenerated hole by an oxidizable, adsorbed species can occur. The oxidized organic then undergoes rapid chemical reaction. Subsequent formation of the final

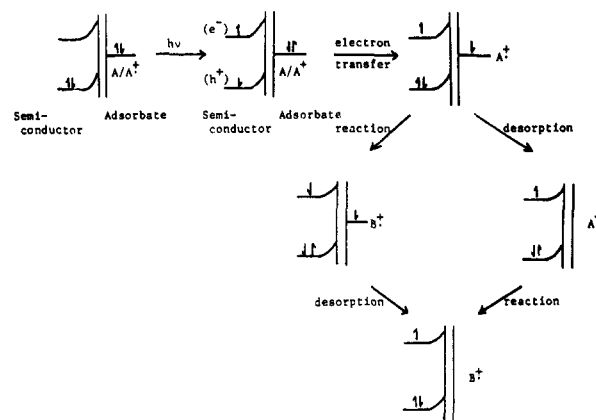


Figure 3. Photoinduced oxidation.

Table I
Band Positions^a for Some Common Semiconductor Photocatalysts (ref 10, 13)

semiconductor	valence band (V vs. SCE \pm 0.1 V)	conduction band (V vs. SCE \pm 0.1 V)
TiO ₂	+3.1	-0.1
SnO ₂	+4.1	+0.3
ZnO	+3.0	-0.2
WO ₃	+3.0	+0.2
CdS	+2.1	-0.4
CdSe	+1.6	-0.1
GaAs	+1.0	-0.4
GaP	+2.2	-1.0
SiC	+1.6	-1.4

^a Band positions in water at pH 1.

products and desorption from the surface completes the usual reaction sequence.

Assuming that single-electron oxidation initiates a demonstrable chemical conversion and that the rate of this chemical reaction is at least competitive with back electron transfer, this model predicts that sensitized oxidation will occur for any organic molecule having an oxidation potential less positive than the semiconductor valence band. Thus, band gap irradiation renders the semiconductor an effective oxidant. Whether oxidation-initiated chemistry can be stimulated by excitation of a given semiconductor may be predicted by comparing the oxidation peak potential of the compound of interest with the valence band position of the sensitizer. Typical values for band positions in a number of common semiconductors are listed in Table I and some representative oxidation potentials for several organic functional groups are listed in Table II. Even a peripheral examination of the relative potentials points to a number of possible interesting photocatalyzed electron transfer that should be amenable to semiconductor sensitization under favorable conditions.

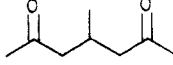

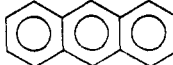
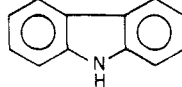
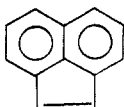

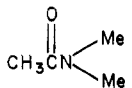
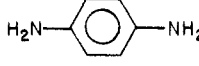

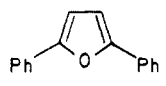

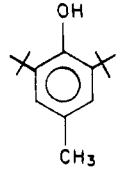

Similar considerations should apply to photosensitized reductions. An excited semiconductor with an electron in its conduction band (Figure 2) can potentially function as an effective reductant. Indeed, claims have been made that even the most difficult of inorganic reductions, e.g., carbon dioxide¹⁵ and nitrogen,¹⁶ can be observed upon semiconductor photocatalysis.

(15) (a) Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. *Nature (London)* 1979, 277, 637. (b) Halmann, M. *Ibid.* 1978, 275, 115.

(16) (a) Schrauzer, G. N.; Guth, T. D. *J. Am. Chem. Soc.* 1977, 99, 7189. (b) Miyama, H.; Fujii, N.; Nagae, Y. *Chem. Phys. Lett.* 1980, 74, 523.

(14) Dunn, W. W.; Aikawa, Y.; Bard, A. J. *J. Am. Chem. Soc.* 1981, 103, 3456.

Table II
Representative Oxidation Potentials for Some
Organic Functional Groups^a

compd	oxid pot. (V vs. SCE)	compd	oxid pot. (V vs. SCE)
	1.56		0.76
	1.09		1.16
	1.21	(PhCH ₂) ₂ NH	1.08
PhPh	1.48	Et ₃ N	0.66
	2.31		1.02
CH ₃ CO ₂ H	1.6		0.18
	1.51		1.29
	1.84		1.21
	1.82		

^a Measured in acetonitrile.

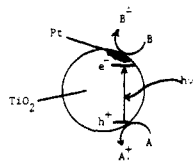


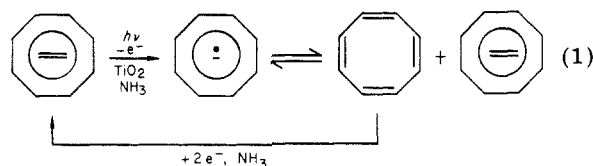
Figure 4. Schematic view of a metallized semiconductor powder.⁹

The application of these concepts to organic redox reactions has received only minimal testing in the laboratory and can therefore provide a potentially fruitful area for investigation. Because of the dearth of well-documented examples involving semiconductor-sensitized reductions, however, the remainder of this Account will emphasize oxidatively initiated organic transformations.

