Photo-oxidation of some benzylic alcohols sensitized by colloidal TiO$_2$ in CH$_3$CN. A kinetic mechanistic study through quantum yield determinations

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ABSTRACT: The quantum yields (ϕ_{obs}) relating to the colloidal TiO$_2$-sensitized photo-oxidation of ring methoxy-substituted benzylic alcohols (D) were determined. The true quantum yields (ϕ_0) were obtained from a Langmuir–Hinshelwood isotherm treatment of ϕ_{obs} at different [D]. In the light of the suggested photo-oxidation mechanism, an equation was deduced where ϕ_0 is expressed as a function of the electron transfer (k_{et}), back electron transfer (k_{-et}) and benzylic deprotonation (k_p) rate constants. In particular, the lower ϕ_0 value of 3-CH$_3$O-*vs* 4-CH$_3$O-benzyl alcohol (**1**, with lower E_p) should principally depend on the difference in k_{et}, while the decrease in ϕ_0 on going from alcohol **1** to the α-methyl derivative (**4**) should be due to the difference in k_p (stereoelectronic effect). The adsorption equilibrium constants under irradiation (K_D) were also obtained from the above equation and the values are similar for the considered substrates, except for **4**. In fact, this substrate shows a lower K_D value, probably because of the steric hindrance of the methyl group to the OH adsorption (preferential site) on TiO$_2$. Finally, both the inter- and intramolecular deuterium isotope effect ($k_H/k_D = 1.8$ and 1.6, respectively) are consistent with a kinetically significant C$_α$—H bond breaking following the electron-transfer step. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: TiO$_2$; photo-oxidation; benzylic alcohols; quantum yields; electron transfer

INTRODUCTION

Heterogeneous photochemical processes, sensitized by semiconductors such as TiO$_2$, have gained wide popularity because of their application, principally in water or atmospheric detoxification, conversion or storage of solar light energy, photography and synthetic or mechanistic organic chemistry.[1] In the latter, photo-oxidation reactions of organic compounds sensitized by TiO$_2$ in aerated CH$_3$CN have been studied, generally using the semiconductor as a suspended powder; in this solvent, suitable for solubilizing organic substrates and not competitively oxidizable, the operation of an electron-transfer mechanism between the photogenerated hole (h$^+$) and the substrate (giving a radical cation as intermediate) is recognized.[1c]

In this research area, some studies have been reported on oxidation photosensitized by TiO$_2$ (as powder) of benzylic derivatives, generally in aerated and/or in deaerated CH$_3$CN, using oxygen[1c] or silver ions[2] as acceptors of photogenerated electrons. In particular, in a deaerated TiO$_2$–Ag$^+$ system, the photochemical reaction is a significantly efficient process and it has also been possible to study the chemical properties of radical cation intermediates, also in connection with the heterogeneous phase.[2] Generally, mechanistic investigations have been performed by product analysis and/or competitive kinetic methods. In a few cases these studies have been carried out in CH$_3$CN by absolute kinetic measurements[3] and, in one case,[3c] the quantum yields or, more precisely, the quantum efficiencies have been determined. For the latter, it must be noted that, in the presence of the suspended powder (a heterogeneous medium), it was not easy to measure quantum yields (a typical mechanistic test for homogeneous photochemical reactions). In fact, as reported in the literature[4] for heterogeneous photocatalysis in aqueous medium, it is only possible to refer to quantum efficiencies, which are always lower than true quantum yields, due to reflective and refractive loss of light incident on the powder. A reliable way to circumvent this problem in the presence of powder is the determination of true quantum yields by a modified integrated sphere method.[5]

True quantum yield determinations can be also carried

out by considering colloidal TiO$_2$, a light-transparent medium. Many of these reported measurements were made in water, where some additives (acids, polymers) were added to avoid rapid TiO$_2$ coagulation.[6] Only a few studies on colloidal TiO$_2$ in CH$_3$CN have been reported[7] and only two studies[7a,f] concerned the photo-oxidation of an organic substrate (in other cases,[7b,c,d,g] the reductive process induced by the photogenerated electron was investigated). In this solvent colloidal solutions can be prepared that are stable for nearly 10 days in the absence of additives,[7b,c] which allows a mechanistic study without secondary undesired reactions promoted by these species.

