Titanium Dioxide Photocatalysed Oxidation of Benzyltrimethylsilanes in the Presence of Silver Sulfate

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In the presence of Ag_2SO_4, the TiO_2-mediated photochemical oxidation of substituted benzyltrimethylsilanes in acetonitrile leads to diarylethanes (50–74%) with a significant intermolecular selectivity ($\rho = -2.5$).

Oxidation of organic compounds at irradiated semiconductor surfaces is a topic of great practical and theoretical interest.[1] Light adsorption by the semiconductor induces electron-hole (e^-, h^+) pair formation, followed by an electron transfer from the adsorbed substrate to the hole: the ensuing chemistry is, therefore, that of the formed organic radical cation. Crucial for the efficiency of the process is a very fast chemical reaction of the radical cation, which can compete with back electron transfer, as well as the capture of the photogenerated electron by a reducible species (*i.e.* O_2).

Recent work has clearly shown that benzyltrimethylsilane cation radicals undergo a very fast C–Si bond cleavage leading to benzyl radicals.[2,3] These compounds should, therefore, be suitable substrates for photochemical reactions induced by semiconductors and accordingly a study of the TiO_2-catalysed photochemical oxidation of ring-substituted (H, *p*-Me, *m*-Me, *m*-CF_3, *m*-Cl) benzyltrimethylsilanes in acetonitrile has been carried out. The valence band potential of TiO_2 in acetonitrile is 2.3 V [*vs.* saturated calomel electrode (SCE)],[4] sufficiently positive to induce rapid electron transfer from the adsorbed silanes.

When the TiO_2-sensitized photochemical reactions of benzyltrimethylsilanes are carried out in acetonitrile, in the presence of O_2 (as the reducible species), using a 500 W high-pressure mercury lamp, very modest yields of products are obtained. Thus, after 20 h, only 10% of benzaldehyde is formed from benzyltrimethylsilane. The yield in 4-methoxybenzaldehyde becomes 25% (together with 6% of 4-methoxybenzoic acid) with 4-methoxybenzyltrimethylsilane, but no reaction at all takes place with *m*-Cl and *m*-CF_3 derivatives.

A substantial improvement has, however, been observed when O_2 is replaced by Ag^+ (as Ag_2SO_4). Under these conditions a quite efficient process [eqn. (1)] occurs leading to diarylethanes in fair to good yields (from 50 to 74%) and with a satisfactory material balance (*ca.* 85%) even when electron-withdrawing substituents (*m*-Cl and *m*-CF_3) are present. The results are given in Table 1 together with the data of relative reactivity obtained in a kinetic investigation of this reaction by using the competitive method.

$$ArCH_2SiMe_3 \xrightarrow[MeCN]{h\nu,\ TiO_2,\ Ag_2SO_4} \underset{50\text{–}74\%}{ArCH_2CH_2Ar} \qquad (1)$$

An important observation is that the rate of the reaction is very sensitive to the nature of the ring substituent, being increased by electron-donating groups and depressed by the electron-withdrawing ones. A quantitative assessement of the phenomenon is provided by the ρ^+ value (-2.5, $r = 0.98$) calculated by the log k_{rel}/σ^+ plot. This is the most negative value ever observed in a TiO_2-catalysed oxidation of aromatic compounds. It compares with ρ^+ values of -0.56 and -0.7 for

Table 1 Products yields and relative rates in the TiO_2-catalysed photochemical reaction [eqn. (1)] of ring-substituted benzyltrimethylsilanes in acetonitrile in the presence of Ag_2SO_4[a]

Substituent	Irradiation time/h	Diarylethane yield (%)[b]	Relative rate[c] at 25 °C
H	3	74	1
p-Me	2	71	3.7
m-Me	2	51	1.5
m-Cl	10	58	0.14
m-CF_3	20	50	0.023

[a] Reactions have been carried out by external irradiation (500 W high-pressure mercury lamp, Pyrex filter), under stirring, of a N_2-purged acetonitrile (HPLC grade) solution (20 ml) of substrate (0.2–0.25 mmol), in the presence of 100 mg of TiO_2 (anatase, dried at 110 °C) and 0.2–0.25 mmol of Ag_2SO_4, at room temp. No reaction takes place if the substrate solution is irradiated in the absence of either TiO_2 or Ag_2SO_4. [b] With respect to the starting substrate, taking the stoichiometry of eqn. (1) into account. Determined by NMR spectroscopy in the presence of an internal standard. Products were identified by GC–MS and NMR spectroscopy (comparison with authentic specimens and literature data[9,10]). The unreacted substrate was determined by GC in the presence of an internal standard. [c] Determined at 25 °C by the competitive method. Solutions, generally containing equimolar amounts of two substrates, A_0 and B_0, were irradiated and the amounts of unreacted A and B at various times (A_t and B_t, respectively) determined by GC.

the TiO_2-mediated photochemical oxidation of alkenes[5] and thioethers,[6] respectively. To adapt these low ρ values to an electron-transfer mechanism, diffusion-controlled electron transfer, adsorption effects and/or the involvement of solvent assistance were suggested.

Clearly the above problems seem to be absent in reaction (1) where the ρ value as well as the nature of the reaction products are well in line with the mechanism described in [eqns. (2–6)] (Nu = MeCN).

$$TiO_2 \xrightarrow{h\nu} h^+ + e^- \tag{2}$$

$$e^- + Ag^+ \longrightarrow Ag \tag{3}$$

$$h^+ + ArCH_2SiMe_3 \longrightarrow [ArCH_2SiMe_3]^{+\bullet} \tag{4}$$

$$[ArCH_2SiMe_3]^{+\bullet} + Nu \longrightarrow ArCH_2^{\bullet} + Me_3Si\text{-}Nu^+ \tag{5}$$

$$2\ ArCH_2^{\bullet} \longrightarrow ArCH_2CH_2Ar \tag{6}$$

Dimerization of the benzyl radical is presumably favoured, over competing processes (*i.e.* oxidation[7]), by the development of a relatively high concentration of this species adsorbed onto the surface of the semiconductor. The relatively large ρ value also suggests that the electron-transfer step plays an important role with respect to the overall reaction rate.

In the proposed mechanism Ag^+ scavenges the photogenerated electron [eqn. (4)] and accordingly we have observed that metallic silver is formed during the irradiation. Moreover, the yield of products decreases if Ag_2SO_4 is added in less than an equimolar amount with respect to the substrate. For example, with benzyltrimethylsilane the yield in 1,2-diphenylethane drops from 74 to 44% when the Ag^+ : substrate molar ratio is 0.5. Since, in the presence of Ag_2SO_4, yields of products are significantly higher than those observed in the presence of O_2, Ag^+ appears to be more efficient than O_2 in the trapping of the photogenerated electron. However, some beneficial effect of the deposition of reduced silver on TiO_2 is also possible,[8] and work aimed at getting more information on the role of Ag^+ as well as on the possible use of other metal ions is in progress.

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