Organic Photoelectrocatalysis on Semiconductor Electrodes

Photoelectrochemical cells have so far been the mainstay for investigations of these semiconductor-catalyzed reactions. If a full kinetic description of the electron-transfer processes or a quantitative rendering of photopotentials, photovoltages, or time dependence of redox equilibration is desired, a complete electrochemical apparatus will be required. In fact, our group's initial interest in organic transformations induced at irradiated semiconductor surfaces was related to the general problem of sensitization of photocurrents in photoelectrochemical cells¹³ and to our investigation of the photochemical properties of organic anions.¹⁷⁻¹⁹ We

showed, for example, that the cyclooctatetraene dianion, a participant in a reversible organic redox couple, could be used as a sensitizer for photogalvanic effects (eq 1).²⁰



Closed-shell monoanions could be similarly photo-oxidized. We showed, for example, that a net endothermic oxidative coupling could be driven by light absorption either by the tetraphenylcyclopentadienide anion adsorbed on a single crystalline TiO₂ electrode or by the semiconductor itself.²¹

Simplified Photoelectrocatalysis

If one is concerned, however, simply with developing new methods for bringing about organic reactions in solution, a much simpler experimental setup can suffice. In particular, the entire electrochemical apparatus can be condensed to a particle that has oxidizing and reducing sites. Picture, for example, a powder granule of a typical semiconductor material upon which small islands of a metal have been deposited (Figure 4). Since the semiconductor and metal are in direct contact, this particle can be thought of as a short-circuited photoelectrochemical cell in which an oxidizable species donates electrons at the semiconductor surface and a reducible species picks up electrons on the metal sites. Immersion of this particle into a liquid phase containing the redox couple of interest and irradiation with photons of greater than band gap energy can initiate exactly analogous redox reactions as found with the macroscopically scaled three-electrode photoelectrochemical cell, but without external current flow.

On a powder, the sites for oxidation and reduction are close together, and such a powder makes impossible the separation of the products of reduction and oxidation into separate half cells. The generation of two reactive species in close spatial proximity, however, may allow for different or directed chemical reactions after the initial electron transfer.

While the depiction of the particle in Figure 4 implies critical kinetic differentiation for the oxidation and reduction, it is often found in practice that a separate metal-reducing site is unnecessary for photocatalysis. Thus, untreated nonmetallized powders have been used to carry out a variety of oxidative transformations. In view of the simplicity inherent in the use of powders to effect such catalyses, particularly in preparative applications, many of the studies to be discussed below have used this technique.

Oxidative Cleavages

One of the first reported oxidative cleavages of an organic molecule induced by long-wavelength ultraviolet

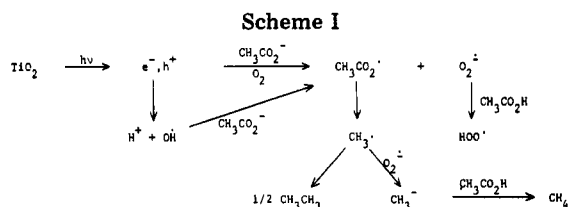
(17) Fox, M. A. *Chem. Rev.* 1979, 79, 253.

(18) For example, see the following: Fox, M. A. *J. Am. Chem. Soc.* 1979, 101, 4008. Fox, M. A.; Voynick, T. A. *Tetrahedron Lett.* 1980, 3943. Fox, M. A.; Owen, R. C. *ACS Symp. Ser.* 1981, 146, 337. Fox, M. A.; Singletary, N. J. *J. Org. Chem.* 1982, 47, 3412. Fox, M. A.; Ranade, A. C.; Madany, I. *J. Organomet. Chem.* 1982, 239, 269.

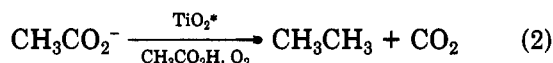
(19) Fox, M. A.; Singletary, N. J. *Sol. Energy* 1980, 25, 225.

(20) Fox, M. A.; Kabir-ud-Din. *J. Phys. Chem.* 1979, 83, 1800.

(21) Fox, M. A.; Owen, R. C. *J. Am. Chem. Soc.* 1980, 102, 6559.



irradiation of a semiconductor involved the photo-decarboxylation of acetic acid (eq 2).²²⁻²⁶ This photo-



Kolbe reaction was studied at the surface of an irradiated *n*-TiO₂ single-crystal or polycrystalline electrode immersed in acetonitrile containing tetrabutylammonium acetate.²² Since the overall reaction is thermodynamically down hill, such a reaction is photocatalytic rather than photosynthetic.

