

True quantum yields and adsorption constants as tools for a mechanistic study of the TiO₂-sensitized photooxidation of benzylic derivatives

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Abstract

The quantum yields (Φ) of the colloidal TiO₂-sensitized photooxidation of 4- (**1**) and 3-methoxybenzyl alcohol (**2**) together with 4-methoxybenzyltrimethyl- (**3**) and 4-methoxybenzyltriisopropylsilane (**4**) were determined in CH₃CN, in the presence of HClO₄ for **3** and **4**. The true quantum yields (Φ_0) of **1**, **2** and **3**, obtained from a Langmuir–Hinshelwood isotherm treatment of Φ at different substrate concentrations, are linearly correlated with $I_A^{-1/2}$, where I_A is the light intensity. According to the previously suggested mechanisms for alcohols and silanes, a kinetic scheme that justifies this correlation is suggested. It is shown that the ratio of the slopes (from the Φ_0 versus $I_A^{-1/2}$ plots) for **1** and **2** is equal to the Φ_0^1/Φ_0^2 ratio at any I_A ; this ratio depends on the rate constants in the kinetic scheme, in this case principally on the electron transfer constant, k_{et} . On the contrary, the Φ_0^3/Φ_0^4 ratio depends on k_p , the cation radical desilylation rate constant, confirming a steric hindrance to nucleophilic assistance in the C–Si fragmentation by the bulky isopropyl group in the SiR₃ moiety. Differently from Φ_0 , the adsorption constants on the semiconductor under irradiation (K_D , obtained from the above isotherm treatment) are independent of I_A . Moreover, as $K_D^1 = K_D^2$ and $K_D^3 = K_D^4$, the structural modifications within the two alcohols and within the two silanes should be far enough away from the adsorption site. For all the substrates, K (the dark adsorption constant) is five times greater than K_D , showing that this change does not depend on the substrate structure but is the result of different experimental conditions. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Mechanistic investigations on the primary oxidation steps related to the TiO₂-sensitized photooxidation of organic compounds could provide useful information about the degradation pathways involved in the mineralization of organic pollutants in waste water [1].

A simplified starting approach involves studying the process in CH₃CN [2] that, unlike water, is an inert solvent, under the considered oxidative reaction conditions. However, as we have previously shown, at least with alkylaromatic substrates, the same primary chemical events, subsequent to the photoinduced production of the hole (h⁺), should occur in both solvents [3].

In recent years, many mechanistic details have been collected about this TiO₂-sensitized oxidative process starting with benzylic derivatives (arenes, alcohols, ethers, silanes, sulphides, . . .) in CH₃CN [4]. The semiconductor has been used as suspended powder, photoanode and transparent colloid in the presence of oxygen, Ag⁺ and Li⁺ as sacrificial electron acceptors.

Among the different approaches to the reaction mechanism, quantum yield measurements relative to the photooxidation of benzyl alcohols to benzaldehydes, sensitized by colloidal TiO₂ in aerated CH₃CN, [4g] provided further details about the kinetically significant steps of the previously suggested mechanism [4e,f,i].

In particular, treating the observed quantum yield values (Φ) at various initial substrate concentrations with the Langmuir–Hinshelwood adsorption isotherm, the Φ_0 (the true quantum yield related to the intrinsic reactivity) and the K_D (the adsorption constant under irradiation) of some methoxybenzyl alcohols were determined at a constant value of adsorbed light intensity ($I_A = 9.1 \times 10^{-9}$ einstein s⁻¹)

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[4g]. This treatment implies that prior to the reaction the substrate to be photooxidized in the presence of TiO_2 must be adsorbed at the semiconductor surface. The observed quantum yields should therefore be dependent on the association established (Eq. (1)) between the semiconductor and the substrate (D, electron donor). The adsorption constant (K_D in Eq. (2)) is expressed as a function of $\{\text{TiO}_2 \dots \text{D}\}$, the number of sites that are occupied by D, and $\{\text{TiO}_2\}$, the sites that are free on the semiconductor.



$$K_D = \frac{\{\text{TiO}_2 \dots \text{D}\}}{\{\text{TiO}_2\} [\text{D}]} \quad (2)$$

The Langmuir–Hinshelwood treatment allows Eq. (3) to be obtained, where θ is the fraction of occupied sites on the semiconductor and Φ_0 is the true quantum yield.

