SHORT PAPER

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The photoelectrochemical oxidation of benzyl derivatives at Ti/TiO_2 anodes. A mechanistic approach through current efficiency and density measurements[†]

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The mechanism of the photoelectrochemical sensitised oxidation of 4- and 3-methoxybenzyl alcohols and silanes at Ti/TiO_2 'anatase' and 'rutile' photoanodes has been investigated through current efficiency and density measurements.

Keywords: titanium dioxide, photoelectrochemistry, benzyl alcohols, benzyl silanes

The TiO_2-sensitised photomineralisation of organic compounds as pollutants in waste water is an environmentally friendly system.[1] In this context, it is useful to acquire further information about the mechanistic behaviour of differently functionalised substrates. In particular, knowledge about the kinetically significative steps of the primary oxidation products and of the reaction stoichiometry (the number of electrons exchanged per molecule of reacted substrate) is useful. The use of the TiO_2 photoanode (as a film supported on a conducting material) in an electrolytic cell could be a way to evaluate both of these aspects. In effect, this photoelectrochemical technology allows the experimentally-observed electrical parameters (current efficiency and density) to be used to acquire further mechanistic information relative to the process. To date, this technology has been principally used in aqueous medium.[2] In some works, acetonitrile was considered as an alternative solvent;[3] this organic solvent, in contrast to water, does not signficantly compete with the substrate oxidation and therefore allows current efficiencies nearer to unity to be obtained,[3a,b] making the process more useful for both synthetic and mechanistic purposes. It has also been shown that the TiO_2-photosensitised oxidation mechanism should be the same as in aqueous medium, at least with respect to the primary oxidation steps of low reduction potential substrates.[4]

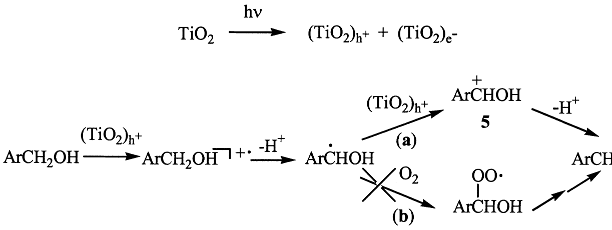
In this work we have undertaken a study in CH_3CN of the photoelectrochemical oxidation of 4- (**1**) and 3-methoxybenzyl alcohol (**2**) together with 4- (**3**) and 3-methoxybenzyltrimethylsilane (**4**) sensitised by TiO_2 (with 'anatase' or 'rutile' crystal structure), as a film supported on titanium anodes prepared as reported.[5] The analysis of the reaction products together with current efficiency (yield) and density measurements have provided further information about the mechanistic behaviour of these photoelectrochemical processes.

Results and discussion

Current efficiency: The photooxidation reaction of some phenyl-substituted benzyl alcohols sensitized by TiO_2 as powder[6] or as colloid[7] in CH_3CN and in the presence of Ag^+ (deaerated medium) or O_2 (aerated medium) as an electron acceptor, respectively, gives the corresponding benzaldehydes.

When the reaction is performed with alcohols **1** and **2** in a photoelectrolytic cell with Ti/TiO_2 anode (see Experimental) the corresponding aldehyde is again the only observed product in both aerated and deaerated medium (see Table 1), presumably formed through the same mechanism reported with the dispersed semiconductor.

In particular, the current efficiency (defined as the amount of current passed in relation to the number of electrons exchanged per molecule of the product formed or the substrate consumed, provided that a quantitative material balance is observed) allows further information to be acquired about the reaction stoichiometry and, in particular, about the last steps of the mechanism. In effect, the current efficiency for the reaction of **1** at the Ti/TiO_2 'anatase' anode in deaerated medium (entry 1) is nearly 100% (at least until *ca* 20% of substrate conversion) when it is assumed that two photogenerated electrons, $(TiO_2)_{e}$-, are transferred to the electron acceptor (probably Li^+ at the cathode[5]); this fact is in line with the involvement of the first photogenerated hole, $(TiO_2)_{h}$+, to yield the radical cation (Scheme 1) and a second hole that oxidises the α-OH-substituted benzylic radical to give the protonated aldehyde (Scheme 1, path **a**).



Scheme 1

The same results are obtained with Ti/TiO_2 'rutile' (entry 2), showing that the different crystalline structure does not influence the reaction.

It must be noted that, even if the process is carried out in an undivided cell, the anodic and the cathodic processes do not interfere with each other. In effect, experiments performed utilising WO_3 as cathode[5] in a divided cell (where the cathodic process is $Li^+ + e \rightarrow Li$[8]) show the same current efficiency (compare entry 3 with 2).