The true catalytic nature of this conversion could be demonstrated by observing current-potential curves obtained under illumination. The photoassisted oxidation was found to proceed at potentials approximately 2.4 V negative of where oxidation occurs on platinum, and a quantum efficiency of about 65% was estimated for this photoconversion. After the reaction, the behavior of the electrode was unaltered.

When the same irradiation was conducted on platinumized TiO₂ (anatase) or WO₃ powders in aqueous acetic acid, methane became the major organic product.²⁴ Other saturated carboxylic acids could be similarly photocatalytically decarboxylated, even if the α -carbon of the carboxylic acid were sterically congested.²⁵ As with the formation of ethane, the overall reaction is exothermic.

The proposed reaction mechanism for this conversion, shown in Scheme 1, begins with electron-hole pair separation in the irradiated semiconductor. The organic oxidation is effected by capture of the photogenerated hole at the surface of the semiconductor powder by the adsorbed acid (or carboxylate). Loss of CO₂ by the carboxylate radical leads to the formation of the alkyl radical, which can either dimerize or be reduced to an anion. Protonation of the latter leads to monomeric decarboxylation product.

The critical difference between the irradiated powders and the irradiated electrode surface probably relates to differences in the space-charge layers in the two experiments. In powders, the existence of a significant space-charge region is unlikely, and photoinduced charge separation is thought to occur mainly on the particle surface. Under such circumstances, the newly formed radical remains rather isolated from other radicals generated in the same fashion, persisting on the surface where back electron transfer ultimately generates the anion. The critical involvement of alkyl radicals could be demonstrated in spin-trapping experiments,²⁶ but the eventual protonation of an anion was established by deuterium-labeling studies.²⁵

- (22) (a) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* 1977, 99, 7729.
 (b) Kraeutler, B.; Bard, A. *J. Nouv. J. Chim.* 1979, 3, 31.
 (23) Sato, S. *Chem. Commun.* 1982, 26.
 (24) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* 1978, 100, 2239.
 (25) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* 1978, 100, 5985.
 (26) Jaeger, C. D.; Bard, A. J. *J. Phys. Chem.* 1979, 83, 3146.

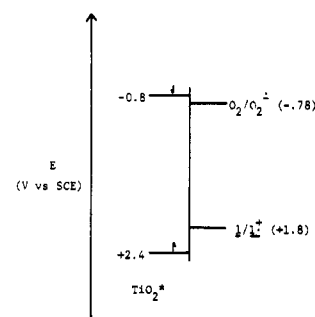
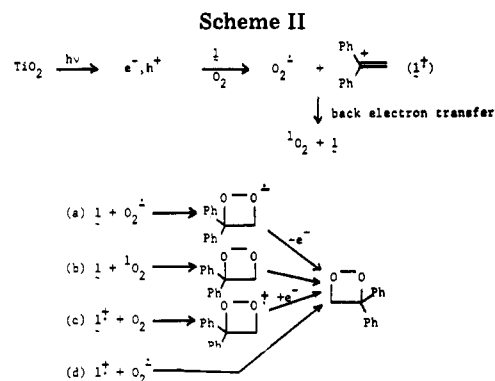


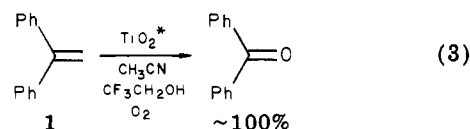
Figure 5. Energetic ordering for the photocatalyzed oxidation of 1.^{27,28}



Olefin Oxidative Cleavage

This pioneering work by the Bard group inspired us to search for other organic reactions that might be photoelectrochemically initiated by excitation of a semiconductor. Tokumaru and co-workers reported at about that time that 1,1-diphenylethylene, 1, could be converted in modest yield to a mixture of benzophenone, 1,1-diphenyloxirane, and 2-methoxy-1,1-diphenylethanol upon irradiation of an oxygenated suspension of TiO₂ or CdS in polar organic solvents.²⁷ The observed inhibition of the photocatalyzed reaction by hydroquinone and by 2,6-di-*tert*-butyl-4-methylphenol led the authors to suspect the involvement of radicals, but little mechanistic information regarding these reaction was available.

We chose to investigate the heterogeneous-photocatalyzed oxidative cleavage of arylated olefins in more detail in order to evaluate whether the predictions of semiconductor band theory were relevant to organic photoelectrochemical oxidations occurring in nonaqueous solvents. We soon established that upon optimizing reaction conditions (identity and form of the semiconductor powder photocatalyst, solvent polarity, and irradiation time) that we could observe efficient, sometimes virtually quantitative, oxidative cleavage of a family of olefins, e.g., eq 3.^{28,29} To set up a working



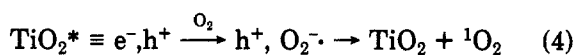
hypothesis, we first considered the thermodynamics of the required electron transfers.

- (27) Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* 1980, 21, 467.
 (28) Fox, M. A.; Chen, C. C. *J. Am. Chem. Soc.* 1981, 103, 6757.
 (29) Fox, M. A.; Chen, C. C. *J. Photochem.* 1981, 17, 119.