$$\Phi = \Phi_0 \theta = \Phi_0 \frac{K_D [\text{D}]}{1 + K_D [\text{D}]} \quad (3)$$

In Eq. (4), the inverse of Eq. (3), a linear correlation between $1/\Phi$ and $1/[\text{D}]$ can be observed. From the corresponding plot, it is possible to evaluate Φ_0 and K_D from the intercept and the intercept/slope ratio, respectively.

$$\frac{1}{\Phi} = \frac{1}{\Phi_0} + \frac{1}{\Phi_0 K_D} \frac{1}{[\text{D}]} \quad (4)$$

In this paper we report a more detailed investigation that considers 4- (1) and 3-methoxybenzyl alcohol (2) at different I_A values (from 1.6 to 26×10^{-9} einstein s^{-1}) to evaluate the dependence of Φ_0 and K_D on light intensity. The photooxidation of other benzyl derivatives such as 4-methoxybenzyltrimethyl (3) and 4-methoxybenzyltriisopropylsilane (4) with colloidal TiO_2 was also studied to test the dependence of different structural effects on the reaction rate and substrate adsorption, under irradiation (K_D) and in the dark (K).

2. Results and discussion

2.1. Benzylic alcohols

The results of this study show that the Φ_0 values for photooxidation of 4- (1) and 3-methoxybenzyl alcohol (2) sensitized by colloidal TiO_2 in aerated CH_3CN are almost constant at higher I_A values while, at lower I_A values, this parameter significantly increases (see for example Fig. 1 relative to 4-methoxybenzyl alcohol). In light of the previously suggested mechanism [4e,f,g,i] (Scheme 1), we suggest a kinetic pattern that could justify the dependence of Φ_0 on I_A (Scheme 2).

Under irradiation (I_A), the semiconductor with the preadsorbed substrate, designated as $\text{TiO}_2 \dots \text{D}$, yields an equal amount of photogenerated holes, $(\text{TiO}_2 \dots \text{D})_{\text{h}^+}$, and electrons, $(\text{TiO}_2 \dots \text{D})_{\text{e}^-}$. The holes can either recombine with

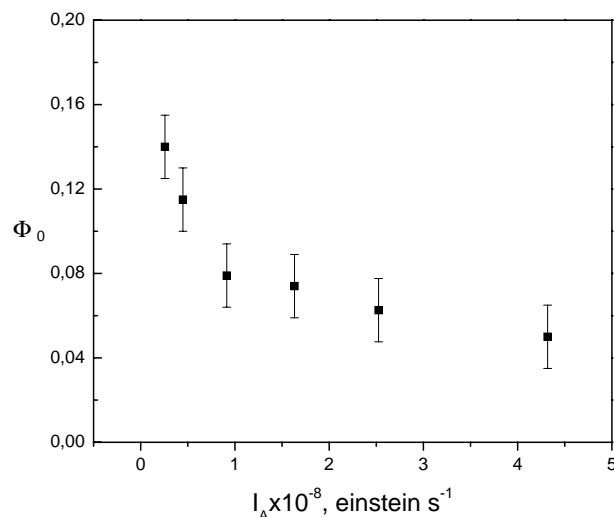
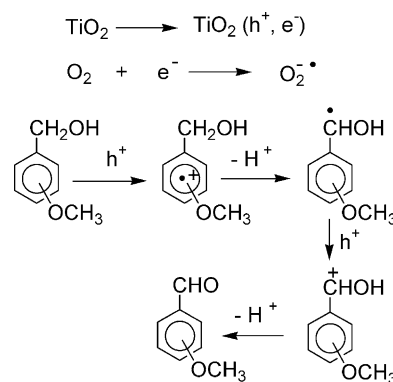
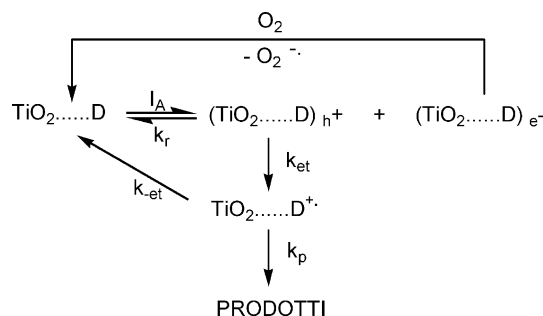


Fig. 1. True quantum yield of 4-methoxybenzyl alcohol photooxidation sensitized by TiO_2 as a function of light intensity.



