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RADICAL CATION INTERMEDIATES IN THE FORMATION OF SCHIFF BASES ON IRRADIATED SEMICONDUCTOR POWDERS

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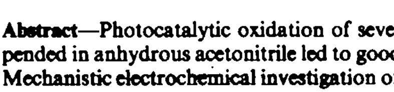
Abstract—Photocatalytic oxidation of several primary aliphatic amines on irradiated TiO_2 powders suspended in anhydrous acetonitrile led to good yields of the corresponding symmetrical N-alkylidene amines. Mechanistic electrochemical investigation of the reaction revealed intermediate formation of an immonium cation in an ECE route. This species is generated via electrooxidation of an α-amino radical formed by deprotonation of the primary oxidation product, an aminium cation radical. The influence of the metal oxide surface on radical cation reactivity is discussed.

INTRODUCTION

The amino functionality represents one of the most widely dispersed and chemically significant organic groups. Its ability to act as an effective electron donor has fascinated mechanistic chemists for many years, and its tendency to activate a geminate covalent bond in photochemical, free radical, electrochemical, chemical, and enzymatic transformations makes it a rich source for interesting mechanistic study.[1] Moreover, its one electron oxidation product, the aminium cation radical 1 (Eq. 1),



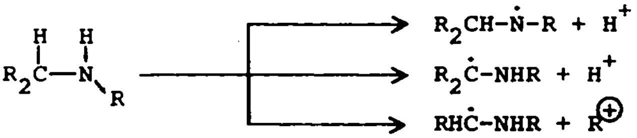
(1)

has been extensively studied by spectroscopic[2] and electrochemical[3] methods because of its significant biological importance.[4]

Amine excited states[5] are often involved in photoinduced electron transfer schemes, having been characterized as early as 1963 as donors in fluorescent exciplexes.[6] Depending on solvent polarity, charge separation within the exciplex pair can be extensive[7,8] (Eq. 2),

$$R_3N + A \xrightarrow[A=\text{acceptor}]{h\nu} [R_3\overset{+\cdot}{N}A] \rightleftharpoons R_3\overset{+\cdot}{N} + A^{\dot{-}} \qquad (2)$$

leading to formation of the free radical ions. With pulse excitation, the donor or acceptor radical ion can sometimes be characterized by optical spectroscopy and the kinetics of subsequent rapid chemical steps can be determined.[9-11] Whether the observed cleavage involves an α-C—H,[12-14] an N—H,[14] or an α-C—C[15] bond to release protons or carbocations and aminyl or α-amino radicals (Eq. 3),



(3)

depends on the structure of the intermediate aminium ion and on the reaction conditions, particularly solvent polarity.

This diversity of reaction paths from a common intermediate prompted our interest in aminium ions. In particular, we wished to investigate whether chemoselectivity in amine oxidations could be observed if the aminium ion were generated as a metal oxide surface-adsorbed species and whether synthetically useful transformations of amines could be effected upon ultraviolet irradiation of an appropriate photocatalyst.

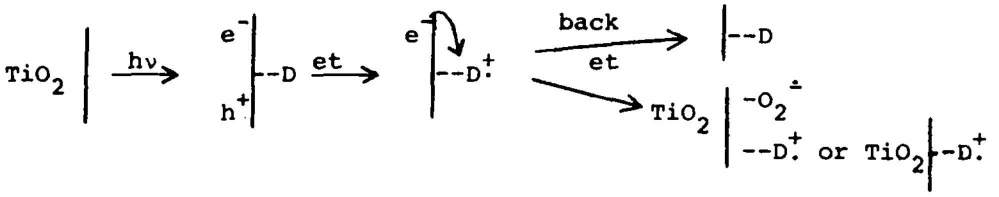
We had previously established that surface-bound radical ion intermediates are involved in semiconductor mediated phototransformations of a wide array of organic functional groups.[16] This conclusion was based not only on product analysis, but also on mechanistic refutation of several other possible oxidative routes,[17] on kinetic effects of substituents,[18] and on direct spectroscopic observation of radical cations upon flash photolysis of colloidal suspensions of the metal oxide semiconductor.[19]