The relevant band positions for excited TiO_2 powders in acetonitrile¹³ together with the reported potentials for the electrooxidation of 1,1-diphenylethylene,³⁰ chosen as a representative arylated olefin, and the electroreduction of molecular oxygen³¹ are shown in Figure 5. The energetic ordering is consistent with formation of the olefin radical cation and/or the superoxide anion in the primary electron transfer.

Band gap irradiation of anatase powders could therefore initiate reactivity by a number of routes. A control experiment demonstrated that admixture of TiO_2 powder with the dioxetane derived from 1 led to clean oxidative cleavage. Several routes to this potential intermediate are represented in Scheme II. The possible involvement of homogeneous superoxide as the primary oxidant, path a, was made unlikely by the observation that solubilized potassium superoxide was ineffective in inducing oxidative cleavage of 1 in the absence of irradiated TiO_2 powder. Furthermore, the reaction rate remained unaffected by the presence of dissolved superoxide or of phenylglyoxylic acid, a known superoxide quencher. Such observations do not, of course, rule out the involvement of superoxide adsorbed on the surface of the photocatalyst.

The possibility that singlet oxygen functioned as the primary oxidant required evaluation since 1 could be efficiently converted to benzophenone by singlet oxygen generated independently by dye sensitization. Since singlet oxygen can be produced by oxidation of superoxide, its formation under the conditions of the photoreaction also seemed plausible: under the influence of irradiated semiconductor powders, singlet oxygen could be formed by back electron transfer from superoxide to either the olefin radical cation or to the photogenerated hole in the catalyst (eq 4). Such re-



versible electron transfers obviate spin restrictions encountered in the conversion of ground-state oxygen to singlet oxygen.

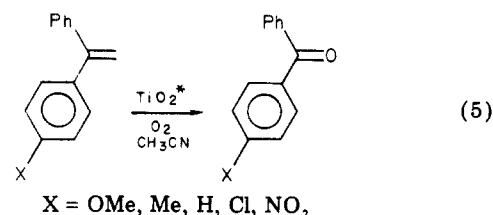
Nonetheless, contrasting chemical behavior was observed when the course of olefin oxidation induced by powder irradiation was compared with that known to occur upon reaction with singlet oxygen. For example, no ene product (known to be formed upon reaction with singlet oxygen) was observed in the oxidative cleavage of tetramethylethylene.^{27,28} Likewise, *trans*-stilbene, an alkene that suffered relatively efficient oxidative cleavage upon irradiation of semiconductor powder suspensions, has been reported to be inert toward singlet oxygen. We conclude that singlet oxygen need not be involved in these conversions.

The other two paths shown in Scheme II both involve the formation of a radical cation. It was important therefore to establish whether formation of these intermediates did indeed occur in nonaqueous solutions. Our observation that a solvent of high dielectric constant was required if efficient photoconversion were to be obtained was consistent with a highly polar transition state.

Relative rates of reaction of a series of olefins should reflect the stability of the one-electron oxidation

product if radical cations are involved. Indeed, reduced reactivity of the olefin was found to accompany decreased π -electron density of the double bond. Thus, 2-methoxy-1,1-diphenylethylene and 2-methyl-1,1-diphenylpropene were as easily oxidized as 1. 4-Methoxystyrene was oxidized more slowly and olefins substituted with electron withdrawing groups, e.g., ethyl cinnamate, benzylideneacetone, and cinnamitrile, could be recovered unchanged.²⁷ Similarly, there exists a rough parallel between the irradiation time required for the oxidative cleavage of a series of substituted naphthalenes and their oxidation peak potentials.³²

The classical demonstration of the involvement of charged intermediates invokes the Hammett relationship. When para-substituted derivatives of 1 were subjected to the TiO_2 -catalyzed oxidative cleavage (eq 5), a linear relationship with a negative slope could be observed between the relative rate of the reaction and σ^+ .³³



More direct evidence for the involvement of radical cations was sought by direct spectroscopic techniques. This requirement necessitated the use of optically transparent heterogeneous catalysts. We achieved this seemingly contradictory goal by synthesizing colloidal TiO_2 in acetonitrile. When such colloidal catalysts were flashed with a nitrogen laser in the presence of *trans*-stilbene, transient formation of an intermediate with spectral properties and a lifetime identical with those reported for the stilbene radical cation could be observed.³⁴ Furthermore, the possibility of using the photocatalyst as a reducing site was established by the observation of the formation of the reduced monocation derived from methyl viologen when the latter species was present in the irradiation mixture.^{34,35}

While none of these results taken alone is compelling, the accumulation of evidence does seem to imply that radical cations may be significant intermediates in these reactions and, thus, that semiconductor band theory may be a useful predictive tool for organic photoelectrochemical reactivity. Further elaboration of the route(s) by which the radical cation is converted to oxidative cleavage product is even more difficult, however.