Scheme 1.

the photogenerated electrons in the conduction band (k_r) or oxidize the alcohol to the corresponding cation radical (k_{et}). This intermediate either undergoes a fragmentation process (k_p , deprotonation in the case of alcohols) or it undergoes a back electron transfer process ($k_{-\text{et}}$) by reacting with electrons present in the valence band. The true quantum yield, Φ_0 , can be defined as the ratio between the reaction rate and the photon adsorption rate (Eq. (5)), where the symbol $\text{D}^{+\bullet}$



Scheme 2.

has been used for $\text{TiO}_2 \cdots \text{D}^{+\bullet}$, for simplicity purposes.

$$\Phi_0 = \frac{k_p \{D^{+\bullet}\}}{I_A} \quad (5)$$

Assuming a steady state approximation for this intermediate and for $(\text{TiO}_2 \cdots \text{D})_{h^+}$, indicated as h^+ , the Eqs. (6) and (7) are obtained.

$$k_{et}\{h^+\} = k_{-et}\{D^{+\bullet}\} + k_p\{D^{+\bullet}\} \quad (6)$$

$$I_A = k_r\{h^+\}^2 + k_{et}\{h^+\} \quad (7)$$

The value of $\{h^+\}$ and $\{D^{+\bullet}\}$ can be obtained from the simplified Eq. (7) ($I_A = k_r\{h^+\}^2$) and the simplified Eq. (6) ($k_{et}\{h^+\} = k_{-et}\{D^{+\bullet}\}$), respectively; these simplifications should be valid since it can be assumed that $k_{-et} \gg k_p$ in Eq. (6) and $k_r \gg k_{et}$ in Eq. (7) due to the low observed Φ values (see for example the values in Fig. 1). In this way, it is possible to express Φ_0 in Eq. (5) as a function of k_p , k_{et} , k_{-et} , k_r and I_A according to Eq. (8) for which the plot Φ_0 versus $I_A^{-1/2}$ is a straight line with no intercept. This relationship was previously observed for TiO_2 -sensitized photooxidations in aqueous phase [5].

$$\Phi_0 = \frac{k_p k_{et}}{I_A^{1/2} k_{-et} k_r^{1/2}} \quad (8)$$

The plots relative to the photooxidation of **1** and **2** (Fig. 2) show a linear correlation with a different slope. The ratio of the slopes ($= 2.3 \pm 0.3$), corresponding to the ratio of Φ_0 at any I_A , is expressed by Eq. (9) and allows the kinetic constants (k_p , k_{et} and k_{-et}) of the two alcohols to be compared (in the last equation k_r is not present because it is independent from the substrate).

$$\frac{\text{slope}^1}{\text{slope}^2} = \frac{k_p^1 k_{et}^1 / k_{-et}^1}{k_p^2 k_{et}^2 / k_{-et}^2} = \left(\frac{\Phi_0^1}{\Phi_0^2} \right)_{\text{at any } I_A} \quad (9)$$

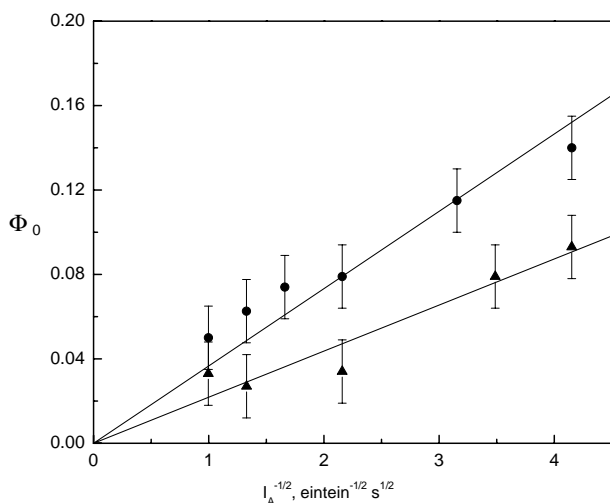
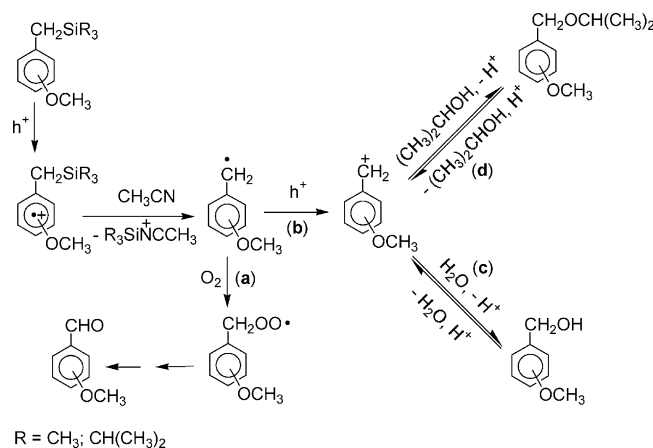