The current efficiency value obtained for 4-methoxy derivative (**1**) in the presence of O_2 (entry 4) is again nearly 100% (two transferred electrons per molecule). It can therefore be suggested that oxygen does not participate in the reaction of **1** and, therefore, the mechanism is the same as in a deaerated medium. In other words, the known[9] fast coupling process between a benzylic radical and oxygen to the corresponding

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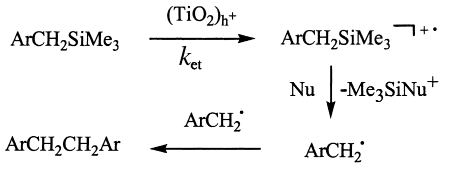
peroxyl radical that evolves into the aldehyde (without the intervention of a further hole, Scheme 1, path **b**) cannot compete with the oxidation by $(TiO_2)_h+$ of the benzylic radical when it is α-OH substituted (Scheme 1, path **a**); this behaviour is probably due to the low reduction potential of this radical,[10] in line with the significant stability of the cation **5** (Ar = 4-MeOPh).

When the reaction is carried out with alcohol **2** in aerated medium (entry 5), the current efficiency (again two electrons per molecule) is practically quantitative (at least until 10% substrate conversion). This behaviour could be explained by assuming a low reduction potential for the α-hydroxylated 3-methoxybenzyl radical, that should make the oxidation to the cation easier with respect to the coupling with oxygen (Scheme 1). This means that the stabilising effect of α-OH on the cation **5** is also high when the substituent on the ring is electron-withdrawing (Ar = 3-MeOPh).

The photoelectrochemical oxidation of benzylic silanes **3** and **4** on Ti/TiO_2 was also performed. In the past, the photooxidation reaction of some phenyl-substituted benzyltrimethylsilanes sensitised by TiO_2 in CH_3CN were studied utilizing the semiconductor as a powder in both deaerated (in the presence of Ag^+)[11] and aerated medium.[12]

The only product obtained from the electrochemical photooxidation of silane **3** in deaerated CH_3CN, with both TiO_2 'anatase' and 'rutile' anode, is reported in Table 1 (entries 6–8). It is a dimer [1,2-bis(4-methoxyphenyl)ethane] with the same structure as those obtained with TiO_2 as powder.[11] It is reasonable to suggest that this 1,2-diarylethane is obtained through the same mechanism (Scheme 2). The observed nearly quantitative current efficiency, assuming that only one photogenerated electron is transferred to the electron acceptor, confirms the suggested mechanism.

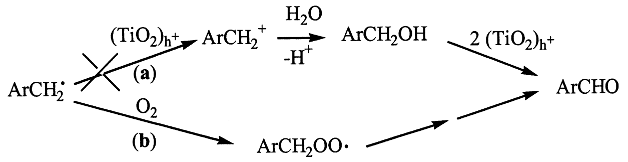


Scheme 2

When the photoelectrochemical reaction of **3** and **4** is carried out in aerated CH_3CN (entries 9 and 10) the only observed product is 4-methoxybenzaldehyde and the current efficiency is nearly quantitative considering one hole is involved per molecule of formed product. This suggests that the benzylic radical (formed as in Scheme 2) is quickly trapped by the adsorbed oxygen[9] (no holes are involved, Scheme 3, path **b**). In other words, this reaction should be more efficient than the benzyl radical oxidation to the corresponding cation that produces the aldehyde through the involvement of other holes (Scheme 3, path **a**).

In conclusion, it must be noted that the different fate of 3- and 4-methoxybenzyl radicals with respect to the α-OH-substituted ones (compare Scheme 3 with Scheme 1) is in line with the lower oxidisability of the former intermediates (in effect, it is known that the 4-methoxybenzyl radical has a higher E_p value than the α-OR-substituted one[13]).

Current density: This electrical parameter can be utilised to evaluate the relation between the organic substrate structure and the photoelectrochemical efficiency of the process.[14] The current density values relative to alcohols **1** and **2** together with those of silanes **3** and **4** are reported in Table 1.



Scheme 3

It must be noted that the current density, a measure of the transfer rate of the electrons from the anode to the cathode through the electric circuit, should be related to the product formation (or the substrate disappearance) rate only when the current yield is practically quantitative (we suggest > 80%). Since this rate should depend on both the adsorption preequilibrium constant (K_D) of the substrate at the TiO_2 surface and the rate constants of the steps following this preequilibrium,[7] in this work we have compared the current density values of only those compounds with the same functional group (that should reasonably have similar K_D; see, for example, the values for **1** and **2**[7]). In this context, by comparing the current density values of alcohols **1** and **2** or silanes **3** and **4** (in the same photoelectrochemical reaction conditions) it can be observed that the reactivities of the 4-methoxy derivatives are higher than those of the 3-methoxy ones. In particular, the relative reactivity of alcohols (current density ratio = 1.4, comparing entries 4 and 5 in Table 1) is in line with that (quantum yield ratio = 2.3) measured in the photooxidation reactions sensitised by colloidal TiO_2.[7] The lower selectivity, derived from current density measurements, could be ascribed to the higher photocatalytic efficiency[5] of the semiconductor when an anodic potential (0.5 V *vs* SCE) is applied. The relative reactivity observed for **3** and **4** (current density ratio = 1.5 by the comparison of entries 9 and 10) can be explained as for alcohols[7]: the reactivity ratio should depend principally on the electron transfer step according to the corresponding E_p values [k_{et}(**3**)> k_{et}(**4**) in Scheme 2 is in line with E_p(**3**)(1.22V *vs* SCE) < E_p(**4**)(1.43V)].