In this context, here we report quantum yield determinations from the photo-oxidation of benzylic alcohols **1–6** sensitized by colloidal TiO$_2$ in aerated CH$_3$CN, prepared in the absence of stabilizing agents.

CRR'OH
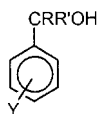
Subst.	Y	R	R'
1	4-CH$_3$O	H	H
2	4-CH$_3$O	H	D
3	4-CH$_3$O	D	D
4	4-CH$_3$O	CH$_3$	H
5	4-CH$_3$O	CH$_3$	CH$_3$
6	3-CH$_3$O	H	H

Previously[2f] we studied the oxidation of a series of ring-substituted (4-CH$_3$O, 4-CH$_3$, 4-Cl, H, 3-Cl, 3-CF$_3$, 4-CF$_3$) benzyl alcohols (to form the corresponding benzaldehydes) photosensitized by powdered TiO$_2$ suspended in deaerated CH$_3$CN and in the presence of Ag$^+$ (from Ag$_2$SO$_4$) as an electron acceptor. It has been shown that the step involving the electron transfer from the substrate to the photogenerated hole (h$^+$) is kinetically significant. The cation radical should undergo C$_\alpha$—H fragmentation to give an α-OH-substituted benzyl radical that should easily lose an electron[2e,f] to yield the protonated form of the aldehyde (Scheme 1).

In the present work all the experiments were carried out using O$_2$ (the most generally used electron acceptor) in place of Ag$^+$, this ion (a more efficient acceptor) being insoluble in its reduced form (Ag). Otherwise it has been
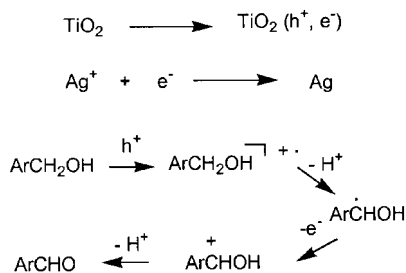
recently observed that O$_2$ does not participate to the oxidation mechanism; in particular, we have shown that, at least with 4- and 3-methoxybenzyl alcohol in aerated CH$_3$CN [from current yield measurements in photoelectrochemical experiments, using a Ti/TiO$_2$ photoanode in an electrolytic cell (results to be published)], the corresponding aldehyde does not derive from the expected reaction[2f] between benzylic radical and oxygen, but this intermediate is oxidized to cation as in Scheme 1 (by h$^+$).

To confirm and complete the reaction mechanism, we have undertaken a kinetic study based on quantum yield determinations. In this way some quantitative information was obtained about the influence of the substrate structure on reactivity (the ring and side-chain substituent effects, by comparing quantum yields of **1** and **6** and **1** and **4**, respectively).

Moreover, taking into account a recent paper about the competition between C$_\alpha$—H and O—H deprotonation paths of α-hydroxy-substituted alkylaromatic radical cations in different media,[8] the intermolecular deuterium isotope effect was determined by comparing the quantum yields of **1** and **3**. In this context, intramolecular (product distribution from **2**) and intermolecular (kinetic competitive experiments between **1** and **4** and **1** and **5**) selectivity studies were also performed.

RESULTS AND DISCUSSION

The TiO$_2$ colloidal solution in CH$_3$CN (0.08 g dm^{-3}) was prepared from titanium(IV) 2-propoxide[7b] (see Experimental); in Fig. 1, as an example, the UV–visible absorption spectrum in the presence of **1** is reported.

The products and the yields from the photo-oxidation of compounds **1** and **4–6**, sensitized by TiO$_2$ as colloid (entries 1–4) and as powder (entries 5–8) in aerated CH$_3$CN, are reported in Table 1. In both media, the corresponding aldehyde is the product from **1** and **6**;
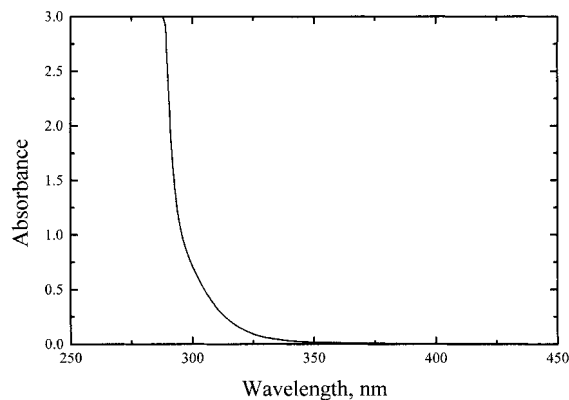