Fig. 2. True quantum yields of 4- (●) and 3-methoxybenzyl alcohol (▲) photooxidation sensitized by TiO_2 as a function of inverse square root of light intensity.



Scheme 3.

It must be noted that the expression of the slope ratio is identical to the expression of the Φ_0 ratio obtained at $I_A = 9.1 \times 10^{-9}$ einstein s^{-1} in a previous paper and, consequently, the obtained value is identical within experimental error [4g]. Therefore, the previously suggested mechanistic interpretation of this ratio remains valid (the reactivity ratio $1/2$ should depend principally on the electron transfer step, k_{et} , according to the different corresponding E_p values) [4g].

Using the $1/\Phi$ versus $1/[D]$ plots, the adsorption constants under irradiation (K_D) for alcohols **1** and **2** were evaluated (see Eq. (4)) at all the considered I_A values; the K_D values are practically constant as the I_A values change and are the same for the two alcohols ($150 \pm 50 \text{ M}^{-1}$ is the average of the values measured at different I_A). The K_D values are identical to those previously reported for the two alcohols at $I_A = 9.1 \times 10^{-9}$ einstein s^{-1} [4g].

2.2. Benzylic silanes

Some mechanistic information was collected previously about the photooxidation reaction sensitized by TiO_2 , as suspended powder or anode, of benzyltrimethylsilanes ($\text{XPhCH}_2\text{Si}(\text{CH}_3)_3$ where $\text{X} = 3\text{-CH}_3\text{O}, 4\text{-CH}_3, 3\text{-CH}_3, 3\text{-Cl}, 4\text{-Cl}, 4\text{-F}, 3\text{-CF}_3$) in CH_3CN [3,4a,i,k,6].

The products and their distribution obtained from the photooxidation of 4-methoxybenzyltrimethyl- (**3**) and 4-methoxybenzyltriisopropylsilane (**4**) sensitized by colloidal TiO_2 in aerated CH_3CN under different experimental conditions are reported in Table 1. The principal product obtained from **3** is the corresponding benzaldehyde accompanied by small amounts of 4-methoxybenzyl alcohol (entry 1). In Scheme 3 the previously suggested mechanism for the TiO_2 (as powder)-sensitized photooxidation to benzaldehyde (path a) is reported [3,4a,i,k,6]. The alcohol, not present as a reaction product in the previously studied silanes, can be easily justified if one takes into account, besides the capture of oxygen (path a), the oxidation of the easily oxidizable 4-methoxybenzyl radical intermediate (path b); the obtained benzylic cation should give the

Table 1

Product yield in the photooxidation of 4-methoxybenzyltrimethyl- (**3**) and 4-methoxybenzyltriisopropylsilane (**4**) sensitized by colloidal TiO₂ in aerated CH₃CN^a

Entry	TiO ₂ (mg ml ⁻¹)	Substrate	Isopropyl alcohol (M)	HClO ₄ (M)	<i>t</i> (h)	Products yield (%) ^b		
						ArCHO	ArCH ₂ OH	ArCH ₂ OCH(CH ₃) ₃
1	0.08	3	3 × 10 ⁻²	–	6	10	<2	–
2	0.4	3	0.15	5 × 10 ⁻⁴	1.5	30	2	<2
3 ^c	0.4	3	0.15	5 × 10 ⁻⁴	3	30	2	<2
4	0.4	4	0.15	5 × 10 ⁻⁴	1.5	15	<2	<2
5 ^d	6.0	3	–	–	3	26	2	–
6 ^d	6.0	4	–	–	3	7	<2	–
7 ^d	6.0	3	0.15	5 × 10 ⁻⁴	1.5	35	14	2
8 ^{d,e}	6.0	3	0.15	5 × 10 ⁻⁴	1.5	33	9	9

^a 500 W high pressure Hg lamp.