Our understanding of electron exchange at the semiconductor–liquid interface is well developed.[20-24] Semiconductors possess a characteristic band structure in which a filled valence band is separated by an energy gap from a vacant conduction band. Upon excitation with a photon of energy greater than the band gap, a hole is generated in the valence band and a highly mobile electron is placed in the conduction band. Although band bending (to achieve bulk Fermi level equilibration of the semiconductor and the redox couple contained within the electrolyte) influences the motion of these charge carriers to and from the interface, the overall thermodynamics for the requisite electron exchange is controlled by the band positions. Thus, any substrate whose oxidation potential lies less positive than the valence band edge can act as an effective electron donor and any substrate whose reduction potential lies positive of the conduction band edge can act as an effective electron acceptor (Fig. 1). This simple picture can be altered, of course, by interfacial kinetic effects but these band levels and redox potentials provide a starting point for the design of allowable redox systems.

Chemical transformations which meet these thermodynamic requirements will occur on a synthetically useful scale if two additional requirements are met:

(1) if mass transport and/or adsorption phenomena allow for delivery of the oxidizable species to the electrode surface before recombination of the charge separated pair can occur;

(2) if chemical reaction of the radical ion so generated can compete kinetically with back electron transfer (Eq. 4).



(4)

If either of these requirements is not met, the efficiency of the photoredox reaction will be decreased. This requirement for rapid chemical reaction means that reactivity can be finely tuned by providing an appropriate surface bound reactant. In fact, we have found it possible to completely divert radical cation fragmentation observed in solution by generating the radical ion by photoelectrochemical methods on an irradiated semiconductor surface.[25,26]

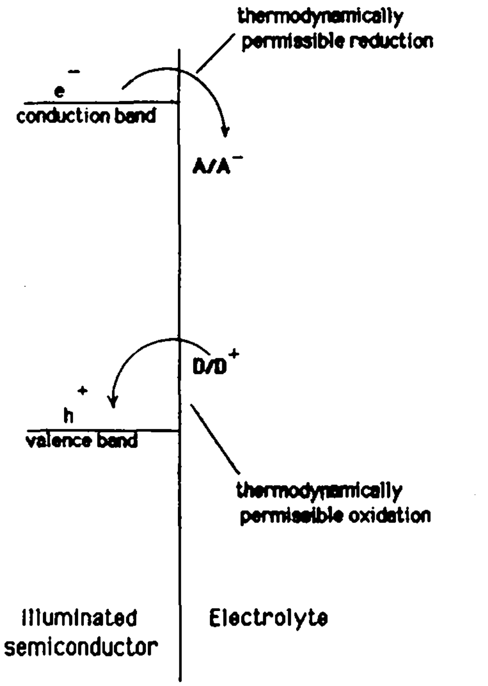


Fig. 1. Energetically permissible electron transfers on semiconductor surfaces.

For these reasons, we have investigated photochemically activated semiconductor suspensions as redox catalysts for the oxidation of primary amines bound to a secondary carbon. We report here observation of photoelectrochemical Schiff base formation and offer a mechanistic scheme for their formation.

RESULTS AND DISCUSSION

In a typical experiment the amine **1** was dissolved in oxygen-saturated anhydrous acetonitrile containing a catalytic portion of TiO_2 suspended in the solution by sonication. The reactions were kept under a positive pressure of oxygen during a 24 h irradiation period at 350 nm. Although the amines show tailing absorption in this region, the consumption of starting material was at least five times faster in the presence of the catalyst than in its absence. No reaction occurred in argon purged mixtures or in oxygenated heterogeneous suspensions stirred in the dark for 24 h. Thus, the presence of oxygen, catalyst, and light are necessary for efficient conversion (Table 1).

The major products formed from photocatalytic oxygenation of amines **1a–c** were the corresponding N-alkylidene amines **1a–c** (Table 2). In addition, smaller yields of carbonyl products could be observed. Structures were determined by ^{1}H-NMR and IR and were confirmed by comparison with authentic samples synthesized by unambiguous routes.

