

Selectivity in the TiO₂- Mediated Photocatalytic Oxidation of Thioethers

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Abstract: The relative rates of photooxygenation of substituted diphenyl sulfides on irradiated TiO₂ powders suspended in oxygenated acetonitrile correlate linearly with σ^+ , as is consistent with formation of a surface bound cation radical in the primary photoprocess. Substituted dibenzyl sulfides, in contrast, suffer C-S cleavage upon photocatalyzed oxidation. Factors disposing these reactions toward preferential sulfoxide formation or bond cleavage are discussed.

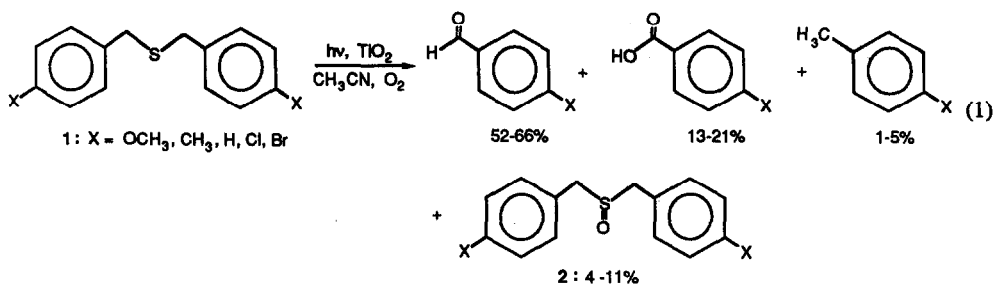
Introduction

Our continued interest in selective photocatalysis at irradiated semiconductor surfaces prompts us to report our recent investigation of the TiO₂-mediated photocatalytic oxidation of benzyl and aryl sulfides. The primary photochemical process in such conversions often involves interfacial transfer of a single electron from an adsorbed substrate to a photogenerated hole.^{1,2} If this route transpires in the photocatalytic conversions of sulfides, a surface-bound thioether cation radical would be formed. When generated in homogeneous solution, such a cation radical is known to be captured by oxygen or superoxide,³ forming an intermediate whose involvement is signaled by formation of sulfoxide and sulfone products. The well-known alpha cleavage of a thioether cation radical⁴ would be expected, however, to lead to oxidative cleavage.

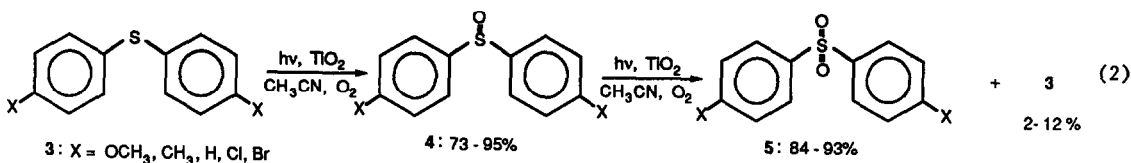
Selectivity in oxidation mode can be influenced frequently by the environment in which a singly oxidized species is generated, reflecting kinetic influences on reaction partitioning by the metal oxide,⁵ adsorption effects,⁶ and trapping of surface-bound reactive intermediates.⁷ This study sought to establish whether analogous effects might be operative in the photocatalytic reactions of thioethers. A preliminary study by Davidson⁸ had shown that such substrates are photoelectrochemically oxidized via a route not involving singlet oxygen, but product analysis and mechanistic details are still lacking. Thus, we report herein the effect of electronic perturbation of the surface-bound cation radical and more clearly delineate the factors controlling the course of semiconductor-mediated photooxidations.

Results and Discussion

C-S cleavage dominates the photocatalytic degradation of dibenzyl sulfide 1, eqn 1, with sulfoxide 2



being formed only as a minor product, whereas sulfoxide formation ensues from diaryl sulfides 3, eqn. 2.⁹



As might be expected with primary electron-hole formation, control experiments demonstrated that light, TiO₂, and O₂ were necessary for efficient photocatalysis. With symmetrically substituted diaryl sulfides, the relative rates of photooxygenation, Table 1, for two diaryl sulfides competing for a common reaction site on a suspended TiO₂

Table 1. Chemical Yields^a in the TiO₂-Photocatalyzed Oxidation of Thioethers^b

Compound	Relative Rate ^c	Products: Yields (%)
1 (X=H)		C ₆ H ₅ CHO: 61, C ₆ H ₅ CO ₂ H: 13, C ₆ H ₅ CH ₃ : trace, 2 (X=H): 11
3 (X=H)	1.0	4 (X=H): 89
3 (X=OMe)	2.8	4 (X=OMe): 92
3 (X=Me)	1.5	4 (X=Me): 73, H ₃ CC ₆ H ₄ SC ₆ H ₄ CHO: 27
3 (X=Cl)	0.65	4 (X=Cl): 84
3 (X=Br)	0.63	4 (X=Br): 95
4 (X=H) under O ₂		5 (X=H): 95
4 (X=H) sealed under air		5 (X=H): 66, 3 (X=H): 28

^a Observed yields are dependent on conversion since the products are also oxidizable. The reported yields are those obtained by extrapolation to zero conversion for three reactions conducted on separately prepared catalysts.

