hole in the valence band.[10,11] Since secondary and tertiary amides are oxidized at 1.8 and 1.2–1.5 V, respectively,[12] electron transfer from amide to semiconductor would be thermodynamically possible.

Since the reactants are inert to photolysis in the absence of a suitable oxidant such as O_2 or Cu(II), these reagents presumably serve as electron acceptors to maintain the charge neutrality of the semiconductor. Considering the potential of the conduction band electron, the reduction of oxygen to H_2O ($E = 0.57$ V), H_2O_2 ($E = 0.024$ V), or $O_2^{-}\cdot$ ($E = -0.39$ V)[13] are all thermodynamically possible. Since the latter two reduction products are oxidizing agents, it is at least plausible that these reagents serve to oxidize the organic reactant rather than the excited semiconductor. The following facts, however, are not consistent with this interpretation.

First, H_2O is known to rapidly quench $O_2^{-}\cdot$ and indeed, where photocatalytically generated $O_2^{-}\cdot$ has been implicated in hydrogen abstraction, the rate of oxidation was observed to decrease significantly upon addition of H_2O to the suspension.[14,15] Accordingly, the observed increase in amide oxidation upon addition of H_2O to acetonitrile suspensions of TiO_2 is inconsistent with significant oxidation by this species. Second, although the reduction of O_2 to H_2O_2 is thermodynamically favorable, its formation has only been observed upon irradiation of reduced TiO_2 powders[16,17] —conditions which do not enhance the rate of amide oxidation. Furthermore, control experiments in the presence of added H_2O_2, but in the absence of TiO_2, or in the presence of TiO_2 but without irradiation were accompanied by a 10-fold decrease in imide formation. Accordingly, direct oxidation by photocatalytically generated H_2O_2 is, at most, a minor pathway in these reactions. Finally, oxidation of **5** with concomitant reduction of Cu(II) confirms that oxidizing agents photocatalytically generated from added molecular oxygen are not a prerequisite for amide reaction.

The increase in oxidation upon addition of H_2O to the reaction medium might also suggest that H_2O is scavenging valence band holes to generate HO· or H_2O· radicals which are, in turn, responsible for amide oxidation. Although such radicals have been detected during irradiation of aqueous TiO_2 suspensions and have been implicated in the photocatalytic hydroxylation of benzene,[18,19] such species do not appear to be responsible for amide oxidation in the present case. Thus, when a nitrogen-purged 0.2 M aqueous solution of Cu(II) containing 100 mg of suspended TiO_2 was irradiated for 6 h in the absence of amide **5**, no reduction of Cu(II) could be detected. Accordingly, the rate at which water scavenges valence band holes cannot account for the yield of reaction in the presence of amide **5**. Similarly, although Bard and colleagues have observed only very low yields of Cu(II) reduction after 24 h of irradiation at much higher light intensities, the reaction yield was greatly enhanced by the addition to the solution of acetate, a species known to efficiently scavenge valence band holes.[20]

As revealed by the mass balance shown in Table I, these photocatalytic reactions show a high degree of selectivity for oxidation at the carbon α to the amide nitrogen. Although in this respect they resemble direct electrochemical oxidations at platinum surfaces[21] and benzophenone sensitized oxidations,[22] reactions at TiO_2 do not yield mixtures of imides and hydroxy lactams as are obtained in the former reactions. Further work directed toward the mechanistic details and synthetic applications of these photocatalytic oxidations is in progress.[23]

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(10) Gerischer H. In "Solar Power and Fuels"; Bolton, J. R., Ed.; Academic Press: New York, 1977.

(11) All potentials in this paper are relative to SCE at pH 7.

(12) O'Donnell, J. F.; Mann, C. K. *J. Electroanal. Chem.* **1967**, *13*, 157; **1967**, *13*, 163.

(13) Meisel, D. *Chem. Phys. Lett.* **1975**, *34*, 263.

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

(20) Reiche, H.; Dunn, W. W.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 2248.

(21) Okita, M.; Wakamatsu, T.; Ban, Y. *J. Chem. Soc., Chem. Commun.* **1979**, 749.