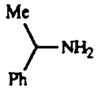
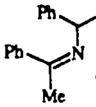
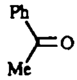
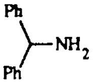
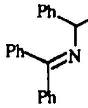
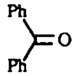
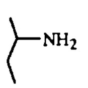
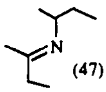
A reaction pathway parallel to that proposed for the N-formylation of primary aliphatic amines bound

Table 1. Control experiments for the photocatalytic oxidation of **1a**[a] in acetonitrile

Conditions	Reaction period (h)	Percent conversion[b]
TiO_2, light,[c] O_2	24	97
TiO_2, dark, O_2	24	0
TiO_2, light, Ar	24	5
light, O_2	6	10
TiO_2, light, O_2	6	53

[a] Concentration of substrate was 0.02 mol l^{-1}.
[b] Determinations made by gas chromatography.
[c] Irradiations at 350 nm.

Table 2. Product distributions of amine oxidations on irradiated[a] TiO_2 powder

Substrate	Concentration (mol l^{-1})	Products (yield)[b]
 **1a**	0.02	 (65) **2a**  (7)
 **1b**	0.02	 (70) **2b**  (5)
 **1c**	0.02	 (47) **2c**

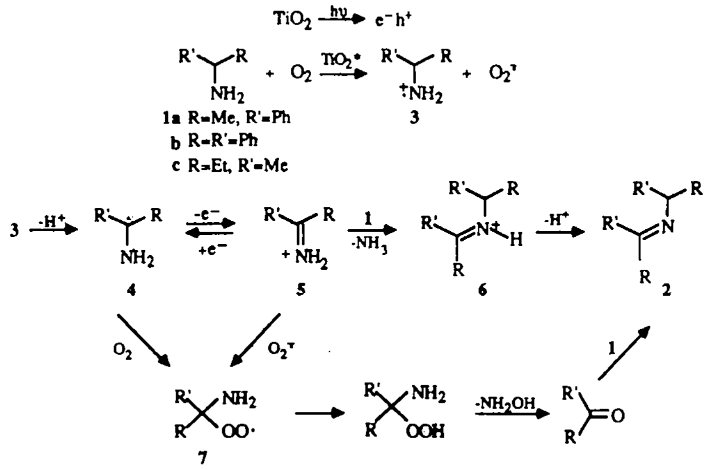
[a] Irradiations at 350 nm for 24 h.

[b] Products were identified by IR and ^{1}H-NMR and yields were calculated against an internal standard using HPLC.

to primary carbon atoms on photoexcited TiO_2[7] is consistent with the products observed in these experiments. Scheme 1 illustrates this mechanism. Exposure of TiO_2 to long wavelength UV irradiation (350 nm) effects electron–hole pair separation. Since the oxidation potentials of the amines are considerably more negative than the valence band of TiO_2, the absorbed amines will be oxidized readily by the photogenerated hole to form an aminium cation radical **3**. Simultaneously, capture of the photogenerated electron by molecular oxygen creates superoxide. The organic cation radical can rapidly deprotonate to form a stabilized α-aminoalkyl radical **4**. Analogous intermediates have been documented in electron transfer photoreductions of transition metal complexes[28] and aromatic hydrocarbons[12,29] by alkyl-substituted amines. Electron loss by radical **4** generates an immonium cation **5**. Nucleophilic attack on **5** by a molecule of starting material leads to a coupled immonium ion **6**. Subsequent deprotonation forms the observed imine adduct **2**. Alternatively, capture of **4** by molecular oxygen generates hydroperoxy radical **7** ultimately leading, after formal loss of hydroxyl amine, to the skeletally corresponding carbonyl. Alternatively, nucleophilic attack of superoxide on **5** could also generate **7**. Condensation of the ketone product with starting amine provides an alternate route to the imine.

The necessity for oxygen for the induction of photoreactivity follows from the requirement for a suitable electron acceptor. In the absence of such a species the adsorbed aminium cation radical **3** would be rapidly reduced, thus quenching photoinduced charge separation. Oxygen serves to reduce unproductive back electron transfer allowing observable chemistry to ensue.

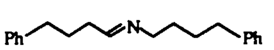
In contrast to the results observed here, the straight chain primary aliphatic amine **7** is known to suffer further oxidation in non-aqueous dispersions of TiO_2 generating N-formylated product in moderate yield.[27]



Scheme 1. Proposed mechanistic pathway for photocatalytic amine oxidation.