^b With respect to starting material.

^c Multilamp photoreactor.

^d TiO₂ as powder.

^e Distilled CH₃CN.

alcohol reacting with water adsorbed at the semiconductor surface (path **c**) [4j,k].

The results relative to the photooxidation of **3** and **4** with colloidal TiO₂ in the presence of HClO₄ (entries 2–4) are also reported in Table 1. This mineral acid must be added in order to perform the Φ measurements because, without it, the optical properties (from UV-Vis spectrum) of the TiO₂ colloidal solution change in the time needed to evaluate this parameter. In effect, in the presence of HClO₄: (i) the colloidal TiO₂ becomes stable enough to perform Φ measurements for longer periods of time; (ii) a transparent colloidal solution can be prepared with a higher amount of TiO₂ and this could enhance the substrate reactivity. Regarding the latter point, it can be observed in Table 1 that the reaction of silane **3** in the absence of acid (TiO₂ amount, 0.08 mg ml⁻¹) gave only a small amount of benzaldehyde (entry 1) after 6 h; on the other hand, in the presence of HClO₄ (TiO₂ amount, 0.4 mg ml⁻¹) **3** yielded, the same product distribution after 1.5 h but in significantly higher yields (entry 2). It must be noted that another product, benzyl isopropyl ether, was present in the acid medium that should be derived from the reaction of the benzylic cation with isopropyl alcohol, used as co-solvent in the colloid preparation (Scheme 3, path **d**). When the reaction was performed with the multilamp photoreactor (the nearly monochromatic apparatus utilized for Φ determination, see Section 3), the same product distribution was obtained although the yield diminished with respect to the irradiation with 500 W lamp (compare entries 2 and 3). The reaction with **4** gave lower yields of the same product distribution as **3** (compare entries 4 and 2 in Table 1).

For the sake of comparison, experiments in the presence of TiO₂ powder which more generally used in photochemical oxidation sensitized by this semiconductor, again showed a higher reactivity of **3** with respect to **4** (see entries 5 and 6). When isopropanol and HClO₄ were added at the same concentration as that in the presence of colloidal TiO₂, the ether was again observed in addition to aldehyde and alco-

hol, (entry 7). Under these latter experimental conditions it was shown that the product distribution remained unchanged in the presence of both atmospheric or bubbled oxygen and whether the reaction mixture was worked up or not. In contrast the ether increased with respect to the alcohol when distilled CH₃CN was used (compare entries 7 and 8). In effect, the distillation should reduce the amount of water with respect to the isopropanol thus disfavoring path **c** with respect to path **d** in Scheme 3.

As previously reported for alcohols, [4g] the Φ values for benzyl silane **3** (in acidic conditions) were obtained by product analysis at a low substrate conversion ($\leq 5\%$). A relationship between Φ_0 and I_A , similar to that depicted in Fig. 1 for alcohols **1** and **2**, is observed and Φ_0 versus $I_A^{-1/2}$ plot is again linear. The kinetic pattern in Scheme 2 should therefore be valid, where k_p is relative to the radical cation desilylation step reported in Scheme 3.

While evaluating the effect of modifying the silane structure on the SiR₃ moiety (R = CH₃ or CH(CH₃)₂) by using Eq. (9), the Φ_0 of silane **4** was also considered.

