

Photocatalytic Oxidation of Multifunctional Organic Molecules. The Effect of an Intramolecular Aryl Thioether Group on the Semiconductor-Mediated Oxidation/Dehydrogenation of a Primary Aliphatic Alcohol

A remote thiophenyl group retards the TiO_2 -mediated photocatalytic oxidation of the alcohol group in 4-thiophenyl-1-butanol. Model studies implicate intramolecular bridging in the adsorbed cation radical and/or hole trapping by sulfur in the primary oxidative photoprocess at the photocatalyst-liquid interface. © 1990 Academic Press, Inc.

INTRODUCTION

Site selectivity in catalytic oxidations of multifunctional organic molecules remains a significant challenge. Our investigations of irradiated semiconductor surfaces show them to be promising vehicles for controlling photocatalytic oxidations. Such studies can also probe the catalytic features which can direct reactivity along a desired pathway.

Photocatalysis begins by band gap excitation of a metal oxide semiconductor powder, generating a surface-bound electron-hole pair. In the presence of adsorbed oxygen, the electron, which is poised at the potential of the conduction band edge, is trapped, leaving a free surface-localized hole which can effect a single-electron oxidation of an oxidizable adsorbate (1, 2). When photocatalytic oxidations are conducted as aqueous suspensions, water is the dominant adsorbate, and the primary product of this interfacial electron transfer is often an adsorbed hydroxy radical (3). Long known for its high reactivity, this species can indiscriminately attack coadsorbates bearing abstractable hydrogens, thus producing adsorbed free radicals. It is also possible, although less likely in most systems, that $\text{OH}\cdot$ can diffuse from the surface into the contacting solution, where analogous reactions can ensue.

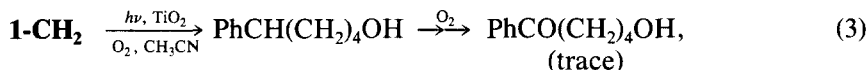
In the presence of oxidatively inert solvents, this reaction mode is inhibited, how-

ever, and direct oxidation of adsorbed substrates, with better oxidative specificity, can represent the major route for photoinitiated reactivity. A polar, nonhydroxylic solvent thus presents the best opportunity for controlling oxidative reactivity at the interface between a liquid reaction mixture and a solid irradiated photocatalyst. This reactivity can occur either by photooxidative formation of surface-bound cation radicals or by hydrogen transfer at a metal island deposited on the semiconductor surface to introduce a junction to assist in separation of the electron-hole pair. In molecules bearing more than one oxidizable functionality, oxidative selectivity can be influenced by adsorption effects, band-edge redox energetics, light flux effects, and the kinetics of electron-hole recombination and back electron transfer from adsorbed redox reagents (4). We describe herein product analysis and kinetic competition experiments which allow us to define the photocatalyst characteristics which govern site selectivity in the photocatalytic oxidation of 4-thiophenyl-1-butanol **1-S** and in several model compounds.

METHODS

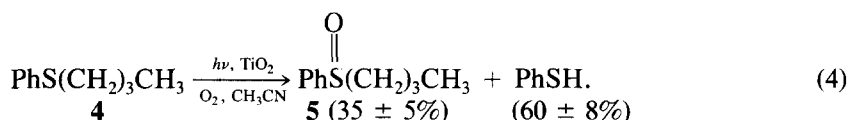
Titanium dioxide (MCB technical grade, anatase powder or DeGussa P-25 powder) and platinized (1% metal loading) TiO_2 (5) were dried overnight in a vacuum oven at 120°C and were stored under nitrogen before use. Oxygen or air was dried by passage through a drying tube containing dry cal-

Similarly, since only trace quantities of 4-hydroxyvalerophenone could be detected from **1-CH₂**,

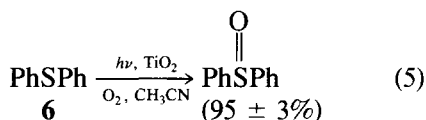


oxidation at the alcohol was at least an order of magnitude more efficient than abstraction at the benzylic position, despite literature precedent for TiO₂ activation of the benzylic hydrogens in alkyl-substituted benzenes (11, 12).

In contrast, the nonalcoholic analog **4** was converted to the corresponding sulfoxide **5** in a lower yield process, with C-S cleavage (signaled by the formation of thiophenol) representing the major competing route.



This route is thus analogous to that observed with diphenylsulfide **6** itself (13),



except that in **4** C-S cleavage, ultimately producing mineralization, intervenes to a much greater extent than in Eq. (5).

The relative rates for photocatalytic oxidation on irradiated TiO₂ and of dehydrogenation on Pt/TiO₂ for this family of compounds are summarized in Table 1.