The corresponding imine was postulated as a likely precursor to the final product based on the detection of trace quantities of **8** in the photolysis mixture. While similar formylated products were not observed in this study, further oxidation cleavage of n-alkyl substituted imines such as **8** is quite reasonable as these compounds are generally unstable; competing polymerization often makes their isolation difficult even under mild conditions.[30] Conversely, substrates **1a–c** form stable Schiff bases. Each imine has been previously prepared and isolated in good to excellent yield.[31] It is not surprising, then, that **2a–c** are resistant to oxidation while **8**,or its tautomeric enamine, cleaves readily.


7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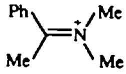
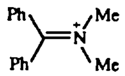
A logical extension of the study of semiconductor-mediated electron transfer reactions involves the electrochemical generation and observation of the reactive cation radicals at electrode surfaces. In order to further evaluate the validity of Scheme 1, the electrochemical behavior of substrates **1a** and **b** as probed using cyclic voltammetry as a diagnostic tool. These experiments were conducted in deaerated acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate with the reported potentials referenced to the $Ag/AgNO_3$ electrode. The voltammograms were obtained between 1.6 and −2.3 V beginning at 0 V and initially scanning anodically. At a scan rate of 50 mV s^{-1}, amines **1a** and **b** displayed an irreversible oxidative wave at 1.09 and 1.18 V, respectively (Figs 2(a) and 3(a)). These oxidative waves are typical of those observed in voltammograms of primary amines in aprotic solvents[3] and presumably correspond to two one-electron oxidations separated by an intervening chemical step.[32,33] This ECE mechanism ultimately produces the immonium cation,

$$RCH_2NH_2 \xrightarrow{-e^-} RCH_2NH_2^{+\cdot} \underset{}{\overset{-H^+}{\rightleftarrows}} R\dot{C}HNH_2 \xrightarrow{-e^-} RCH{=}NH_2^+ \qquad (5)$$

Upon increasing the scan rate to 1000 mV s^{-1}, a new quasireversible couple, undetectable on a slower time scale, appeared in the voltammograms of both amines (Figs 2(b) and 3(b)). This new reductive wave appeared at −1.50 V in a solution of **1a** and at −1.22 V in a solution of **1b**. These peaks are assigned to the reduction of the corresponding immonium cations of each amine, **5a** and **b** based on the excellent correlation between these peak potentials and the polarographic half wave potentials reported by Andrieux and Saveant[34] for immonium salts **9** and **10**. That the N-dimethylated salts serve as appropriate model compounds for **5a** and **b** is supported by the small influence of the N-alkyl substituent on the electrochemical properties of these cations.[34]


9

$E_{1/2}$ = -1.49 V


10

$E_{1/2}$ = -1.17 V

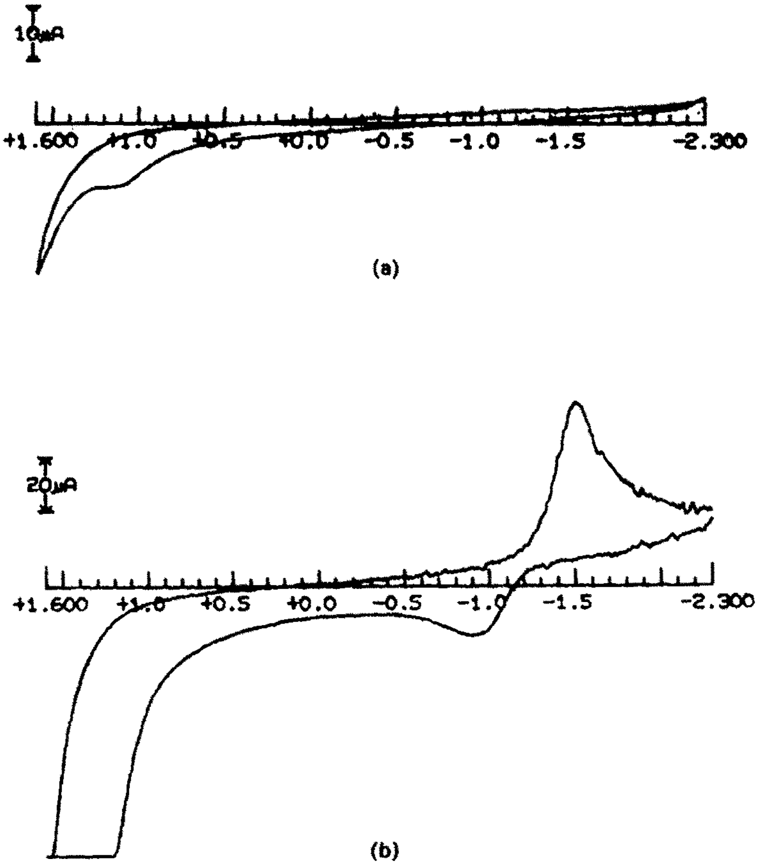
The reduction of immonium cation **5b** proceeds with a higher degree of reversibility than **5a** with a 360 mV separation between the anodic and cathodic peaks as compared with a 550 mV difference for **5a**. This behavior is in qualitative agreement with that observed by Andrieux and Saveant and can be rationalized based on the enhanced stability of diphenyl substituted α-amino radicals relative to their monophenyl analogs.