Unfortunately, the reactivity of this compound was so low that the amounts of products were only measurable at the maximum I_A value ($\Phi_0 = 3.7 \times 10^{-2}$ at $I_A = 2.6 \times 10^{-7}$ einstein s⁻¹) and then it was not possible to verify the Φ_0 versus I_A dependence for this substrate. Nevertheless, as shown above for alcohols, the Φ_0 ratio should be independent of I_A and the $\Phi_0(\mathbf{3})/\Phi_0(\mathbf{4})$ ratio at $I_A = 2.6 \times 10^{-7}$ einstein s⁻¹ (2.2) should be equally significant allowing the effect of the above silane structure modification on the reactivity to be evaluated. In particular, the lower Φ_0 value relative to the triisopropylsilyl derivative **4** should be ascribed (Eq. (9)) to a difference in k_p , since **3** and **4** have similar E_p values (1.22 and 1.27 V versus SCE, respectively), and consequently they should have similar k_{et} and k_{-et} values. This behavior is expected since, in line with a previous suggestion, [7] the isopropyl group, which is bulkier than methyl, should exert a steric hindrance on the nucleophilic assistance of the solvent (CH₃CN) in the C–Si

fragmentation process of the radical cation intermediate which is a kinetically significant process (Scheme 3).

From the $1/\Phi$ versus $1/[D]$ plots (Eq. (4)) the K_D values under irradiation were also obtained for **3** (at all the considered I_A values) and **4** (at the highest I_A value, where Φ was measurable, see above). The K_D values for **3** at different I_A values remained unchanged within the experimental error with an average value of $110 \pm 50 \text{ M}^{-1}$, which is the same, within the experimental error, as for **4** ($160 \pm 50 \text{ M}^{-1}$). Both substrates, adsorbed on the semiconductor through the π system, [4j,k] probably assume a conformation where the SiR_3 group is far enough away from the TiO_2 surface (in this case a bulky R as $\text{CH}(\text{CH}_3)_2$ does not exert a steric hindrance on the adsorption).

As previously reported for benzyl alcohols **1** and **2**, [4k] the adsorption constants at the TiO_2 surface in the dark (K) were also determined by a Hiemans–Langmuir treatment for silanes **3** and **4** in CH_3CN , but in this case, it was in the presence of HClO_4 (the same medium used to determine Φ_0 and K_D). As observed above for K_D , the K values of **3** and **4** are identical ($520 \pm 140 \text{ M}^{-1}$), confirming the hypotheses on adsorption suggested above for K_D . As previously reported for alcohols **1** and **2**, [4k] K is nearly five times higher than K_D ; this fact confirms the previous hypothesis [4k] that this change is independent of the substrate structure and can be due to the different experimental conditions with TiO_2 as powder or as colloid (the competitive adsorption of isopropanol, the co-solvent used in the colloid preparation, probably lowers the adsorption constant).

It must be noted that the contribution of intrinsic reactivity (Φ_0) and/or of K_D to the increase of the reaction rate (Φ) observed in the presence of HClO_4 with respect to the non-acid medium cannot be evaluated because it is not possible to perform quantum yields in the absence of acid. However, the measurement of 'dark' adsorption constants (K) of **3** and **4** in the two media allows at least the role of adsorption on reactivity to be evaluated. In effect, the K values of **3** and **4** ($520 \pm 140 \text{ M}^{-1}$) in the acid medium are higher than the K values in the absence of acid; the latter are too low ($K < 100 \text{ M}^{-1}$) to be evaluated by the reported experimental method [4k]. This observation shows that a contribution to the reactivity (Φ) enhancement observed in acid medium should be given by a higher adsorption extent in the presence of HClO_4 . A suitable explanation of the adsorption increase in the latter medium could be the smaller size of semiconductor particles as observed by light scattering measurements (the diameter of the particles dispersed in CH_3CN was nearly 30 nm while in the same medium, but in the presence of HClO_4 , this measurement was not possible and so the diameter was $< 2 \text{ nm}$).

3. Experimental

^1H NMR spectra were run on a Bruker AC 200 (200 MHz) spectrometer, with solutions in CDCl_3 with TMS as inter-

nal standard. GC-MS analyses were performed on a Hewlett Packard 6890A gas-chromatograph (HP-Innovax capillary column, 15 m) coupled with an MSD-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-Vis spectra were measured on an 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 $\text{CH}_3\text{CN-LiClO}_4$ (0.1 M).

3.1. Materials

TiO_2 (anatase, Aldrich-99.9% or P-25, Degussa-99.5%, both dried at 110°C), titanium(IV) 2-propoxide, 2-propanol, CH_3CN (HPLC grade, was used as such or distilled from CaH_2 , water content 0.02% from Karl–Fischer coulometry), 4-methoxybenzyl alcohol (**1**) and 3-methoxybenzyl alcohol (**2**) and 4-methoxybenzaldehyde were commercial samples. 4-Methoxybenzyltrimethylsilane (**3**), [4i] 4-methoxybenzyltriisopropylsilane (**4**) [4i] and isopropyl 4-methoxybenzyl ether [8] were prepared as previously described.