In path c, the radical cation is captured by molecular (triplet) oxygen, while in path d, this species is attacked by superoxide. The first of these routes has good chemical precedent in Nelsen's observation of stable oxidation products formed upon the single electron oxidation of adamantyladamantylidene, a highly hindered olefin, in the presence of oxygen.³⁶ Formation of an analogous dioxetane from 1 would, under our

(32) Fox, M. A.; Chen, C. C. *J. Am. Chem. Soc.*, submitted for publication.

(33) Fox, M. A.; Chen, C. C. *Tetrahedron Lett.* 1983, 24, 547.

(34) Fox, M. A.; Lindig, B. A.; Chen, C. C. *J. Am. Chem. Soc.* 1982, 104, 5828.

(35) Watanabe, T.; Honda, K. *J. Phys. Chem.* 1982, 86, 2617.

(36) Nelsen, S. F.; Akaba, R. *J. Am. Chem. Soc.* 1981, 103, 2096.

(30) Arnold, D. R.; *J. Am. Chem. Soc.* 1976, 98, 5931.

(31) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker: New York, 1970; p 247.

reaction conditions, lead to the formation of oxidative cleavage product since treatment of the independently generated dioxetane derived from 1 gave rise to benzophenone in high chemical yield. Additional precedent for the reaction of hydrocarbon radical cations with triplet oxygen has recently been elaborated in many studies undertaken after Barton's discovery³⁷ of a reaction now interpreted as involving the capture of a diene radical cation with molecular oxygen.³⁸

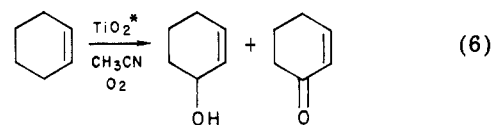
Little is known about the efficiency of reaction of radical cations with triplet oxygen, although the reversibility of many hydrocarbon electrooxidations (at least on a cyclic voltammetric time scale) in solutions from which oxygen has not been rigorously excluded certainly implies that some barrier to the reaction does exist. In order to better evaluate whether the reaction of a radical cation with oxygen might be a reasonable route along this heterogeneous reaction pathway, we turned to semiempirical calculations. Using the unrestricted Hartree-Fock version of MNDO,³⁹ we have evaluated barriers for several routes for the combination of the radical cation of ethylene with molecular oxygen to form the dioxetane radical cation.⁴⁰ This conversion is exothermic and can proceed most easily via two sequential single-bond-forming steps.

Most of the activation enthalpy can be attributed to the eclipsing interactions introduced as the initially highly twisted cation radical⁴¹ assumes the optimal geometry of the dioxetane radical cation. Although these calculations do not estimate the effect of surface adsorption, the relatively low barriers to reaction encountered even without surface activation provide confidence in the assignment of comparable reactivity during the photocatalysis. It is surely reasonable therefore to consider the capture of the photogenerated radical ion by molecular oxygen or superoxide as a possible step in the oxidative cleavage.

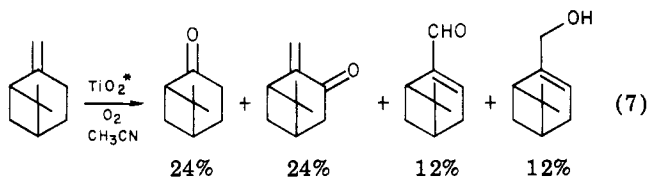
Several photocatalytic studies of hydrocarbon oxidations on semiconductor oxides have also implicated lattice oxygen as the source of oxygen atoms in oxidized products,⁴² but no comparable studies have yet been completed in solution where exchange with solvent and/or gaseous oxygen may be significant. Since oxidative cleavage can also be observed upon photocatalytic sensitization with CdS, the availability of lattice oxygen is surely not absolute. A choice between paths c and d in Scheme II is not yet possible, therefore, but either route seems to be permissible.

Photoelectrochemical principles would predict that only those olefins whose oxidation potentials lie positive of the valence band of the irradiated semiconductor should be subject to photocatalyzed oxidative cleavage. Since simple olefins display oxidative waves positive of 2.5 V, a different reaction course might be expected. These predictions are borne out in the observed photocatalyzed oxidation of nonarylated olefins.³⁸ For example, allylic oxidation is observed when cyclohexene

is subjected to analogous TiO₂ powder photocatalysis (eq 6). With β -pinene, both oxidative cleavage and



allylic oxidation are observed (eq 7).^{28,43} The oxidation



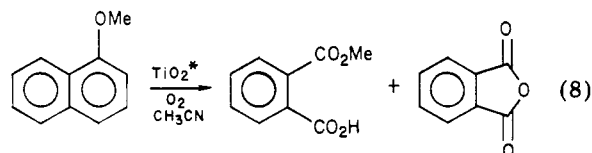
of propylene as a gas stream over powdered metal oxides has also been reported, giving CO₂ as well as products of intermediate oxidation level.⁴⁴

Since single-electron oxidation would be endothermic with these alkenes, it is probable that the reaction proceeds instead by capture of the photoelectron by oxygen, perhaps inefficiently, to give superoxide. If this species is converted to hydroperoxide, a radical chain allylic oxidation can be initiated.