This qualitative voltammetric study provides support for the generation of the immonium cation upon two-electron oxidation of **1a** and **b**. A similar electron transfer pathway has been implicated in the electrooxidation of a series of primary aliphatic amines in acetonitrile.[32] Controlled-potential coulometry affords the corresponding aldehyde as the primary organic product, presumably by hydrolysis of the corresponding immonium salt (Eq. 5). Translation of these electrochemical pathways to the heterogeneous systems under study here is reasonable in view of experiments establishing the formation of organic cation radicals on irradiated powder surfaces.[16] Thus, operation of the pathway **3** → **4** → **5** proposed in Scheme 1 is quite probable in the photooxygenation of amines on TiO_2.

This work is not the first description of the oxidative conversion of nitrogen-containing organic substrates on illuminated semiconductor suspensions. The conversions of toluidines to azo coupling products[35] and amines to imides[36] has been reported in aqueous mixtures of semiconductor powders. Heterogeneous photooxidation of alkyl amines in aqueous dispersion of ZnO[37] or platinized TiO_2[38] are reported to yield the corresponding dialkyl amines in modest yields (24–33%). Small quantities of N-ethylideneethylamine detected by gas chromatography in the oxidation of ethylamine[38] implied that photoreduction of an imine adduct was critical in product formation. Photoelectrochemical reactions conducted in water, however, almost certainly involve formation of the highly reactive, non-selective hydroxyl radical and yields of electron transfer-mediated products are almost always lower than those observed under our experimental conditions. Overoxidation, moreover, which is common in aqueous suspensions, is not a significant problem here.

Although the intermediacy of an imine has been previously suggested in heterogeneous oxidations of amines, the experiments reported here represent the first study where imines stable under the photocatalytic conditions have been prepared and isolated in high yields.

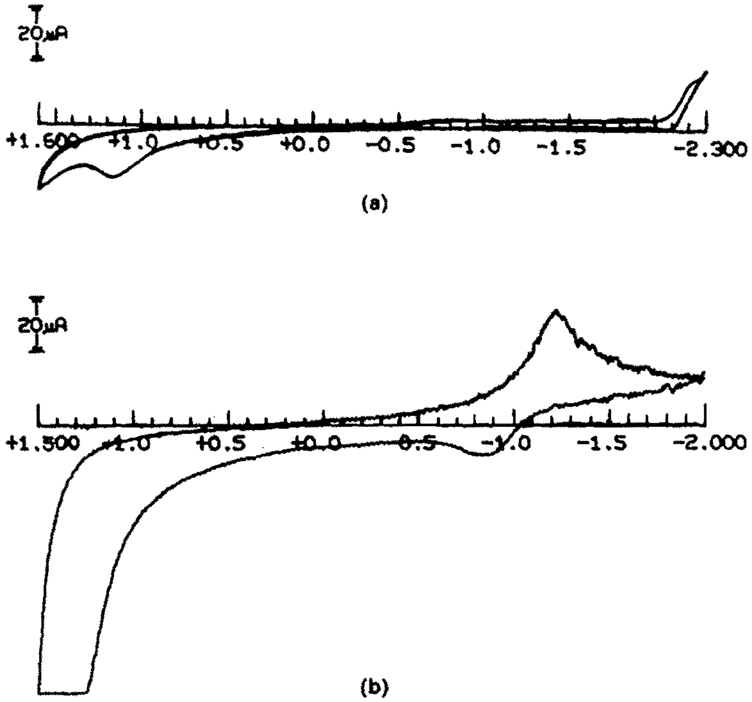
We conclude that non-aqueous semiconductor-mediated oxidations of primary aliphatic amines proceed through an immonium cation formed by two one-electron oxidations by a pathway analogous to that observed in previously studied amine electrooxidations. The major organic product isolated from the photolysis depends on the structure of the starting substrate. Stable Schiff bases generated by coupling of the immonium cation with starting amine are isolated in good yields while unstable imines suffer further oxidative cleavage as previously described.[27] Imines formed in organic suspensions do not undergo reduction to amines as observed in aqueous solution. This work, thus, provides an important mechanistic characterization of non-aqueous photocatalytic electron transfer oxygenations of amines as well as expands the scope of organic functional group transformations occurring on irradiated semiconductor surfaces.



