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PHOTOCATALYTIC DECONTAMINATION OF SULFUR-CONTAINING ALKYL HALIDES ON IRRADIATED SEMICONDUCTOR SUSPENSIONS

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Factors influencing the efficiency of the photocatalytic oxygenation of two mustard simulants (2-chloroethyl methyl sulfide and 2-chloroethyl ethyl sulfide) on irradiated suspensions of TiO_2 in aerated acetonitrile are described. Product analysis indicates that sulfoxide formation is the dominant process in acetonitrile and that TiO_2 is a much better photocatalyst than SnO_2, ZrO_2, or ZnO.

1. Introduction

The strong physiological response induced by contact of mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$) with human skin or lung tissue can be substantially reduced if this sulfur-activated alkyl chloride is oxidized or hydrolyzed [1]. Previous investigations have shown that many organic molecules [2], including specifically thioethers [3,4] and alkyl halides [5], suffer catalytic oxidative degradation at the solid-liquid interface of irradiated metal oxide surfaces immersed in aerated polar organic solvents. We report herein our investigation of the factors influencing the photocatalytic efficiencies of irradiated metal oxide suspensions in the catalytic photooxidative detoxification of two mustard simulants 2-chloroethyl methyl sulfide **1** and 2-chloroethyl ethyl sulfide **2**. The principal variables studied were: a) the effect of the solvent system on product distribution; b) the dependence of the reaction rate on substrate concentration; and c) the influence of the surface composition of the catalyst on observed reactivity.

2. Methods

The procedure employed is similar to that described previously for the photocatalytic oxygenation of other organic substrates [1,6]. Titanium dioxide (MCB technical grade, anatase powder or DeGusa P-25 powder) and zinc oxide (Aldrich) were dried overnight in a vacuum oven at about 125 °C. Tin oxide and zirconium oxide powders were a gift of Professor P. Pichat and were used as supplied. Oxygen or air were dried by passage through a drying tube containing dry calcium chloride. Acetonitrile (Fisher, hplc grade) was distilled and stored under vacuum until use. Water was triply distilled.

In general, a 0.001 to 0.025 M solution of the simulant was prepared in the desired solvent, and a weighed quantity of the photocatalyst (usually 5 to 10 mg/100 mL of solvent) was added to the solution. The mixture was transferred to a pyrex reaction vessel and was sonicated in an ultrasonic bath while bubbling with the purging gas (oxygen, air, or nitrogen). The resulting suspension was then placed inside a double-walled glass cylindrical support equipped to accommodate a 1 cm pathlength chemical filter. Control experiments demonstrated that direct photolysis of the simulants also resulted in decomposition of the substrates. Thus, a bismuth acetate filter was employed to minimize direct excitation of the simulants while allowing photocatalytic process derived from electron-hole formation in the semiconductor photocatalyst to proceed. A one cm pathlength of a 0.004 M optical filter solution (6 g $Bi(OAc)_3$ in 3.5 L of water containing 350 mL conc. HCl) produced a 360 nm cut-off: under these conditions, only negligible direct photodecomposition occurred on the timescale of the photocatalytic experiment.

Irradiation of the suspension was then conducted for a measured period in a Rayonet photochemical reactor equipped with phosphor-coated low pressure mercury vapor lamps blazed at 350 nm. The suspension composition was maintained by stirring with a magnetic stirrer and by a slow stream of purging gas. The light flux of the reactor had previously been calibrated by actinometric measurements with potassium ferrioxalate and agreed within 10% in all cases to manufacturer's specifications (24 watts, about 90% in the 350 ± 10 nm range, 1.5 to 5×10^{16} photons/sec/cm^3).