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(23) These studies are part of an interdisciplinary collaborative study with the Advance Technology Laboratory of GTE Laboratories, Inc., Waltham, MA. We greatly appreciate their financial support and collaboration.

Mechanistic Features of the Semiconductor Photocatalyzed Olefin-to-Carbonyl Oxidative Cleavage

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We wish to report our mechanistic investigation of a high-yield selective oxidation of organic olefins which occurs upon irradiation of platinized or metal-free TiO_2, ZnO, or CdS. Our approach combines photoelectrosynthesis[1] (semiconductor band theory[2]) with recent developments in synthetic applications of photoinduced electron-transfer reactions.[3] Our work is the first clear demonstration that sensitized organic photoxidations do, in fact, occur at the semiconductor–liquid interface rather than in bulk solution.

Tokumaru and co-workers recently described the irradiation of TiO_2 or CdS suspended in solutions containg 1,1-diphenylethylene or its simple derivatives [2-methyl-1,1-diphenylpropene or 2-methoxy-1,1-diphenylethylene] which afforded the corresponding epoxides and benzophenone.[4] Our own studies extend these results to other arylated and nonarylated olefins, delineate the mechanistic possibilities for these conversions, and allow for cleaner preparation of carbonyl derivatives than found under the previously described conditions.[4]

Typically, the semiconductor powder (ca. 5 mg) in its native[5] or platinized[6] form was suspended in a solution of olefin (ca. 200 mg, 0.01 M) in a dry acetonitrile–trifluoroethanol (20:1) mixture. The stirred suspension was irradiated under a slow, constant stream of air bubbles at room temperature at 350 ± 30 nm. Under these conditions, essentially no direct excitation of the organic molecules occurs (<1% of incident light). Product formation was monitored by gas–liquid chromatography (GLC) or high-pressure liquid chromatography (HPLC). Parallel results were obtained usually with ZnO and CdS, and relative rates and yields for the oxidation of 1,1–diphenylethylene as a function of semiconductor catalyst and catalyst type were identical within a factor of 2. A typical conversion is shown in eq 1.

If neat acetonitrile is used as solvent, additional oxidation product(s) were formed. For **1**, for example, irradiation with suspended TiO_2 (an air-saturated 0.01 M solution of **1** in acetonitrile) gave rise to a mixture of benzophenone (~64%), 1,1-diphenyloxirane (~32%), and 2,2-diphenylacetaldehyde (~4%) at 50% conversion of starting material. Upon prolonged irradiation, these products were converted, essentially quantitatively, to benzophenone. Product distributions obtained in acetonitrile with several other olefins are shown in Table I. Here, too, prolonged irradiation and/or the use of $CH_3CN-CF_3CH_2OH$ solvent mixture leads to carbonyl compounds in high yield.

We consider first the possibility that the observed oxygenation occurs by generation of an active specie or species at the photoexcited catalyst surface which desorbs into solution where reaction occurs. Band gap irradiation of TiO_2 in acetonitrile causes

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(1) Bard, A. J. *Science (Washington, D.C.)* **1980**, *207*, 139.

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

(3) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609.

(4) Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1980**, 467.

(5) The semiconductor powders were dried overnight at 110 °C before use (TiO_2: Matheson-Coleman-Bell technical grade, powder).

(6) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4317.

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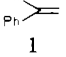
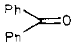
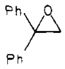
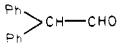
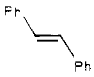
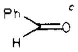
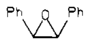
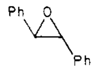
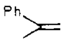
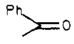
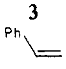
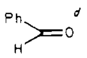
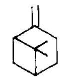
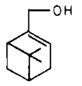
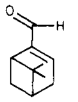
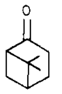
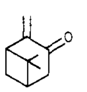
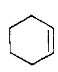
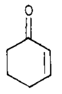
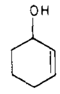
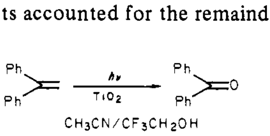
Table I. Photooxidation of Olefins on TiO_2 in Air-Saturated CH_3CN[a]

olefin	% conversion	products (chemical yields %[b])
 1	85	 (84)  (14)  (2)
 2	85	 (33)[c]  (11)  (42)  (14)
 3	50	 (100)
 4	43	 (17)[d]
 5	29	 (12)  (12)  (24)  (24)
 6	10	 (60)  (40)