(a)

(b)

Fig. 2. Cyclic voltammograms of **1a** in degassed acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate at a scan rate of: (a) 50 mV s^{-1}; (b) 1000 mV s^{-1}.



(a)

(b)

Fig. 3. Cyclic voltammograms of **1b** in degassed acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate at a scan rate of: (a) 50 mV s^{-1}; (b) 1000 mV s^{-1}.

EXPERIMENTAL

Instrumentation. ^{1}H-NMR were obtained at ambient probe temperature on a Varian EM-390 90 MHz spectrometer with chemical shifts reported in ppm downfield from TMS as internal standard. IR spectra were recorded on a Perkin–Elmer 298 IR spectrophotometer. GC–MS analyses were performed on a Finnigan Model 4023 automated GC–MS with an INCOS data system using a 50 m DB-1 capillary column. HPLC was performed using a Waters 6000A solvent delivery system equipped with an R401 Differential Refractometer and a μ-Porasil 27477 analytical column or a Porasil semipreparative column. GLC analyses were obtained with a Varian Aerograph 1400 instrument equipped with a flame ionization detector and a 40 m SGE BP-1 capillary column. Peak intensities were monitored with a Hewlett–Packard 3390A Integrator. UV absorption spectra were obtained on a Cary 17 spectrophotometer.

Irradiations were conducted in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Company) equipped with a cooling fan and lamps emitting maximally at 350 nm. Alternatively, the light source was a Hanovia 450 W medium pressure mercury lamp immersed in a reaction vessel and cooled by circulation of an aqueous soln 0.1 M in KNO_2 at pH 10 which filters light of wavelengths shorter than 380 nm.

Cyclic voltammetry was conducted with a Bioanalytical Systems BAS-100 Electrochemical Analyzer equipped with a Houston Instruments DMP-40 digital plotter. Alternatively, electrochemical measurements were conducted using an EG&G Princeton Applied Research (PAR) Model 173 Potentiostat with a Model 179 Digital Coulometer. Excitation wave forms were programmed using a Model 175 Universal Programmer, and current–voltage curves were plotted on a Houston Instruments Model 2000 x–y recorder. A one compartment cell was used. The acetonitrile solns contained 0.1 M tetra-n-butylammonium perchlorate as the supporting electrolyte and were degassed and kept under a positive pressure of Ar during the run. Silver–silver nitrate (0.1 M in acetonitrile) served as the reference electrode and a platinum disk and coil were the working and counter electrodes, respectively. Positive feedback for IR compensation was utilized in all runs to minimize the solution resistance between the working and reference electrodes. The supporting electrolyte acetonitrile solutions were scanned prior to the addition of substrate to insure the absence of electroactive impurities.

Solvents and reagents. TiO_2 (MCB technical grade, anatase powder) was dried overnight at 110° and stored in a vacuum desiccator containing indicating silica gel. Oxygen gas was dried by passage through a drying tube (2 × 20 cm) containing dry calcium chloride. EM Reagents 250–400 mesh silica gel was used in flash column chromatography separations. Acetonitrile (HPLC grade, Fisher Scientific) was used without further purification.

Amines **1a–c** were obtained from Aldrich and vacuum distilled prior to use. Tetra-n-butylammonium perchlorate (Southwestern Analytical Chemicals) was recrystallized twice from Skelly B–EtOAc. Acetophenone (MCB) was used as received.