Arene Oxidations

Our next concern involved establishing that the principles operative in controlling the oxidative cleavage of olefins are operative with other organic functional groups. We have investigated so far oxidative cleavages of arenes and amines. With powdered TiO₂ photocatalysis, both functional groups suffer efficient phototransformation.

The photocatalyzed cleavage of substituted naphthalenes proceeds as shown in eq 8.³² The relatively



high yields of oxidized product obtained make this route viable as a synthetic alternative for preparation of ortho-substituted benzenes. Dialkylated naphthalenes react similarly, leading to ketones or to noncleaved oxidation products. When 2,3-dimethylnaphthalene is similarly treated, cleavage of either ring can be observed with a regiochemical preference reflective of charge density calculated for the radical cation.

Other simple benzene derivatives have similarly been subjected to photocatalytic oxidation. For example, toluene can be oxidized to benzyl alcohol upon irradiation of a suspension of powdered anatase in the neat liquid.⁴⁵ In the gas phase, the analogous reaction gives aldehydes,⁴⁶ while as an aqueous suspension, both oxidation and coupling products are observed (eq 9).⁴⁷ Even benzene can be oxidized. Upon irradiation of

(37) Barton, D. H. R.; Haynes, R. K.; LeClerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin. Trans. 1* 1975, 2055.

(38) (a) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc.* 1979, 100, 5248. (b) Landis, M. E.; Madoux, D. C. *Ibid.* 1979, 101, 5106. (c) Haynes, R. K.; Probert, M. K.; Wilmut, I. D. *Aust. J. Chem.* 1978, 31, 1737. (d) Haynes, R. K. *Ibid.* 1978, 31, 121, 131.

(39) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99, 4899.

(40) Fox, M. A.; Chen, C. C. *J. Comput. Chem.*, 1983, in press.

(41) Bellville, D.; Bauld, N. L. *J. Am. Chem. Soc.* 1982, 104, 294.

(42) Courbon, H.; Formenti, M.; Pichat, P. *J. Phys. Chem.* 1977, 81, 550.

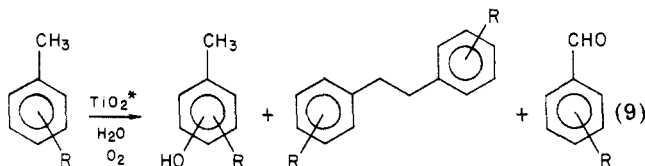
(43) It is noteworthy that no cationic rearrangement products are observed in this photooxygenation. This observation is consistent with the reduced proclivity for rearrangement in radical cations compared with that in closed-shell cations.

(44) Pichat, P.; Herrmann, J. M.; Disdier, J.; Mozzanega, M. N. *J. Phys. Chem.* 1979, 83, 3122.

(45) Fujihara, M.; Satoh, Y.; Osa, T. *J. Electroanal. Chem.* 1981, 126, 277.

(46) Mozzanega, M. N.; Herrmann, J. M.; Pichat, P. *Tetrahedron Lett.* 1977, 2965.

(47) Fujihira, M.; Satoh, Y.; Osa, T. *Nature (London)* 1981, 293, 206.

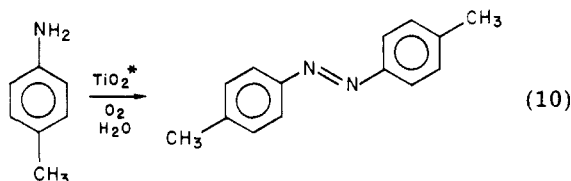


benzene-saturated aqueous suspensions of TiO_2 , phenol formation can be observed, although the main product isolated is carbon dioxide obtained by further indiscriminate oxidation.^{48,49}

While the authors propose a mechanism involving radical cation formation in organic solvents, reactions done in water almost certainly proceed through initial solvent oxidation. The hydroxy radical generated in this fashion is highly reactive and quite unselective, so that limited control observed in the latter reaction is surely understandable. In fact, the formation of the hydroxy radical on irradiated aqueous semiconductor suspensions is well-documented. The use of this mechanistic imperative in devising new routes to photo-Fenton reactions is obvious.⁵⁰

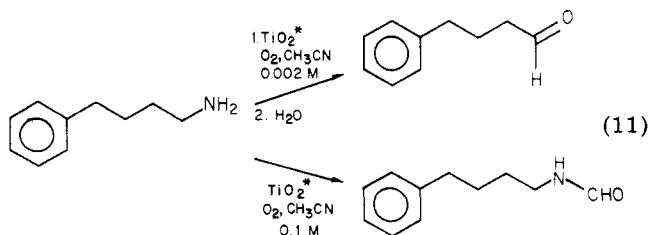
Amine Oxidations

Similar considerations apply to the oxidative cleavage of amines. In the photocatalyzed oxidation of toluidines, for example, azo products are formed (eq 10).⁵¹