^b These reactions were conducted as 5 × 10⁻³ M solutions of the sulfide dissolved in 5 mL of anhydrous air- or oxygen-saturated acetonitrile containing 50 mg of suspended TiO₂ (Aldrich, anatase). The suspensions were irradiated with continuous stirring in a Rayonet photochemical reactor equipped with phosphor-coated lamps emitting maximally 350 nm. A bismuth acetate solution-phase cut-off filter (λ > 350 nm) was employed to obviate direct excitation of the substrates, which all possess broad tailing absorption bands. Products were identified by comparison with authentic samples and were quantitated against a pentamethylbenzene internal standard added after the irradiation.

^c Ratio of rates of disappearance of starting materials from a 1:1 mixture of 3X and 3 (X=H), extrapolated to zero conversion. Reported value is an average of five measurements.

powder showed a linear dependence on substituent σ^+ values with a slope of -0.7 ($R=0.969$). This value is close to that observed in the semiconductor-mediated oxidative cleavage of diaryl ethylenes.⁹ A lower kinetic sensitivity ($0 < \rho < -0.1$) to substituent was observed in similarly substituted dibenzyl sulfides.

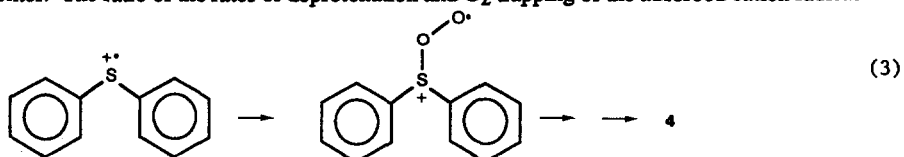
The observation of C-S oxidative cleavage in dibenzyl sulfides is consistent with the expected order of cation stability. From a thioether cation radical, bond cleavage proceeds to preferentially apportion electrons to a thioalkyl radical and an alkyl cation.⁴ The order predicted from cation stabilities is observed for the isomeric dibutylsulfides (*t*-butyl > *n*-butyl),⁸ despite the more facile adsorption of the less sterically encumbered primary thioether. The close similarities in the observed rates may reflect counter-balancing contributions from adsorption effects and the involvement of SN_2 -like assistance by acetonitrile¹⁰ in breaking the C-S bond in the photogenerated di-*n*-butyl sulfide cation radical.

The resistance of the diaryl sulfides to such photooxidative cleavage would then presumably result from the destabilizing influence of the incipient phenyl cation in the transition state for the homolysis and to the impossibility of nucleophilic assistance via back side attack in this cyclic structure. The appreciable positive charge developing at sulfur in the adsorbed cation radical would be more sensitive to ring substituents than in the benzylic analogs. Sulfoxide formation also dominates in the photocatalytic activation of $(p\text{-CH}_3\text{-C}_6\text{H}_4)_2\text{S}$, where deprotonation of the methyl group, ultimately producing aldehyde via oxygen trapping of the initially formed benzylic radical, might have been expected had the cation radical been formed in homogeneous solution. A similar preference for oxygenation of the π -system also led to ring- rather than side chain- oxidation in methyl naphthalenes.⁵

Upon continued photooxygenation, the initial diaryl sulfoxide **4** is converted to sulfone **5**, eqn 2, also in a high yield process. This secondary photooxygenation must at least partially involve oxygen transfer from the sulfoxide, since the starting sulfide is also reformed in this secondary reaction when insufficient surface-bound O_2 is available, Table 1.

We conclude, as in previous studies,¹ that these photocatalytic reactions are initiated by formation of a surface bound cation radical generated by interfacial electron transfer. The photogenerated hole localized at the surface of the irradiated semiconductor is trapped by an adsorbed organosulfur compound, generating an adsorbed cation radical. The small, negative ρ value observed in the oxygenation of the *p*-substituted diaryl sulfides is consistent with either positive charge localization in the rate determining step⁹ or with electronic perturbation of a pre-photocatalytic adsorption equilibrium.⁷ This localization of positive charge at sulfur would be expected either in the transition state leading to the initial oxygen adduct, eqn. 3, or by Bronsted or Lewis acid complexation respectively with acidic or Ti^{4+} sites on the metal oxide surface. The competition between C-S cleavage (as observed in dibenzyl sulfide) and oxygenation (as

observed in the diarylsulfides) is controlled by the stability of the possible fragments and by access of a nucleophile¹⁰ to the developing cation center. The ratio of the rates of deprotonation and O₂ trapping of the adsorbed cation radical



is presumably mediated by the semiconductor surface, bringing together both the photogenerated cation radical and either O₂ or superoxide.⁵ This study thus provides an example of specific, controlled oxidative chemistry in organic substrates adsorbed on photoactivated TiO₂ surfaces. With continuing effort, these heterogeneous photocatalytic oxidations are likely to assume increasing importance as practical methods for environmental decontamination.^{11,12}

Acknowledgement.

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