General procedure for semiconductor-mediated photooxygenations. In a 25 × 250 mm Pyrex test tube 1 mmol of organic substrate was dissolved in 50 ml of acetonitrile and treated with 2.5 mg of semiconductor catalyst. The mixture was sonicated for 5 min to give an opaque suspension; then, bubbled with oxygen for 30 min. The tube was sealed with a rubber stopper wrapped in alumium foil and irradiated for a measured period (24 h, unless otherwise indicated). After reaction, the catalyst was removed by vacuum filtration using a Kimax fine fritted filter. The resulting filtrate was concentrated by rotary evaporation.

Photocatalytic oxidation of α-methylbenzenemethanamine (**1a**). Purification of the crude mixture by flash column chromatography (4:1 Skelly B–EtOAc) gave a colorless liquid, α - methyl - N - (1 - phenylethylidene)benzenemethanamine (**2a**): IR 1632 (C═N) cm^{-1} [lit.[31b] IR 1630 cm^{-1}]; ^{1}H-NMR ($CDCl_3$) δ 7.75–7.90 (m, 2H), 7.15–7.50 (m, 8H), 4.80 (q, 1H, $J = 6$ Hz), 2.20 (s, 3H), 1.50 (d, 3H, $J = 6$ Hz) and acetophenone: IR 1685 (C═O) cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ 7.75–8.00 (m, 2H), 7.20–7.50 (m, 3H), 2.45 (s, 3H). Quantitative analysis by HPLC (4:1 Skelly B–EtOAc, phenol, internal standard) showed 65% **2a** and 6% acetophenone. Independent preparation of imine **2a** by condensation of amine **1a** with acetophenone[31b] yielded a liquid with spectral characteristics identical to those of the isolated product.

Photocatalytic oxidation of α-phenyl benzenemethanamine (**1b**). Separation of the filtered mixture by flash column chromatography (4:1 Skelly B–EtOAc) yielded a white crystalline solid, **2b**: m.p. 150–152°; IR ($CHCl_3$) 1625 (C═N) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.65–7.85 (m, 2H), 7.00–7.45 (m, 18H), 5.55 (s, 1H) [lit.[31a] m.p. 150–151°; IR ($CHCl_3$) 1625 cm^{-1}; ^{1}H-NMR δ 7.80 (m, 2H), 7.35 (m, 18H), 5.60 (s, 1H)] and benzophenone: IR (CCl_4) 1680 (C═O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.70–7.90 (m, 4H), 7.20–7.60 (m, 6H). HPLC analysis (4:1 Skelly B–EtOAc, phenol, internal standard) indicated 70% **2b** and 5% benzophenone.

Photocatalytic oxidation of 2-butanamine (**1c**). GC–MS analysis of the filtrate indicated **2c** present in 47% yield: MS, *m/e* (rel. intensity) 127 (0.6), 112 (2.0), 111 (8.2), 98 (9.9), 97 (98.5), 84 (31.1), 83 (68.1), 70 (100.0), 56 (80.5).

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REFERENCES

[1] See F. D. Lewis, T. I. Ho and J. T. Simpson, *J. Org. Chem.* **46**, 1077 (1981) and refs cited therein.

[2] A. J. Bard, A. Ledwith and H. J. Shine, *Adv. Phys. Org. Chem.* **13**, 156 (1976).

[3] R. C. Reed and R. M. Wightman, *Encyclopedia of Electrochemistry of the Elements* (Edited by A. J. Bard and H. Lund), Vol. XV, Chap. 1. Marcel Dekker, New York (1984).

[4] See, for example, R. Traver, H. E. A. Kramer and P. Hemmerich, *Pure Appl. Chem.* **54**, 1605 (1982).

[5] C. von Sonntag and H. P. Schuchmann, *Adv. Photochem.* **10**, 59 (1977).

[6] H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.* **67**, 791 (1963).

[7] F. D. Lewis, *Accts Chem. Res.* **12**, 512 (1979).

[8a] R. A. Beecroft, R. S. Davidson, D. Goodwin and J. E. Pratt, *Pure Appl. Chem.* **54**, 1651 (1982); [b]R. S. Davidson, *Adv. Phys. Org. Chem.* **19**, 1 (1983).

[9] W. Hub, S. Schneider, F. Dorr, J. I. Simpson, J. D. Oxman and F. D. Lewis, *J. Am. Chem. Soc.* **104**, 2044 (1982).

[10] K. S. Schanze, C. Giannotti and D. G. Whitten, *J. Am. Chem. Soc.* **105**, 6326 (1982).