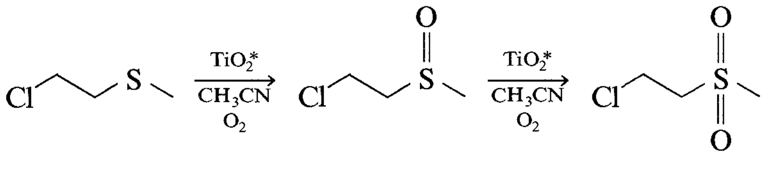
After a measured irradiation period, the photocatalyst was separated from the reaction mixture by filtration through a medium porosity frit and the products were either analyzed directly or were concentrated by evaporative removal of volatile solvent. Aqueous acetonitrile solutions were extracted with diethyl ether after concentration. The resulting organic concentrate was analyzed by gas chromatography (gc) on a Hewlett-Packard 5890 A chromatograph equipped with a flame ionization detector and a capillary column or by gas chromatography/mass spectroscopy (gc/ms) on a Finnegan 4023 automated gc/ms with an INCOS data system using a 50 m DB-1 capillary column. Products were identified either by coinjection with authentic materials and/or by comparison with known gc/ms library fragmentation patterns.

3. Results

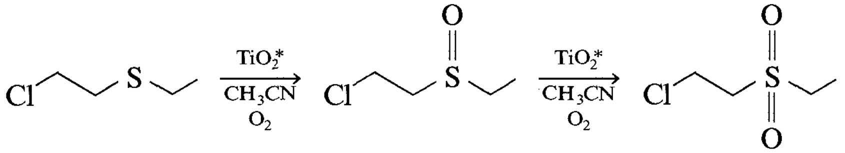
A. SOLVENT EFFECTS ON PRODUCT COMPOSITION AND CONVERSION

Two apparent differences were encountered in comparing the photocatalyzed destruction of the simulants in acetonitrile and in aqueous (10%) acetonitrile. The product mixture was much simpler in neat acetonitrile and the rates of decomposition of the simulant substrates were complicated in water-acetonitrile mixture by concurrent thermal hydrolysis. The simulants proved to be inconveniently insoluble in mixtures containing substantially greater quantities of water.

If the photocatalytic reactions were followed in acetonitrile, the reaction profile shown in fig. 1 was obtained. This figure can be explained by the sequential chemical conversions shown as eqs. (1) and (2), respectively.



1 **1-SO** **$1\text{-}SO_2$** (1)



2 **2-SO** **$2\text{-}SO_2$** (2)

Thus, the sulfide was cleanly converted to a primary product (identified as sulfoxides **1-SO** and **2-SO**, respectively), which in turn suffered further oxidative conversion to the final product (identified as the sulfones **$1\text{-}SO_2$** and **$2\text{-}SO_2$**, respectively). The chemical yields of these two products were conversion-dependent, with maxima observed at approximately 90% conversion of the sulfides to their corresponding sulfoxides [3,4] and of the sulfoxides to the corresponding sulfones. Extrapolation of these reactions to zero conversion shows that the sulfoxide is formed from **1** in $> 95\%$ chemical yield, while the formation of the sulfone from **1-SO** is nearly quantitative at zero conversion. Sulfoxide formation from **2** proceeds in $\sim 92\%$ yield at zero conversion and is similar to that observed in the oxidation of **2-SO** at low conversion.

When the analogous photocatalytic degradations were conducted in aqueous acetonitrile, a much more complex mixture of products was obtained. Complicating the product mixture were substantial amounts of hydrolysis products: $CH_3SCH_2CH_2OH$ and $CH_3CH_2SCH_2CH_2OH$, respectively, and the crude ^{13}C nmr spectra showed appreciable peaks at 23 ppm, which are likely to be hydrolytic dimerization products $CH_3SCH_2CH_2S^+(CH_3)CH_2CH_2X$, where $X =$ Cl or OH [1]. These products could also be detected in a reaction mixture shielded from light, although their rate of appearance was greater during photolysis. Since the average temperature of the Rayonet reactor during operation is approximately 40 °, at least some fraction of this enhanced hydrolysis can be attributed to thermal activation under the photolysis conditions.