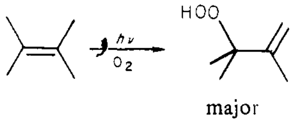
[a] Irradiation in a Rayonet photochemical reactor equipped with RPR-black lights, λ = 350 ± 30 nm; room temperature; irradiation time = 6 h. [b] Yields reported are based on disappeared starting material. [c] Yield of benzaldehyde is based on the expectation of 2 mol of oxidation product derived from 1 mol of stilbene. [d] Oligomeric products accounted for the remainder of consumed starting material.



(1)

the promotion of an electron into the conduction band (band edge ~ −0.8 V vs. SCE)[7] and hence the production of a hole in the valence band (+2.4 V vs. SCE).[8] Thus, oxidation of adsorbed species having oxidation potentials less positive than 2.4 V should be possible, as should reductions of couples with reduction potentials less negative than −0.8 V. Considering an olefin (M)-oxygen couple, three modes of interaction remain possible:[9,10] (a) $M^{+\cdot} + O_2$, (b) $M^{+\cdot} + O_2^{-\cdot}$, and (c) $M + O_2^{-\cdot}$. Of these, mode b allows alternative production of singlet oxygen by reverse electron transfer[11] and, hence, a fourth reaction mode (d) M: + $^1O_2$.

Several recent studies[13-15] have shown that capture of radical cations by triplet oxygen may in fact lead to dioxetanes. Under our reaction conditions, such dioxetanes would cleave to the observed oxidation products.[16] Path a can be evaluated for our systems by generating olefin radical cations in the presence of oxygen. For example, the production of $1^{+\cdot}$ can be accomplished by electrolytic oxidation in acetonitrile saturated with oxygen at the surface of an inert (Pt) electrode. While workup does show the production of some benzophenone (<10% yield), oligomerization is the main reaction pathway. The poor mass balance observed in this electrolysis contrasts sharply with the virtually quantitative oxidation observed with TiO_2 photosensitization. Path b can be excluded by the observation that 0.01 M phenylglyoxylic acid, a known superoxide quencher,[17] fails to influence dramatically the efficiency or product yields in these photooxygenations. The observation that **2** fails to react with a solution of potassium superoxide (0.1 M) in acetonitrile containing 18-crown-6-ether, a species known to solubilize and ionize KO_2,[18] allows the exclusion of path c as a general route to our photooxidations. Much more is known concerning path d. The reaction of singlet oxygen with tetramethylethylene (**7**), for example, has been shown to give mainly ene reaction, together with minor dioxetane and ketone formation (eq 2).[19] The complete absence (<0.5% yield) of ene product derived from **7** under our conditions for catalyzed photooxygenation shows that singlet oxygen cannot be involved.[20] Furthermore, **2**, which efficiently cleaves under our conditions, is known to be essentially inert toward singlet oxygen.[21] Thus, while path a remains possible, but unlikely, we can definitely exclude homogeneous singlet oxygen or superoxide as being active oxidants in our photooxygenations. Tokumaru and co-workers also excluded singlet oxygen in their preliminary studies.[4]



(2)

We can also exclude the possibility that the thermal reversal of initial radical ion pair generation (pathway b) might generate the singlet or triplet excited-state olefins which, upon reaction with oxygen, leads to oxidation products; pathway e: $M^{+\cdot} + O_2^{-\cdot} \rightarrow M^* + O_2$. In no case examined could sensitization of biacetyl emission[22] or product formation known to result from known excited-state chemistry[23,24] be observed. Nor do we find our observed distributions of oxidation products upon direct or sensitized excitation of **1**–**6** in homogeneous solution.

The absence of completely acceptable oxidation mechanisms in homogeneous solution implies that these oxidations may occur instead at the catalyst surface, i.e., at the semiconductor–liquid junction interface. The mechanism at the surface awaits further elaboration and will be the subject of future papers. We note now, however, that in addition to the oxidants discussed above, that several other species (O^-, O_3^-, O_4^-) have been suggested as significant oxidants on such catalyst surfaces.[25] The efficiency of the reaction depends dramatically on the relative positions of the semiconductor valence band and the olefin oxidation potential, the reaction being slowed dramatically as the olefin oxidation potential exceeds the valence band position by more than 0.2 eV and the relative efficiency varying with the identity (and hence

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(7) Frank, S. N.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 7427.