[11a] K. S. Peters, S. C. Freilich and C. G. Schaeffer, *J. Am. Chem. Soc.* **102**, 7566 (1980); [b]K. S. Peters and J. D. Simon, *Ibid.* **103**, 6403 (1981); [c]K. S. Peters, E. Parry and J. Rudzki, *Ibid.* **104**, 5535 (1982).

[12] F. D. Lewis, T. I. Ho and J. T. Simpson, *J. Am. Chem. Soc.* **104**, 1924 (1982).

[13] F. D. Lewis and P. E. Correa, *J. Org. Chem.* **46**, 1077 (1981).

[14] F. D. Lewis and P. E. Correa, *J. Am. Chem. Soc.* **103**, 7347 (1981).

[15] L. Y. C. Lee, C. Giannotti and D. G. Whitten, *J. Am. Chem. Soc.* (1986), in press.

[16] M. A. Fox, *Accts Chem. Res.* **103**, 6757 (1983).

[17] M. A. Fox and C.-C. Chen, *J. Am. Chem. Soc.* **103**, 6757 (1981).

[18] M. A. Fox and C.-C. Chen, *Tetrahedron Lett.* **24**, 457 (1983).

[19] M. A. Fox, B. A. Lindig and C.-C. Chen, *J. Am. Chem. Soc.* **104**, 5828 (1982).

[20] A. J. Nozik, *Ann. Rev. Phys. Chem.* **29**, 189 (1978).

[21] A. J. Nozik (Editor), *Photoeffects at Semiconductor–Electrolyte Interfaces*, ACS Symposium Series No. 146. American Chemical Society, Washington (1981).

[22] A. J. Bard, *J. Photochem.* **10**, 50 (1979).

[23] A. J. Bard, *Science* **207**, 139 (1980).

[24] A. J. Bard, *J. Phys. Chem.* **86**, 172 (1982).

[25] M. A. Fox, C.-C. Chen and J. N. Younathan, *J. Org. Chem.* **49**, 1969 (1984).

[26] M. A. Fox, C.-C. Chen, K. N. Park and J. N. Younathan, *Am. Chem. Soc. Symp. Ser.* **278**, 69 (1985).

[27] M. A. Fox and M.-J. Chen, *J. Am. Chem. Soc.* **105**, 4497 (1983).

[28] P. J. DeLaive, T. K. Foreman, C. Giannotti and D. G. Whitten, *J. Am. Chem. Soc.* **102**, 5627 (1980).

[29] F. D. Lewis and P. E. Correa, *J. Am. Chem. Soc.* **106**, 194 (1984).

[30a] R. W. Layer, *Chem. Rev.* **63**, 489 (1963); [b]S. Dayagi and Y. Degani, *The Chemistry of the Nitrogen–Carbon Double Bond* (Edited by S. Patai), Chap. 2. Wiley, New York (1970).

[31a] K. N. Mehrotra and G. Prasad, *Tetrahedron Lett.* **19**, 4179 (1978); [b]C. G. Overberger, N. P. Marullo and R. G. Hiskey, *J. Am. Chem. Soc.* **83**, 1374 (1961); [c]K. Langheld, *Chem. Ber.* **42**, 2360 (1909).

[32] K. K. Barnes and C. K. Mann, *J. Org. Chem.* **32**, 1474 (1967).

[33] C. K. Mann, *Analyt. Chem.* **36**, 2424 (1964).

[34a] C. P. Andrieux and J.-M. Saveant, *J. Electroanal. Chem.* **26**, 223 (1970); [b]C. P. Andrieux and J.-M. Saveant, *Bull. Soc. Chim. Fr.* 4671 (1968).

[35] H. Kasturirangan, V. Ramakrishnan and J. C. Kuriacose, *J. Catal.* **69**, 216 (1981).

[36] J. W. Pavlik and S. Tantayanon, *J. Am. Chem. Soc.* **103**, 6755 (1981).

[37] S. Yanagida, H. Kizumoto, Y. Ishimaru, C. Pac and H. Sakurai, *Chem. Lett.* 141 (1985).

[38] S. Nishimoto, T. Ohtani, T. Yoshikawa and T. Kagiya, *J. Am. Chem. Soc.* **105**, 7180 (1983).