With both **1** and **2**, sulfoxidation represented a major decomposition pathway in aqueous acetonitrile, although the specific yield was highly variable. Since

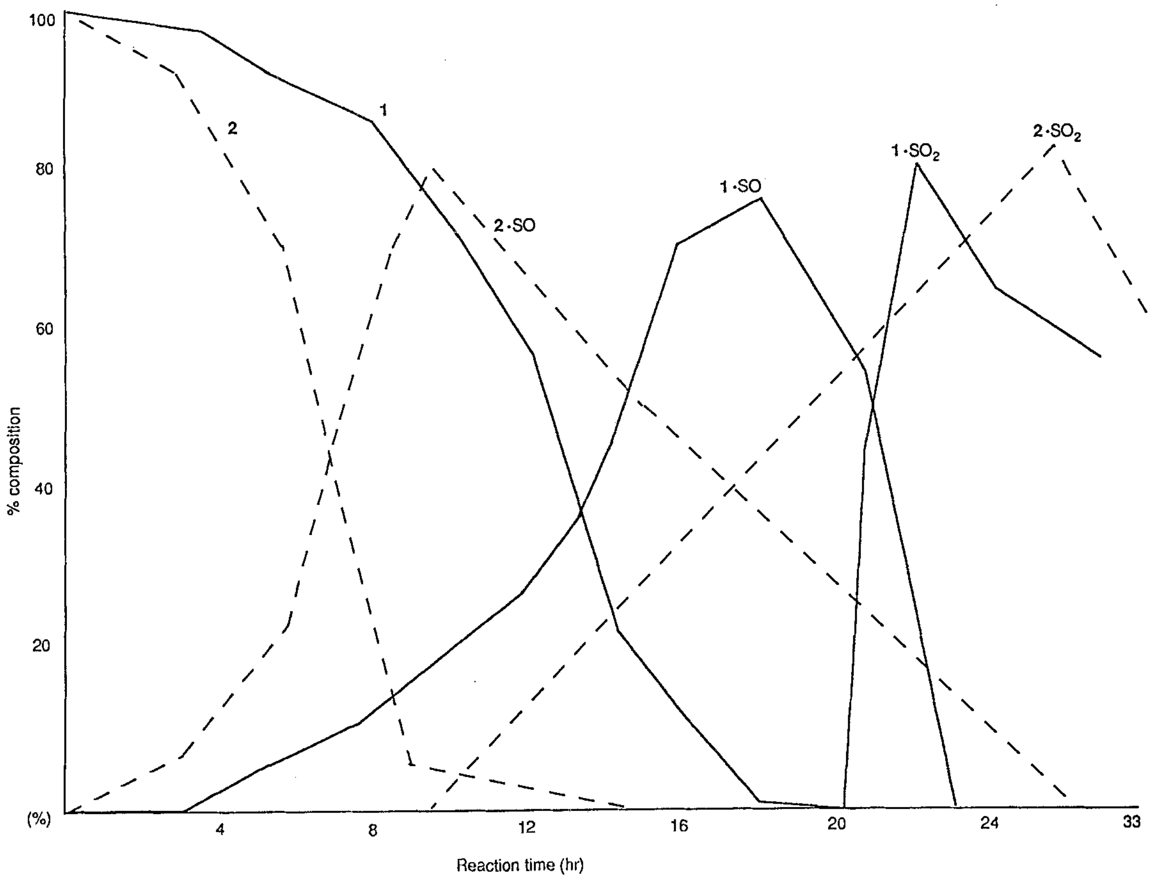


Fig. 1. Evolution of sulfoxidation product in the TiO_2-photocatalyzed oxygenation of simulants **1** (solid curves) and **2** (dashed curves) in anhydrous acetonitrile.

hydroxy radical is a likely primary product in photocatalyzed oxidations conducted as aqueous suspensions [7], the possible involvement of radical chains to destroy the starting material appears likely. Because of difficulties in attaining quantitative reproducibility in aqueous acetonitrile, primary mechanistic attention was focused on the conversions in neat acetonitrile.