(8) Valence band position was calculated by subtracting the band gap (see Nozik, A. J. *Annu. Rev. Phys. Chem.* **1978**, *29*, 189) from the flat band position.

(9) The oxidation potential of diphenylethylene, for example, is +1.52 V vs. SCE: Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455. The oxidation potentials for nonarylated olefins can be estimated from known ionization potentials.

(10) $E_{1/2}(O_2/O_2^{-\cdot})$ = −0.8 V vs. SCE: Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Non-Aqueous System"; Marcel Dekker: New York, 1970; p 497.

(11) Spin restrictions are relaxed in a doublet–doublet recombination so that either singlet–singlet ($M + {}^1O_2$) or singlet–triplet ($M + {}^3O_2$) production may result. Alternatively, dismutation of superoxide is thought[12] to produce singlet oxygen.

(12) Koppenol, W. H.; Butler, J. *Fed. Eur. Biol. Sci. Lett.* **1977**, *83*, 1. But also see: Guiraud, H. J.; Foote, C. S. *J. Am. Chem. Soc.* **1976**, *98*, 1984.

(13) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc.* **1979**, *100*, 5248.

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

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

(16) Richardson, W. H.; Montgomery, F. C., Yelvington, M. B.; O'Neal, H. E. *J. Am. Chem. Soc.* **1974**, *96*, 7525.

(17) San Filippo, J.; Chern., C.-I.; Valentine, J. S. *J. Org. Chem.* **1976**, *41*, 1077.

(18) Lee-Ruff, E. *Chem. Soc. Rev.* **1977**, *6*, 195.

(19) Schenck, G. O.; Schulte-Elte, K. *Ann.* **1958**, *618*, 185.

(20) Control experiments establish that photocatalyzed destruction of this ene product is too slow to account for its absence from the photolysis mixture.

(21) Manring, L. E.; Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 4275.

(22) Wilkinson, F.; Dubois, J. T. *J. Chem. Phys.* **1963**, *39*, 377.

(23) Often, reduction and/or [2 + 2] cycloadditions occur upon excitation of olefins in acetonitrile. For example, we find that reduction product (1,1-diphenylethane) is formed upon direct photoexcitation of **1** in CH_3CN/CF_3CH_2OH.

(24) Geometric isomerization of **2** recovered after partial conversion to carbonyl resulted in a steady-state cis/trans ratio typical of stilbene radical cation equilibration,[25] i.e., *not* that expected from stilbene excited-state equilibration.

(25) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083.

the valence band position) of the semiconductor employed. These observations suggest to us that radical cation formation may be required,[24] i.e., that the (oxidant + adsorbed olefin) complex alone cannot account for the observed reactivity.

This method offers the synthetic chemist interested in olefin oxidations significant advantages over alternate methods for oxidative olefin cleavage. The use of TiO_2 and atmospheric oxygen is cheaper, safer, and more selective than the use of ozone or conventional inorganic oxidants. The workup is particularly easy, the sensitizer being removed by filtration and/or a neutral water wash. We note that a nonaqueous solvent is required for these reactions: further nonselective oxidation is observed in water, presumably because of the generation of the very reactive·OH radical[26] in water.

Clearly, application of the principles of photoelectrochemistry to organic conversions will open a new area of profitable research. Such investigations are continuing in our laboratory.

Acknowledgment. This work was generously supported by the National Science Foundation, the U.S. Department of Energy, and the Robert A. Welch Foundation. M.A.F. gratefully acknowledges support as a Alfred P. Sloan Research Fellow (1980–1982) and as a Camille and Henry Dreyfus Teacher–Scholar (1980–1985).