Coupling to form oxidized products is obviously more important than oxidation of the pendant alkyl groups. Such oxidations are reminiscent of the photocatalyzed oxidation of ammonia reported by Pichat and co-workers.⁵²

While mechanistic details are still uncertain, preliminary results obtained in our group suggest that amine photoreactivity may indeed be controlled by manipulation of reaction conditions. For example, two pathways (eq 11) can be observed in the photocatalyzed oxidation of a primary amine, depending on the initial concentration of the amine and on the nature of the semiconductor photocatalyst.⁵³



(48) Izumi, I.; Dunn, W. W.; Wilbourn, K. O.; Fan, F.-R. F.; Bard, A. J. *J. Phys. Chem.* **1980**, *84*, 3207.

(49) Izumi, I.; Fan, F.-R. F.; Bard, A. J. *J. Phys. Chem.* **1981**, *85*, 218.

(50) Fujihira, M.; Satoh, Y.; Osa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 666.

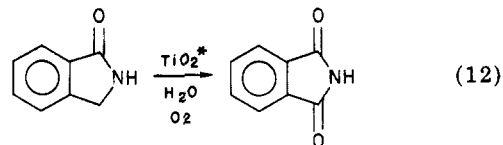
(51) (a) Hema, M. A.; Ramakrishnan, V.; Kuriacose, J. C. *Indian J. Chem., Sect. B* **1978**, *16*, 619. (b) Kasturirangan, H.; Ramakrishnan, V.; Kuriacose, J. C. *J. Catal.* **1981**, *69*, 216.

(52) Mozzanega, H.; Herrmann, J. M.; Pichat, P. *J. Phys. Chem.* **1979**, *83*, 2251; *Chem. Phys. Lett.* **1980**, *74*, 523.

(53) Chen, M. J.; Fox, M. A. *J. Am. Chem. Soc.*, **1983**, *105*, 4497.

Other Catalyzed Oxidations

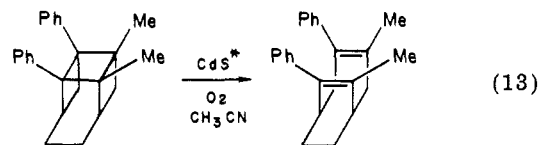
A variety of additional semiconductor catalyzed functional group oxidations have been reported, although scant mechanistic detail is available for these transformations. Foremost among these reactions are the photocatalyzed oxidations of alcohols to aldehydes, ketones, or carboxylic acids⁵⁴ usually as gaseous mixtures in contact with the solid excited photocatalyst. Saturated hydrocarbons can also be photooxidized.⁵⁵ Of greater potential interest to the organic chemist are the photoinduced oxidation of amides to imides⁵⁶ (eq 12) and of bromide to bromine, which can then function



as an electrophilic halogenation agent.^{57,58} Again, mechanistic details are sparse, but both reactions (which have been conducted as aqueous suspensions) may reasonably be assumed to begin by solvent oxidation to generate the hydroxy radical whose subsequent dark chemistry leads to the observed products.

Nonoxidative Photocatalysis

Although semiconductor-photocatalyzed redox reactions have been studied most extensively, several electron-transfer-mediated cycloadditions and reversions have also been described. So far, an examples of a [2 + 2] retrocycloaddition has appeared (eq 13)⁵⁹ as has



an inefficient photocatalyzed dimerization of phenyl vinyl ether.⁶⁰ A single example of a [4 + 4] photocycloreversion, the cleavage of the anthracene photodimer, has also been reported.⁶⁰ The authors suggest that these conversions proceed through photocatalytic oxidation to produce a radical cation. Isomerization of this intermediate and recapture of an electron then leads to the observed products. That these conversions involved electron-transfer sensitization was established by quenching studies and by the isolation of identical products from alternate, known oxidative routes.

A related bond cleavage has been described in the CdS-photocatalyzed dealkylation of methylene blue and rhodamine B.⁶¹ Again electron-transfer sensitization was postulated because of similarities between the CdS-photocatalyzed reaction and that observed with Fe^{3+} sensitization. Singlet oxygen was specifically ex-

(54) For example, see the following: Cunningham, J.; Meriaudeau, P. *J. Chem. Soc., Faraday Trans. 1* **1976**, 1499. (b) Cundall, R. B.; Rudham, R.; Salim, M. S. *Ibid.* **1976**, 1642. (c) Teratani, S.; Nakamichi, J.; Taya, K.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1688.

(55) (a) Djehri, N.; Formenti, M.; Juillet, F.; Teichner, S. T. *Discuss. Faraday Soc.* **1975**, *58*, 184. (b) Courbon, H.; Herrmann, J. M.; Pichat, P. *J. Catal.* **1981**, *72*, 129.

(56) Pavlik, J. W.; Tantayanon, S. *J. Am. Chem. Soc.* **1981**, *103*, 6755.