B. RELATIVE REACTION RATES

In acetonitrile, **2** was photocatalytically decomposed somewhat faster than **1**, figure 1. Control experiments demonstrated the requirement of photocatalyst, light, and oxygen for efficient photodecomposition, table 1. When the bismuth acetate chemical filter was employed, photoconversion in the absence of TiO_2 was negligible.

Table 1
Control experiments establishing the photocatalytic degradation[a] of **1** and **2**

Simulant	Conditions	% Simulant remaining (±5%)	Relative Rate[b] (±0.06)
1	Light, N_2	100	0.00
	Light, air	98	0.01
	TiO_2, light, N_2	95	0.06
	TiO_2, light, air	81	0.28
	TiO_2, light, O_2	42	0.64
2	Light, N_2	100	0.00
	Light, air	99	0.01
	TiO_2, light, N_2	91	0.10
	TiO_2, light, air	76	0.32
	TiO_2, light, O_2	0	1.00

[a] 0.02 M simulant in dry acetonitrile, irradiated in Rayonet (~350 nm) for 14 h through a 1 cm $Bi(OAc)_3$ filter, 5 mg TiO_2 suspended in 25 mL of solution.
[b] Disappearance of substrate, extrapolated to zero conversion.

The effect of altering the initial ratio of simulant to photocatalyst is described by the data in table 2. Thus, increasing the amount of suspended catalyst (and hence the number of surface active adsorption sites) increases the rate of substrate disappearance. Given the level of quantitative reproducibility of experimental results obtained on heterogeneously suspended catalysts, these results are in reasonable correspondence with those predicted for pre-adsorption via a Langmuir isotherm [8].

The enhanced rate of photooxygenation implied by the data of table 1 upon increasing the adsorbed oxygen concentration, which is proportional to the dissolved oxygen concentration and hence to the oxygen content of the purging gas, is also consistent with a requirement for adsorbed oxygen for efficient

Table 2
Dependence of relative rates of photodecomposition[a] of simulants **1** and **2** on photocatalyst concentration

Simulant	TiO_2 (mg/25 mL)	Relative rate[b] (±0.06)
1	0	0.01
	1	0.22
	5	0.37
	10	0.60
2	0	0.02
	1	0.18
	5	0.61
	10	1.00

[a] 0.02 M simulant in dry acetonitrile, irradiated in Rayonet (~350 nm) for 14 h through a 1 cm $Bi(OAc)_3$ filter, 5 mg TiO_2 suspended in 25 mL of solution.
[b] Disappearance of substrate, extrapolated to zero conversion.

conversion. Again, the Langmuir isotherm model represents a reasonable description of the observed effects.

C. OTHER METAL OXIDES

Neither SnO_2 nor ZrO_2 is photocatalytically active as a suspended irradiated powder for the catalytic photooxidation of **1** or **2**. That is, the very low photooxygenation activity observed with these catalysts could be explained as direct photolysis into the trailing absorption band. ZnO shows approximately one-fifth of the photoactivity of TiO_2. The effects of surface platinization of TiO_2 or ZnO appears to parallel that reported for the photocatalytic oxidation of diols [9], i.e., activity increases modestly with platinum loadings of 0–5 weight % [10].

4. Discussion

A. MECHANISM

The lack of selective oxidation observed in aqueous acetonitrile and water suspensions of TiO_2 probably derives from the involvement of water as the primary oxidant. Thus, photoexcitation produces an electron-hole pair, in which the hole is trapped by adsorbed water, producing the adsorbed hydroxy radical. Evidence for its formation in aqueous solution is available from not only direct esr measurements [11] but also from isotopic labelling studies [12]. The surface-bound hydroxy radical is highly reactive and can attack the starting material at a near statistical distribution of sites.