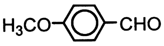
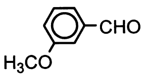
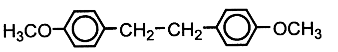
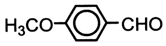
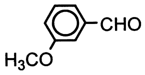
Experimental

^1H-NMR spectra were measured on a Bruker AC 200 (200 MHz) spectrometer. GCMS analyses were performed on a Hewlett Packard 6890A gas-chromatograph coupled with a MSD-HP 5973 mass selective detector (70 eV). GC analyses were carried out on a HP 5890 gas-chromatograph. E_p values were obtained from an AMEL 552 potentiostat controlled by a programmable AMEL 568 function generator (cyclic voltammetry at 100 mV/s, 1 mm diameter platinum disc anode) in $CH_3CN/LiClO_4$ (0.1 M).

Materials: TiO_2/Ti anodes were prepared from surface oxidation of titanium plates (furnished from Titania S.p.A. Terni) as reported.[5] 4-Methoxybenzyl alcohol (**1**), 3-methoxybenzyl alcohol (**2**), 4-methoxybenzaldehyde, 3-methoxybenzaldehyde, H_2SO_4, $LiClO_4$ and Na_2CO_3 were analytical grade commercial products. CH_3CN (99.9%, HPLC grade) contained 0.02% water (from Karl Fisher analysis). 4-(**3**)[15] and 3-methoxybenzyltrimethylsilane (**4**)[4a] were prepared as previously described.[4a]

Photoelectrochemical oxidation: The photoelectrochemical measurements were performed in an undivided cylindrical jacketed cell provided with Ti/TiO_2 anode (20 cm^2), Pt cathode and SCE as reference connected to the AMEL potentiostat. The substrate (0.30 mmoles), $LiClO_4$ (7.5 mmoles), Na_2CO_3 (4.7 mmoles in the reaction of alcohols **1** and **2**) in CH_3CN (150 ml) were placed in the cell and magnetically stirred under nitrogen or oxygen bubbling. The cell was externally irradiated by a 400 W high pressure Hg lamp (Helios Italquartz), cooled by a Pyrex water jacket ($\lambda \geq 300$ nm) positioned in front of Ti/TiO_2 electrode and the apparatus was covered by an aluminium closed cylinder. Current flowed only under irradiation and after 10–30 min (depending of the substrate) it was practically constant. The mixture was concentrated at room temperature, poured into a double volume of water and repeatedly extracted with diethyl ether. The organic layer was washed with NaCl-saturated water, dried on Na_2SO_4 and concentrated. The crude product was analysed by ^1H-NMR and VPC, in the presence of suitable internal standards, and by GCMS. The material recovery (substrate + product) was always

Table 1 Photoelectrochemical oxidation of 4- (**1**) and 3-methoxylbenzyl alcohol (**2**), and 4- (**3**) and 3-methoxybenzyltrimethyl silane (**4**) at Ti/TiO2 anodes in CH_3CN[a]

Entry	Substrate	TiO_2 crystalline form	Bubbled gas	Product	Product /%	Current yield/%	Current density × 10^{-2}/mA/cm^2
1	**1**	Anatase	N_2		21	95[b]	
2	**1**	Rutile	N_2		20	98[b]	
3[c]	**1**	Rutile	N_2		20	98[b]	
4	**1**	Rutile	O_2		20	95[b]	9.5
5	**2**	Rutile	O_2		10	82[b]	6.7
6	**3**	Anatase	N_2		50	81[d]	
7	**3**	Rutile	N_2		45	84[d]	
8[c]	**3**	Rutile	N_2		50	87[d]	
9	**3**	Rutile	O_2		16	88[d]	8.4
10	**4**	Rutile	O_2		5	86[d]	5.7

[a] 0.30 mmoles of substrate in 150 ml of CH_3CN in the presence of $LiClO_4$ (0.05 M) and Na_2CO_3 (4.7 mmoles with alcohols **1** and **2**) to avoid the substrate solvolysis;[5] anodic potential = 0.5 V (*vs* SCE); irradiation by a high pressure Hg lamp, 400W, through Pyrex. [b] Calculated assuming two transferred electrons per molecule of formed product. [c] Divided cell with WO_3 as cathode.[5] [d] Calculated assuming one trasferred electron per molecule of formed product.

≥ 95%. The crude was chromatographed on silica gel eluting with n-hexane. The structure of isolated products was attributed by comparison with authentic specimens (4- and 3-methoxybenzaldehyde) or literature data (1,2-bis(4-methoxyphenyl)ethane[16]).

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