(57) Taniguchi, I.; Nakashima, K.; Yamaguchi, H.; Yasukouchi, K. *J. Electroanal. Chem.* **1982**, *134*, 191.

(58) Frank, S. N.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 4667.

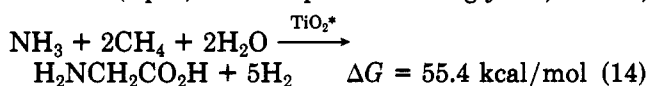
(59) Okada, K.; Hisamitsu, K.; Mukai, T. *Chem. Commun.* **1980**, 941.

(60) Barber, R. A.; de Mayo, P.; Okada, K. *Chem. Commun.* **1982**, 1073.

(61) Takizawa, T.; Watanabe, T.; Honda, K. *J. Phys. Chem.* **1978**, *82*, 1391.

cluded as an important intermediate.

A final example of the photosynthetic potential inherent in the irradiation of semiconductor suspensions containing organic molecules is found in Bard's demonstration of amino acid synthesis. Irradiation of platinized TiO₂ suspensions in aqueous ammoniacal methane (eq 14)⁶² lead to production of glycine, alanine,



serine, aspartic acid, and glutamic acid as well as products of intermediate functionality (methanol, ethanol, and methylamine). The relationship of this observation to chemical evolution is obvious, and the extension of this endothermic reaction⁶³ to other synthetic transformations remains a challenge.

Conclusions

Only recently has the concept of electron-transfer catalysis⁶⁴ been effectively applied in a mechanistic

(62) Dunn, W. W.; Aikawa, Y.; Bard, A. J. *J. Am. Chem. Soc.* 1981, 103, 6893.

(63) Reiche, H.; Bard, A. J. *J. Am. Chem. Soc.* 1979, 101, 3127.

sense to organic reactions. We have shown how electron-transfer-mediated reactions can be initiated by long-wavelength ultraviolet or visible-light irradiation of semiconductor particles. The discovery and characterization of such organic transformations constitute a new area of organic photochemistry, a field replete with both synthetic applications and mechanistic delights. Since such reactions are also of great importance to the larger questions of heterogeneous catalysis, we anticipate that application of this research to many practical organic problems will be forthcoming.

Our research program on photoinduced electron transfer has been generously supported by the National Science Foundation and the Robert A. Welch Foundation. The use of semiconductors as sites for organic photooxidations has been supported by the Fundamental Interactions Branch, Office of Basic Energy Sciences, U.S. Department of Energy. The author is grateful to the Alfred P. Sloan Foundation for fellowship support and to the Camille and Henry Dreyfus Foundation for support as a Teacher-Scholar.

(64) Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 1.

(65) Memming, R. *J. Electrochem. Soc.* 1978, 125, 118.

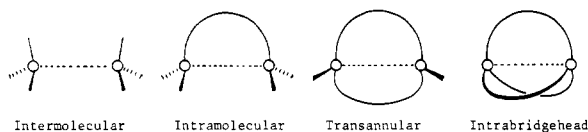
Medium-Ring Bicyclic Compounds and Intrabridgehead Chemistry

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Two-center σ bonding is a cornerstone of chemistry, yet in some senses its limits have been less thoroughly probed than those of π bonding. For elements like carbon and nitrogen it can occur in four topological situations:

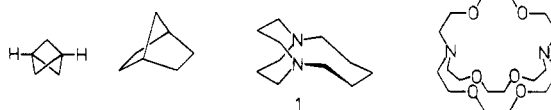


The intrabridgehead situation has important advantages if one wishes to look at weak and exotic σ bonding and antibonding interactions. The two bridgehead atoms can hardly escape from one another, and the structure and stability of the entire molecular species should be relatively independent of the σ interaction we want to examine. The most important point, however, is that close control on orbital alignment is easily

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achieved in the intrabridgehead situation. The compounds needed for these studies should have $\sim 3-5$ atoms¹ in each of the three bridges to permit close approach of the bridgehead atoms without strain; in other words medium-ring (8- to 11-membered) bicyclic compounds.

Organic chemists have put a lot of effort into the preparation of bicyclic compounds containing small (three- and 4-membered) rings in order to probe the limits of bond-angle strain.² Bicyclic compounds containing common-sized rings (5- to 7-membered) are indeed common and important, both as natural products and as "test-beds" for physical organic phenomena. Macrobicyclic compounds containing large (>12-membered) rings have rightly attracted attention recently because of their ability to encapsulate metal ions and other species.^{3,4}



(1) Leonard has discussed the use of trimethylene bridges as spacers for the detection of intramolecular interactions; N. J. Leonard, *Acc. Chem. Res.*, 12, 423 (1979). We think that our work has demonstrated that at least (CH₂)₄ may be an equally effective spacer.

(2) A. Greenberg and J. F. Liebman, "Strained Organic Molecules", Academic Press, New York, 1978.