Figure 1. Absorption spectrum of a colloidal dispersion of TiO$_2$ in CH$_3$CN (0.08 g dm^{-3}) containing 4-methoxybenzyl alcohol (**1**) (10^{-2} M)

Scheme 1:

$$\text{TiO}_2 \longrightarrow \text{TiO}_2\ (h^+, e^-)$$

$$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$$

$$\text{ArCH}_2\text{OH} \xrightarrow{h^+} [\text{ArCH}_2\text{OH}]^{+\cdot} \xrightarrow{-H^+} \text{Ar}\dot{\text{C}}\text{HOH}$$

$$\text{ArCHO} \xleftarrow{-H^+} \text{Ar}\overset{+}{\text{C}}\text{HOH} \xleftarrow{-e^-}$$

Scheme 1

Table 1. Colloidal $TiO_2{}^a$ photosensitized oxidation of **1** and **4–6** in aerated CH_3CN

|				Products(%)[b]	
Entry	Substrate	Time (h)	Unreacted substrate(%)[b]	ArCHO	$ArCOCH_3$
1	**1**	6	62	33	
2	**4**	6	81		12
3	**5**	6	97	—	
4	**6**	6	78	13	
5[c]	**1**	1	33	59	
6[c]	**4**	1	60		38
7[c]	**5**	1	96	—	
8[c]	**6**	1	72	25	

[a] 0.08 g dm^{-3}.
[b] With respect to the starting material.
[c] TiO_2 as powder, 6.3 g dm^{-3}.

acetophenone is obtained from **4** and no products are obtained from **5**. The results obtained have been discussed in the light of the mechanism reported in Scheme 2. It can be noted that the relative reactivity (**1** >**6** and **1** > **4** ≫ **5**) of the considered substrates in the presence of TiO_2 as colloid is similar to that observed with TiO_2 as powder; this behaviour suggests that changes in particle size do not significantly influence the relative photochemical reactivity towards the considered organic substrates. In addition, product conversion with the colloidal semiconductor is less than that with the powder, probably because much less semiconductor (~100 times) is used in the first case (the maximum amount compatible with a transparent solution).
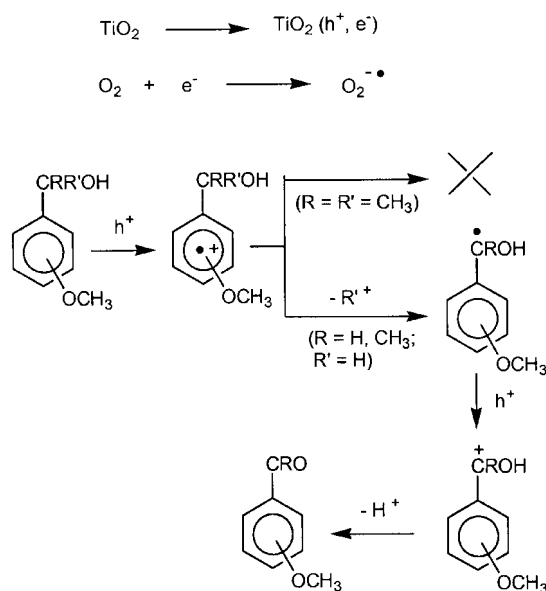
Quantum yield determinations

In the TiO_2-sensitized photo-oxidation processes the substrate must be preadsorbed at the semiconductor surface before the reaction.[1] The quantum yield kinetic data could therefore be treated according to a Langmuir–Hinshelwood-type equation.[7c,g] In other words, the quantum yield should be dependent on the association established between the semiconductor and the electron donor, D:

$$TiO_2 + D \rightleftharpoons TiO_2 \cdots D \qquad (1)$$
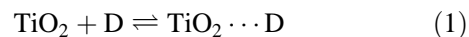
The association constant under irradiation (K_D) [It has been reported that the value of K_D determined through this treatment (under irradiation) is different from that obtained directly from adsorption measurements (in the dark)[9]] is expressed by