TABLE I

Relative Rates of Photooxidative Consumption of 4-Thiophenyl-1-Butanol and Analogs

Compound	Relative rates of disappearance (photocatalyst/atmosphere)	
	TiO ₂ /O ₂	Pt, TiO ₂ /N ₂
1-CH₂	1.6 ± 0.4	1.5 ± 0.2
1-O	1.5 ± 0.2	1.5 ± 0.3
1-S	1.0 ± 0.2	1.0 ± 0.2
4	0.6 ± 0.1	0.3 ± 0.2
6	0.5 ± 0.1	0.0 ± 0.1

DISCUSSION

Photocatalytic oxidation of sulfur-containing aliphatic alcohols occurs mainly at the alcohol group, presumably because the primary interfacial electron transfer at the OH, by virtue of the possibility of proton exchange, is significantly less reversible than at the thioether site. Both photooxidation (occurring on native TiO₂ via direct electron transfer from the oxidizable adsorbate to a photogenerated, surface-confined hole which is likely to chemically resemble a surface-bound oxy radical) and photodehydrogenation (occurring on platinized TiO₂ via hydrogen transfer on the metal surface) follow a similar kinetic profile (Table 1), indicating that the relative reactivity of the adsorbed substrate, rather than the mechanism of the primary photoprocess itself, governs the critical branching ratio which establishes the product distribution observed. The requirement for adsorbed oxygen for efficient photocatalysis presumably derives from the need for an effective trap for the conduction band electron: thus, secondary chemical steps may involve either adsorbed oxygen or superoxide.

The high chemical yields of aldehyde and

carboxylic acid (its secondary oxidation product) observed in these conversions (Eq. (1)) clearly demonstrate the usefulness of this semiconductor-mediated photooxidation as a synthetically viable route for manipulating oxygen functionality in multifunctional molecules, with alcohol oxidation dominating over other possible oxidative modes involving stabilized radicals. Thus, photoelectrochemical activation at neither the α -phenoxy radical discussed in Eq. (2) nor the benzylic radical considered in Eq. (3) can kinetically compete with that at the alcohol functional group.

The lower yield of alcohol oxidation products observed in **1-S**, Eq. 1, together with its lower rate of reaction (Table 1), indicates that the sulfur atom either competes directly with the OH group in the interfacial electron transfer step or acts as an intramolecular nucleophilic trap (14) to stabilize the incipient cation radical at oxygen. In either case, substantial cation radical character develops at sulfur, thus either reducing the observable oxidation rate by facilitating back electron transfer from the negatively charged semiconductor surface or initiating C-S cleavage as a mechanistic alternative. The absence of S-oxidation product in the reaction of **1-S** contrasts with their occurrence in those of **4** and **6**. From the isolated yields in Eq. (1) and (4), respectively, we conclude that in this family of compounds, alcohol oxidation is about 4 times as efficient as C-S cleavage, which in turn is about twice as favorable as sulfoxidation. This latter route becomes the dominant process (Eq. (5)) only when the thioether cation radical is particularly stabilized (as in Ph_2S^+) and

when C-S cleavage forms a particularly unstable fragment, e.g., the phenyl cation.

ACKNOWLEDGMENTS

This work was supported by the US Army Research Office and by the Robert A. Welch Foundation.

REFERENCES

1. Fox, M. A., *Top Curr. Chem.* **142**, 721 (1987).
2. Bard, A. J., *Science* **207**, 139 (1980).
3. Cunningham, J., and Srijaran, S., *J. Photochem. Photobiol. A* **42**, 329 (1988).
4. Fox, M. A., Ogawa, H., and Muzyka, J., *Proc. Electrochem. Soc.* **88-14**, 9 (1988).
5. Pichat, P., Herrmann, J. M., Disdier, J., Courbon, H., and Mozzanega, M. N., *Nouv. J. Chim.* **5**, 627 (1981).
6. Harpp, D. N., Vines, S. M., Montillier, J. P., and Chan, T. H., *J. Org. Chem.* **41**, 3987 (1976).
7. McCurdy, R. M. and Prager, J. H., *J. Polym. Sci., Part A* **2**, 1185 (1964).
8. Protiva, M., Rajnsner, M., Adlerova, E., Seidlova, V., and Vejdelek, Z. J., *Collect. Czech. Chem. Commun.* **29**, 2161 (1964).
9. (a) Kawai, T. and Sakata, T., *Chem. Commun.*, 694 (1980); (b) Fox, M. A., Ogawa, H., and Pichat, P. *J. Org. Chem.* **54**, 3847 (1989).
10. Pincock, J. A., Pincock, A. L., and Fox, M. A., *Tetrahedron* **41**, 4107 (1985).
11. Fujihira, M., Satoh, Y., and Osa, T. *J. Electroanal. Chem.* **126**, 277 (1981).
12. Pichat, P., Disdier, J., Herrmann, J. M., and Vaudano, P. *Nouv. J. Chim.* **10**, 545 (1986).
13. Fox, M. A. and Abdel-Wahab, A. A., *Tetrahedron Lett.*, in press.
14. Dinnocenzo, J. P., Farid, S., Goodman, J. L., Gould, I. R., Todd, W. P., and Mattes, S. L. *J. Amer. Chem. Soc.* **111**, 8973 (1989).

MARYE ANNE FOX
A. A. ABDEL-WAHAB

*Department of Chemistry
University of Texas at Austin
Austin, Texas 78712*

Received April 17, 1990; revised August 13, 1990.