Much cleaner product formation is observed in acetonitrile. The applicability of the Langmuir model leads us to propose the following mechanism as a reasonable route for the catalytic photooxygenation of simulants **1** and **2** in this non-aqueous solvent. Photogeneration of the electron-hole pair again occurs upon absorption by the suspended semiconductor of a photon of greater than band gap energy. The surface-confined hole, poised at the valence band edge of TiO_2, is sufficiently oxidizing to induce interfacial electron transfer from the pre-adsorbed substrate to generate an adsorbed thioether cation radical. Co-adsorbed oxygen acts as an electron trap, inhibiting electron-hole recombination and hence re-reduction of the absorbed cation radical. This latter species is then attacked chemically, either by oxygen or photogenerated superoxide, initiating the series of reactions shown, all of which have secure precedent in known oxygenation electron transfer chemistry [13].

Analogous steps can be repeated to accomplish the secondary conversion of the sulfoxide to the sulfone. Dehalogenation [5] did not compete at low conversion with oxidation at sulfur, although at much longer irradiation times loss of chloride could be noted.

The curves shown in fig. 1 show that over the irradiation periods required for nearly complete destruction of the simulant, nearly equal rates of decomposition (as modified by decreasing adsorption upon consumption of the substrate according to the Langmuir model) are observed throughout the irradiation period. Furthermore, if the catalyst from one reaction is recovered by simple filtration, it exhibits the same level of activity as if exposed to the initial stock solution of the simulant. Thus, photocatalytic activity appears to be retained during the photoconversion of the simulants.

Extrapolation of these laboratory results for field conditions may be risky, however, in that it has been shown in previous studies [1] that continued irradiation of unsaturated hydrocarbons or alkyl halides will give rise to appreciable quantities of surface-adherent polymers, thus producing insulator-coated photocatalysts whose oxidizing activity is lost or diminished. Although the photoinduced reactions of the simulants appear to be quite clean in acetonitrile, other substrate components or impurities may interfere with this clean oxygenation and cause catalyst surface contamination. According to the mechanism discussed above, such coatings will inhibit the reaction at the first step, rendering the proposed photocatalysis useless on a long-term basis. Thus, additional work under field conditions would be necessary in order to establish the practicality of this photocatalytic method as a route for in situ decontamination.

B. PHOTOCATALYTIC EFFICIENCY

Absolute quantum yield determinations in reflective heterogeneous suspensions are difficult because of the necessity for correction of the primary data for reflection and refraction losses of incident light. The simplest solution to this problem instead calculates a quantum yield limit with the assumption that negligible light loss from scattering and reflection can occur. These uncorrected quantum yields thus represent *minimum* values for photoreaction, but are more realistic measures of practical reactivity attainable. That is, the chemist concerned with reaction efficiency will also encounter the same reflection and refraction losses and will be more concerned with the question of how many photons must be supplied in order to achieve a desired photoconversion, rather than with an explicit determination of the efficiency of conversion of the photogenerated electron-hole pair into chemical products. Thus, the quantum yields reported below are *not* corrected for reflection and refraction losses.

The uncorrected quantum yield for the TiO_2-photocatalyzed disappearance of simulant **1** in neat acetonitrile under oxygen was 0.03 ± 0.01. From the relative rate data in table 1, we therefore calculate that the uncorrected quantum yield for disappearance of **2** in neat acetonitrile is 0.05 ± 0.01. These quantum yields are similar to those which have been measured for other surface-induced cation radical photooxygenations [1], which suggests that a competition between interfacial electron transfer and recombination of the photogenerated electron-hole pair governs the photocatalytic efficiency. This relatively inefficient light utilization is likely to be the major barrier to practical implementation of this method under field decontamination conditions.

Comparable rates of disappearance of **1** and **2** in aqueous acetonitrile were also observed, but because of the difficulties encountered in mixed water-acetonitrile solvents, the reaction efficiency cannot be conveniently expressed as a measured quantum yield.

C. CHOICE OF PHOTOCATALYST AS A DETERMINANT OF SELECTIVITY

As in previous studies, TiO_2 proved to be a superior catalyst, even without co-deposition of platinum. Although the presence of the metallic co-catalyst did improve the rate of photooxygenation somewhat, such a small increase in reactivity is attained, however, that the usefulness of adding another (expensive) step to the sequence for catalyst preparation seems debatable.

Acknowledgements

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