$$K_D = \frac{\{TiO_2 \cdots D\}}{\{TiO_2\}\{D\}} \qquad (2)$$

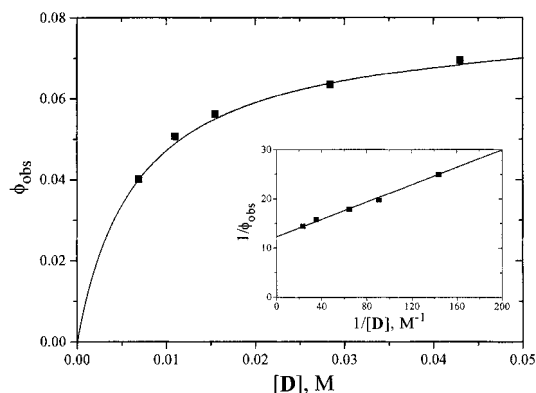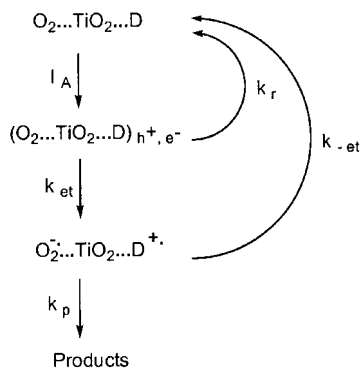where $\{TiO_2 \cdots D\}$ and $\{TiO_2\}$ represent the number of

Scheme 2

Figure 2. Dependence on [D] of the observed quantum yield (ϕ_{obs}) relative to the photo-oxidation of D [4-methoxybenzyl alcohol (**1**)] sensitized by colloidal TiO_2 in aerated CH_3CN. The inset shows the $1/\phi_{obs}$ vs $1/[D]$ dependence

Scheme 3

sites that are occupied and free, respectively, on the semiconductor.

It is reasonable to assume[6c,g] that the oxidation of D occurs only on the adsorbed substrate, $TiO_2 \cdots D$, with a true quantum yield ϕ_0 and that the extinction coefficients of this complex and of TiO_2 are the same at the same excitation wavelength. Therefore, it is possible to relate the observed quantum yield (ϕ_{obs}) to the substrate concentration:

$$\phi_{obs} = \phi_0\theta = \phi_0\frac{K_D[D]}{1 + K_D[D]} \tag{3}$$

where θ is the fraction of occupied sites on the semiconductor. In line with the typical behaviour of absorption pre-equilibrium-dependent kinetics, the plot of ϕ_{obs} *vs* [D] has a curved shape as shown in Fig. 2 (example relative to alcohol **1**).

The equation,

$$\frac{1}{\phi_{obs}} = \frac{1}{\phi_0} + \frac{1}{\phi_0K_D}\frac{1}{[D]} \tag{4}$$

the inverse of Eqn. (3), shows a linear correlation between $1/\phi_{obs}$ and $1/[D]$, where the corresponding plot (inset in Fig. 2) is a straight line. From the plot it is therefore possible to evaluate ϕ_0 and K_D from the intercept and the intercept/slope ratio, respectively.

The ϕ_0 values for the different substrates can be discussed in the light of the suggested reaction mechanism (see Scheme 2) according to the kinetic pattern shown in Scheme 3.

The formalism $TiO_2 \cdots D$ in Eqn. (1) has been substituted by $O_2 \cdots TiO_2 \cdots D$ because the experiments were carried out in atmospheric air and it can be assumed that the amount of adsorbed oxygen on the semiconductor surface is high and nearly constant. The hole and the electron, generated by the light absorption (I_A), can recombine (k_r) or react with donor to give $D^{+\cdot}$ and with O_2 to yield $O_2^{-\cdot}$, respectively (k_{et}). The radical cation formed, $D^{+\cdot}$, should give D again through a back electron

transfer process with $O_2^{-\cdot}$ (k_{-et}) or evolve into the corresponding final products (k_p).

The true quantum yield, ϕ_0, defined as the ratio between the reaction and the photon absorption rates, can be expressed as

$$\phi_0 = \frac{k_p\{O_2^{-\cdot}\cdots TiO_2\cdots D^{+\cdot}\}}{I_A} \tag{5}$$

where $\{O_2^{-\cdot}\cdots TiO_2\cdots D^{+\cdot}\}$ is the number of sites undergoing the electron-transfer process.

