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The Titanium Dioxide Sensitised Photo-Oxidation of Sulphides

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Summary: Titanium dioxide has been shown to photosensitise the oxidation of sulphides to give sulphoxides and sulphones. Evidence is presented against the involvement of singlet oxygen and in favour of the sulphide radical cations as being intermediates.

Semiconductors are finding use as sensitisers for a number of organic photochemical reactions. Recently, the ability of particulate titanium dioxide to sensitise the oxidation of alcohols has been utilised to develop a method for generating hydrogen from cellulose waste.[1] Much work has been carried out on the sensitised decarboxylation of alkanoic acids[2] and on the splitting of photodimers, e.g. the anthracene photodimer.[3] Of particular interest is the ability of semiconductors to sensitise photo-oxidation reactions. Both colloidal[4] and particulate[5,6] titanium dioxide have been shown to sensitise the oxidation of alkenes, alkyl aromatic and related compounds. Cadmium sulphide has been shown to sensitise the oxidative dealkylation of N-methylated aromatic amines[8] and titanium dioxide to sensitise the oxidation of lactams, N-alkylamines[9] and aliphatic amines.[10] The latter undergo N-formylation and α-C-oxidative cleavage upon titanium dioxide catalysed photo-oxidation.

We now report that titanium dioxide can act as a sensitiser for the oxidation of sulphides. Irradiation of a suspension of titanium dioxide (0.05g, Anatase) in oxygenated acetonitrile solution (5 mls) containing a sulphide (5×10^{-3} M) was carried out using fluorescent lamps having a maximal emission at 350 nm (no light was absorbed by the sulphides). The rate of oxidation was monitored by glc analysis and the rates of consumption of sulphide are shown in Table 1. All the allylic sulphides yielded the corresponding sulphoxides and sulphones. However, with the exception of di-n-hexylsulphide the combined yield of sulphoxide and sulphone was always lower than the amount of sulphide consumed in the reaction (Table 1). It would therefore appear that these sulphides are undergoing other reactions. The rates of formation of oxidation products do not correlate with the relative rate constants[11] for reaction of the sulphides with singlet oxygen. Thus if the reaction had been singlet oxygen mediated the following order of reactivity should have been observed:-

di-n-butylsulphide (9.1×10^6 M^{-1} s^{-1}) > 1,4-dithiane (1.5×10^6 M^{-1} s^{-1}) > di-t-butylsulphide ($\sim 1.5 \times 10^5$ M^{-1} s^{-1}) > diphenyl sulphide (1×10^6 M^{-1} s^{-1}) (rate constants are given in brackets[11]) whereas the observed order of reactivity was found to be:-

di-n-hexylsulphide > diphenylsulphide > di-n-butylsulphide > di-t-butylsulphide. This indicates that, as reported[5,6] for the titanium dioxide sensitised photo-oxidation of alkenes, singlet oxygen is not the reactive species responsible for oxidation.

Table 1 **Rates of consumption of sulphide during titanium dioxide catalysed photo-oxidation, in oxygenated acetonitrile solution, and the percentage of reaction which led to the production of sulphoxides and sulphones**

Sulphide	Rate M (s^{-1})	Reaction leading to sulphoxide and sulphone production (%)
di-n-butylsulphide	8.9×10^{-7}	42
di-t-butylsulphide	4.4×10^{-7}	21
di-n-hexylsulphide	2.3×10^{-6}	100
diphenyl sulphide	6.4×10^{-7}	62
1,4-dithiane	5.1×10^{-7}	a

a - not determined

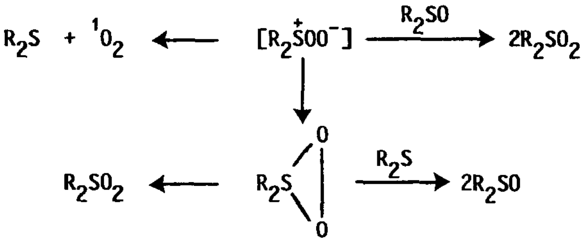
Although the other reactions which lead to consumption of the sulphide remain to be characterised, the finding that small quantities of sulphur are deposited on the oxide surface (characterised by x-ray fluorescence), the observation of disulphides as products (in low yield) from the reaction of di-(n-butyl), di-(t-butyl), diphenylsulphides and biphenyl as an additional product from the latter suggests that some C-S bond cleavage is involved.

We propose that the oxidation of the sulphides occurs as follows:-

$$\begin{aligned}
TiO_2 &\longrightarrow TiO_2(h^+) + e^- \\
TiO_2\,(h^+) + R_2S &\longrightarrow R_2S^{+\cdot} \\
e^- + O_2 &\longrightarrow O_2^{\overset{\cdot}{-}} \\
R_2S^{+\cdot} + O_2^{\overset{\cdot}{-}} &\longrightarrow [R_2\overset{+}{S}OO^-] \longrightarrow \textbf{oxidation products} \\
R_2S^{+\cdot} &\longrightarrow R^+ + RS^{\cdot} \\
R_2S^{+\cdot} &\longrightarrow R^{\cdot} + RS^+ \quad (R = Ph) \\
2RS^{\cdot} &\longrightarrow RS\text{—}SR \\
2R^{\cdot} &\longrightarrow R\text{—}R
\end{aligned}$$

Scheme 1

The photo-oxidation of sulphides is commonly interpreted as occuring via an intermediate of the type $[R_2\overset{+}{S}OO^-]$, in aprotic solvents.[12] Formation of products from such a species is believed to occur as outlined below.



Scheme 2

The formation of sulphide radical cations ($R_2\overset{+\bullet}{S}$) has been postulated as a primary step in the cyanoaromatic, e.g. 9,10-dicyanoanthracene, sensitised electron transfer photo-oxidation of sulphides.[13] In these reactions oxidation products are proposed as occuring via the reaction of the sulphide radical cation with the superoxide radical ion. Products derived via C-S bond cleavage in the titanium dioxide sensitised photo-oxidation of sulphides can be explained on the basis of dissociation of $R_2\overset{+\bullet}{S}$ radical cations as outlined in Scheme 1.

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