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

Time-Resolved Determinations of Deuterium Isotope Effects on $O_2(^1\Delta_g)$ Lifetimes in Solution

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The natural lifetime (τ_Δ) of the lowest excited singlet state of molecular oxygen, $O_2(^1\Delta_g)$, as a function of the solvent and its isotopic composition has been the subject of experimental and theoretical interest over the past decade. Until recently it appeared that the wide range of observed lifetimes[1-10] could be satisfactorily rationalized in terms of a theory based on energy transfer between the electronic levels of O_2 and ground-state vibrational levels of the solvent. New data, however, has appeared which indicate that a reappraisal, especially of the isotope effect, is necessary. Direct, time-resolved[11-13] measurements of the weak $^3\Sigma_g \leftarrow {}^1\Delta_g$ luminescence at 1270 nm have been used to confirm earlier less direct values of τ_Δ in several solvent media and have additionally shown a ratio $\tau_\Delta{}^D/\tau_\Delta{}^H = 3.4$ in chloroform, markedly different from earlier values. Furthermore, recent steady-state photooxidation measurements[14] using diphenylisobenzofuran (DPBF) and rubrene (R) as monitoring substrates lead Ogilby and Foote[14] to report unusually high values for $\tau_\Delta{}^D/\tau_\Delta{}^H$ for the solvents benzene, acetonitrile, acetone and chloroform (fully protiated and fully deuterated species). In this laboratory a time-resolved technique was used[15] for directly monitoring the loss of optical absorption of DPBF owing to the elementary process

$$O_2(^1\Delta_g) + M \xrightarrow{k_m} -M \qquad (1)$$

(M = monitoring substance). These experiments showed that the value $\tau_\Delta(D_2O)$ was 53 μs—significantly higher than hitherto reported. Confirmation of this higher value has been subsequently provided by Matheson and Massoudi.[16] In view of the differences in τ_Δ and $\tau_\Delta{}^D/\tau_\Delta{}^H$ values brought to light by the new data,[11-14] it was considered worthwhile to apply the time-resolved substrate bleaching method to the problem. We have examined the four solvents (protio and deuterio analogues) studied by Ogilby and Foote and have found in only one case good agreement with their data.

In the absence of additional quenching substances, the natural decay of singlet oxygen competes with the process which causes bleaching of the monitor (reaction 1):

$$O_2(^1\Delta_g) \xrightarrow{k_d} O_2(^3\Sigma_g) \qquad (2)$$

Under first-order conditions ($[M]_0 > 10[O_2(^1\Delta_g)]_0$) it follows that

$$k_{obsd} = k_d + k_m[M]$$

where k_{obsd} is the observed first-order rate constant for the bleaching of M. A linear plot of k_{obsd} against [M] shows consistency with the scheme and allows k_d ($= 1/\tau_\Delta$) and k_m to be evaluated from the intercept and the slope, respectively.

We used a previously described laser flash photolysis system[15] comprising a pulsed (8 ns) nitrogen gas laser excitation source coupled with computer controlled kinetic spectrophotometric detection.[17] Acetonaphthone (~10^{-3} mol L^{-1}) was employed as sensitizer to generate $O_2(^1\Delta_g)$ via its triplet state. Singlet oxygen kinetics were monitored by subsequent removel of the chromophores DPBF (415 nm, protio solvent) or rubrene (500 nm, deuterio solvent). Rubrene was preferred over DPBF as monitor in the solvents exhibiting large τ_Δ values owing to its lower rate constant for reaction. This meant that larger monitor concentrations could be used and hence larger bleaching signals (still <10% removal) could be observed. This ensured good signal-to-noise ratios and kept the value of $k_m[M]$ near k_d to lessen the need for extended extrapolation for obtaining the intercept value (k_d).

Experiments were undertaken in aerated solutions at varying monitor concentrations (DPBF, 1–7 × 10^{-5} mol L^{-1}; rubrene, 1.5–13 × 10^{-5} mol L^{-1}) up to a limit governed by monitor concentration at which no more than 30% of the 337-nm excitation light was being directly absorbed by monitor. Neutral density filters were employed to attenuate the laser beam in order to ensure that less than 10% of the monitor was removed. Photolysis by the xenon monitoring arc was prevented by allowing light through the spectrometer for only ca. 10 ms during which time the experiment was conducted. Under the prevailing conditions, the removal of monitor was strictly first order.

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