Assuming a steady-state approximation for both $\{O_2^{-\cdot}\cdots TiO_2\cdots D^{+\cdot}\}$ and $\{(O_2\cdots TiO_2\cdots D)_{h+,e-}\}$, the following two equations:

$$I_A = k_r\{(O_2\cdots TiO_2\cdots D)_{h+,e-}\} +$$
$$k_{et}\{(O_2\cdots TiO_2\cdots D)_{h+,e-}\} \tag{6}$$

$$k_{et}\{(O_2\cdots TiO_2\cdots D)_{h+,e-}\} =$$
$$(k_{-et} + k_p)\{O_2^{-\cdot}\cdots TiO_2\cdots D^{+\cdot}\} \tag{7}$$

are obtained, from which the ϕ_0 expression, as a function of the different rate constants, can be derived:

$$\phi_0 = \frac{k_pk_{et}}{(k_{-et} + k_p)(k_r + k_{et})} \tag{8}$$

In Table 2, the ϕ_0 and K_D values of compounds **1, 3, 4** and **6** are reported [quantum yield determinations were carried out at low substrate conversion ($\leq 5\%$) as the primary oxidation products (i) can absorb the incident light and/or (ii) can be further oxidized; at these conversions the material recovery is always quantitative (see Experimental) and, therefore, the quantum yield based on the unreacted substrate is equal to that referred to the obtained product (aldehyde or ketone); to minimize the experimental error we preferred to determine ϕ_{obs} from the product conversion]. For all the substrates considered, the ϕ_0 values are much lower than unity, which is common in colloidal TiO_2-sensitized photo-oxidation reactions.[7a,f] This probably occurs because (i) a large fraction of the photogenerated h^+ and e^- in the TiO_2 colloid are lost in the very exothermic recombination process $(k_r)^{1d}$ and (ii) the back electron-transfer process (k_{-et}) is usually very fast[10] (both processes are nearly diffusion controlled). Therefore, assuming that k_{et} and k_p are negligible in comparison with k_r and k_{-et}, respectively, Eqn. (8) could be simplified to give.

$$\phi_0 = \frac{k_pk_{et}}{k_{-et}k_r} \tag{9}$$

In line with this equation, the lower true quantum yield value observed for the 3-methoxy (**6**) with respect to the 4-methoxy derivative (**1**) (see Table 2) should be ascribed

Table 2. True quantum yields (ϕ_0) and association constants under irradiation (K_D) determined in colloidal TiO_2 photo-sensitized oxidation of **1**, **3**, **4** and **6** in aerated CH_3CN

Substrate	ϕ_0	K_D	E_p (vs SCE)
1	0.079 ($\pm$0.003)	148 ($\pm$10)	1.52
3	0.044 ($\pm$0.002)	154 ($\pm$18)	
4	0.049 ($\pm$0.002)	105 ($\pm$9)	1.55
6	0.034 ($\pm$0.002)	142 ($\pm$14)	1.66

to a difference in either the k_{et}, and/or k_{-et} and/or k_p values of the two compounds, since k_r is independent of the substrate. We suggest that the k_{et} value is the major factor responsible for the higher ϕ_0 value of **1** with respect to **6**; this rate constant is higher in **1** which has a lower reduction potential (see E_p in Table 2). The radical cation deprotonation step (k_p) may also play a role since the C—H bond-breaking rate measurements from $\mathbf{1^{+\cdot}}$ and $\mathbf{6^{+\cdot}}$ (generated in flash photolysis experiments by the photo-oxidation of the corresponding alcohols with 9,10-dicyanoanthracene–biphenyl in the presence of 2,6-lutidine in CH_3CN) show that $k_p(\mathbf{1^{+\cdot}})$ (4.0×10^7 M^{-1} s^{-1})[11] is *ca* twice $k_p(\mathbf{6^{+\cdot}})$ (1.8×10^7 M^{-1} s^{-1}) (unpublished results). On the other hand, k_{-et} should not play a significant role in this ϕ_0 change because, if it did, ϕ_0 should increase less for **1** than for **6** [see Eqn. (9)]; in fact, it has been suggested that the highly exothermic back electron-transfer reactions are in the Marcus 'inverted region' where the electron-transfer rates decrease with increasing exothermicity[10] [that is, $k_{-et}(\mathbf{1}) < k_{-et}(\mathbf{6})$ when $E_p(\mathbf{1}) < E_p(\mathbf{6})$]. It must be noted that the reliability of our kinetic treatment is evidenced by the fact that the $\phi_0(\mathbf{1})/\phi_0(\mathbf{6})$ ratio (from Table 2) is identical with the relative rate ($k_{rel} = 2.3$) obtained from the competitive experiment involving the two substrates.

The lower reactivity observed for **4** with respect to **1** cannot be ascribed to different rates in the electron-transfer steps (k_{et} and k_{-et}) since the E_p values are comparable (see Table 2). Therefore, this behaviour should be exclusively due to differences in the deprotonation rate (k_p); it is known[11] that the deprotonation rate ratio, $k_p(\mathbf{1^{+\cdot}})/k_p(\mathbf{4^{+\cdot}})$ [obtained by pulse radiolysis experiments where the $\mathbf{1^{+\cdot}}$ and $\mathbf{4^{+\cdot}}$ decay rates (k_p) were measured in sodium peroxodisulfate aqueous solutions], is nearly 2. This behaviour can be explained on the basis that it is more difficult to satisfy the stereoelectronic requirements for the deprotonation reaction in the α-methyl-substituted radical cation ($\mathbf{4^{+\cdot}}$) than in the unsubstituted intermediate ($\mathbf{1^{+\cdot}}$).[12]

The association constants (K_D in Table 2), derived from quantum yield measurements, show that, under irradiation, the physical interaction between alcohol **4** and the TiO_2 surface is weaker than that of **1** [$K_D(\mathbf{1})/K_D(\mathbf{4}) \approx 1.4$], while **1** and **6** are similarly adsorbed [$K_D(\mathbf{1})/K_D(\mathbf{6}) \approx 1.0$]. These results confirm that the OH group is preferentially adsorbed on the TiO_2 surface;[1c, 2f] prob-

ably, when an α-hydrogen is substituted by a larger group (CH_3), a steric hindrance to adsorption should be observed, due to the proximity of the substituent to the OH group, whereas a change in the ring substituent position (far away from this group) should have no effect on K_D.

To verify if the C_α—H is the deprotonation site of the radical cation in our medium and to evaluate the influence of the deprotonation process rate on ϕ_0, the true quantum yield of the α,α-dideutero derivative **3** was measured (Table 2) and the deuterium isotope effect ($k_H/k_D = 1.8$) was determined. This value was obtained from the ϕ_0 ratio of **1** and **3** and corresponds, in Eqn. (9), to the deprotonation rate (k_p) ratio of the two compounds since the alcohols should have similar k_{et} and k_{-et} values. The k_H/k_D value is in line with the previously observed primary isotope effects reported in the literature[8,13] for reactions where a kinetically significant C_α—H bond-breaking (through a reagent-like transition state) follows the electron-transfer step. In contrast, it has been reported that, when the radical cations $\mathbf{1^{+\cdot}}$ and $\mathbf{3^{+\cdot}}$ (generated in aqueous NaOH) undergo a deprotonation process involving the OH group, the k_H/k_D value is 1.0, which indicates that the C_α—H proton loss occurs in a fast subsequent step.[8]

The intramolecular (primary) deuterium isotope effect was also measured from the molar ratio of α-deutero-4-methoxybenzaldehyde (**7**) and 4-methoxybenzaldehyde (**8**) formed in the TiO_2-sensitized photo-oxidation of **2**. The value obtained ($k_H/k_D = 1.6$) is similar to the value of the intermolecular isotope effect (see above); this allows one to hypothesize that the C_α—H deprotonation step, following the electron transfer, is the rate-determining step. Moreover, this result attests that the deprotonation is slower than the back electron transfer ($k_p < k_{-et}$), as supposed above on going from Eqn. (8) to Eqn. (9).

To confirm that the C_α—H bond breaking plays an essential role in the process, competitive kinetic experiments (comparing alcohols **4** and **5** with **1**) were carried out. The fact that the observed rate ratio between alcohol **1** and alcohol **5** (without benzylic hydrogens) is high ($k_{rel} > 150$) supports the contention that the α-OH radical cations undergo C_α—H deprotonation. Otherwise, this very high reactivity gap cannot be justified by a very different electron-transfer rate since the E_p value of **1** (1.52 V) is only slightly lower than that of **5** (1.59 V). Moreover, this gap cannot be attributed to steric hindrance of the two α-methyl groups to the semiconductor surface adsorption of **5**, taking into account that alcohol **4**, with one α-methyl, reacts only slightly slower than the side-chain unsubstituted alcohol **1** ($k_{rel} = 3.0$).

CONCLUSIONS

The quantum yields (ϕ_{obs}) relative to the photo-oxidation of benzyl alcohols sensitized by colloidal TiO_2 in CH_3CN

confirm the previously hypothesized mechanism of TiO_2 powder in the same solvent.

It is possible to separate and evaluate the effects of the substrate structure on intrinsic reactivity (ϕ_o) and on the extent of adsorption at the semiconductor surface under irradiation (K_D). In particular, it has been shown that the different ϕ_o values observed when the ring substituent position is changed (inducing a different E_p value) depend mainly on the electron-transfer rate constant, whereas when an α-alkyl group is introduced (the E_p value is nearly unchanged), the ϕ_o change depends on the deprotonation rate constant. According to the preferential absorption of the OH group on the semiconductor, the K_D value decreases only when the substituent is introduced in the side-chain, next to the absorption site.

Finally, both the inter-and intramolecular deuterium isotope effects confirm that the deprotonation step involves a kinetically significant C_α—H bond breaking following the electron-transfer step.

EXPERIMENTAL

^{1}H NMR spectra were measured on a Bruker AC 200 (200 MHz) spectrometer, from solutions in $CDCl_3$ with TMS as internal standard. GC–MS analyses were performed on a Hewlett-Packard (HP) Model 6890A gas chromatograph (HP-5-MS capillary column, 30 m) coupled with an HP 5973 mass-selective detector (70 eV). GC analyses were carried out on an HP 5890 gas chromatograph using an HP Innovax capillary column (15 m). UV–visible spectra were measured on a HP 8451A diode-array spectrophotometer. E_p values were obtained with an AMEL 552 potentiostat controlled by a programmable AMEL 568 function generator (cyclic voltammetry at 100 mV s^{-1}, 1 mm diameter platinum disc anode) in CH_3CN–$LiClO_4$ (0.1 M).

Materials. TiO_2 (anatase, Aldrich, 99.9%, dried at 110°C), titanium (IV) 2-propoxide, 2-propanol, CH_3CN (HPLC grade, distilled from CaH_2, water content 0.02% from Karl Fischer coulometry), 4-methoxybenzyl alcohol (**1**), 4-methoxy-α-methylbenzyl alcohol (**4**) and 3-methoxybenzyl alcohol (**6**) were commercial samples. α-Deutero-4-methoxybenzyl alcohol (**2**) was prepared by reduction of 4-methoxybenzaldehyde (**8**) with $LiAlD_4$ in anhydrous diethyl ether and chromatographed on silica gel [light petroleum–diethyl ether (1:1, w/w) as eluent] [δ_H 7.28 (2H, d, $J = 9$Hz, ArH), 6.88 (2H, d, $J = 9$Hz, ArH), 4.56 (1H, t, $J = 1.5$Hz, CHD), 3.82 (3H, s, OCH_3); m/z 139 (M$^+$, 100%), 138, 137, 135, 122, 110, 109, 107, 95, 78, 77, 66, 51]. α,α-Dideutero-4-methoxybenzyl alcohol (**3**) was obtained^{14} by reduction of 4-methoxybenzoic acid with $LiAlD_4$ in anhydrous tetrahydrofuran and chromatographed on silica gel [light petroleum–diethyl ether (1:1, w/w) as eluent] [δ_H^{14} 7.28 (2H, d, $J = 9$Hz, ArH), 6.88 (2H, d, $J = 9$Hz, ArH), 3.82 (3H, s,

OCH_3); m/z 140 (M$^+$, 100%), 139, 138, 137, 135, 123, 110, 95, 78, 66, 64, 63, 51]. α,α-Dimethyl-4-methoxybenzyl alcohol (**5**) was prepared by reaction of 4-methoxyphenylmagnesium bromide with acetone in anhydrous tetrahydrofuran and purified by chromatography on a silica gel column [light petroleum–ethyl acetate (1:2, w/w) as eluent] [δ_H^{15} 7.41 (2H, d, $J = 9$ Hz, ArH), 6.86 (2H, d, $J = 9$ Hz, ArH), 3.79 (3H, s, OCH_3), 1.56 (6H, s, CH_3); m/z 166 (M$^+$), 151 (100%), 135, 121, 109, 91, 77, 65, 59, 51, 43].

Colloidal TiO_2. A 10% solution (1 ml) of titanium(IV) 2-propoxide in 2-propanol was prepared and stored (for several days) in a nitrogen atmosphere (dry-box). The solution (50 μl) was added to CH_3CN (20 ml) again under nitrogen (dry-box) with magnetic stirring.

α-Deutero-4-methoxybenzaldehyde (7). A solution of α,α-dideutero-4-methoxybenzyl alcohol (**3**) (210 mg) in CH_3CN (100 ml), containing TiO_2 (600 mg) and Ag_2SO_4 (570 mg), was reacted and worked up as reported below. The crude was chromatographed on a silica gel column [light petroleum–diethyl ether (9:1, w/w) as eluent] [δ_H^{16} 7.85 (2H, d, $J = 9$ Hz, ArH), 7.01 (2H, d, $J = 9$ Hz, ArH), 3.89 (3H, s, OCH_3); m/z 137 (M$^+$), 135 (100%), 107, 92, 77, 66, 51, 50].

Photochemical oxidation sensitized by TiO_2. The reactions were carried out by external irradiation (Helios Italquartz 500 W high-pressure mercury lamp, Pyrex filter) of a TiO_2 colloidal solution or a TiO_2 powder suspension in 20 ml of CH_3CN (0.08 or 6.3 g dm^{-3}, respectively) containing the substrate (0.23 mmol) in a cylindrical flask provided with a water cooling jacket and intensive condenser. After irradiation, the reaction mixture was poured into NaCl-saturated water (after double paper filtration in the case of TiO_2 powder) and extracted with diethyl ether. The analysis of the reaction products and of the unreacted substrate was performed by ^{1}H NMR spectroscopy and/or by GC of the reaction mixture in the presence of an internal standard (bibenzyl). The analysis of the products [α-deutero-4-methoxybenzaldehyde (**7**) and 4-methoxybenzaldehyde (**8**)] obtained from **2** was carried out by GC–MS utilizing bibenzyl as an internal standard; the peaks considered are at m/z 91 (relative to bibenzyl), 136 (relative to **8**) and 137 (relative to **7** corrected for the M + 1 contribution of **8**).

Reaction products. The crude reaction product was chromatographed on silica gel, eluting with light petroleum, light petroleum–diethyl ether (from 9:1 to 1:1, w/w) and diethyl ether. The structure of isolated products was attributed by spectroscopic and GC comparison with authentic specimens [3-methoxybenzaldehyde, 4-methoxybenzaldehyde (**8**) and 4-methoxyacetophenone were commercial samples, α-deutero-4-

methoxybenzaldehyde (**7**) was prepared as described above].

Quantum yield determinations. A spectrophotometric cuvette (optical path = 4.00 cm) containing a suitable substrate [(5–50) × 10^{-3} M] in a colloidal solution of TiO_2 in CH_3CN was placed in a thermostated (25 °C) support placed on a linear optical bench equipped with a Osram high-pressure Hg lamp and a Balzers interference filter ($\lambda = 313$ nm, $\Delta\lambda_{1/2} = 5$ nm). The mixture was irradiated, under magnetic stirring, until ≤5% substrate conversion. The product formation was determined by GC analysis (bibenzyl as an internal standard). Light flux was measured by ferrioxalate actinometry (9.1×10^{-9} einstein s^{-1}). Only the experiments where the material recovery (substrate + aldehyde or ketone) was quantitative ($100 \pm 2\%$) were considered.

Competitive experiments. These kinetic experiments were performed by irradiation (Applied Photophysics multilamp photochemical reactor, $\lambda = 320 \pm 30$ nm) of a TiO_2 colloidal solution containing equimolar amounts of two alcohols (**1** and **4** or **1** and **5**, 0.15 mmol each) placed in a thermostated (25 °C) cylindrical flask. The amounts of the products obtained were determined by GC analysis with respect to an internal standard (bibenzyl).

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