3.2. Colloidal TiO_2

A 10% solution (1 ml) of titanium(IV) 2-propoxide in 2-propanol was prepared and stored under a nitrogen atmosphere (dry-box). The solution (60 μl) was added to distilled CH_3CN (20 ml) again under nitrogen (dry-box) with magnetic stirring (0.08 g dm^{-3}); to prepare the colloid in acid medium the initial solution (250 μl) was added to a mixture of HClO_4 , 10 M (1 μl) and CH_3CN (20 ml).

3.3. Photochemical oxidation sensitized by TiO_2

As previously described for benzyl alcohols, [4g] the reactions with benzylalkylsilanes were carried out by external irradiation (Helios Italquartz 500 W high-pressure mercury lamp, Pyrex filter or Applied Photophysics Multilamp photochemical reactor; 12 lamps at $\lambda = 320 \pm 20 \text{ nm}$) of a TiO_2 colloidal solution (20 ml) or a powder suspension in 20 ml of CH_3CN (6.3 g dm^{-3}) containing 0.23 mmol of the substrate (with silanes, also in the presence of HClO_4 , $5 \times 10^{-4} \text{ M}$) in a cylindrical flask provided with a water cooling jacket and intensive condenser. After irradiation in the presence of oxygen either bubbled or atmospheric, the reaction mixture (after double paper filtration in the case of TiO_2 powder) was analyzed by GC (in the presence of bibenzyl as an internal standard), directly or after treatment with NaCl -saturated water and extraction with diethyl ether. In the latter case the analysis of the reaction products and of unreacted substrate was also performed by ^1H NMR spectroscopy in the presence of an internal standard (bibenzyl). The structure of products was

attributed by ^1H NMR and GC-MS comparisons with authentic specimens.

3.4. Quantum yield determinations

A spectrophotometric cuvette (optical path = 4.00 cm) containing a suitable substrate ($2\text{--}50 \times 10^{-3}$ M) in a colloidal solution of TiO_2 in CH_3CN , alone or containing HClO_4 5×10^{-4} M, was placed in a thermostated (30°C) support placed inside a MLU-18 Multilamp photoreactor (Applied Photophysics Ltd.) fitted with four lamps (mod 3022, peak intensity at 312 nm, range 290–330 nm) or two lamps (as such or differently darkened). The mixture was irradiated under magnetic stirring until $\leq 5\%$ substrate conversion. The product formation was determined by GC analysis (bibenzyl as an internal standard). Light intensity was measured by ferrioxalate actinometry ($1.6\text{--}26 \times 10^{-8}$ einstein s^{-1}). Only the experiments where the material recovery was quantitative were considered.

3.5. Dark adsorption equilibrium constants

Equilibrium constants of benzylic silanes onto TiO_2 (P-25, particle concentration 20 g dm^{-3}) in CH_3CN (HPLC grade) in the presence of HClO_4 5×10^{-4} M were evaluated as for alcohols [4k] by a Langmuir-type treatment using an equation (Eq. (11)) suggested by Hiemans, [9] where C is the equilibrium bulk substrate concentration, n and n_{sat} are the number and the maximum number of moles of substrate adsorbed per gram of TiO_2 , respectively.

$$\frac{C}{n} = \frac{1}{Kn_{\text{sat}}} + \frac{C}{n_{\text{sat}}} \quad (11)$$

The K values were evaluated from different initial substrate concentrations at room temperature. In particular, the initial and final substrate concentrations were measured (by HPLC) after overnight equilibration of the shaken suspensions and filtration (through Millipore filters) as reported [10]. Each K value is the average of two or three determinations.

3.6. Dynamic light scattering measurements

Light scattering measurements were made by using ca. 0.6 ml of sample (TiO_2 colloidal in CH_3CN in the presence or in the absence of HClO_4) in 6 mm diameter Pyrex glass culture tubes. The cylindrical glass sample tube was fixed at the center of a toluene-filled fluorimeter cuvette to provide refractive index matching against stray light reflections. The cuvette was housed in a black-anodized aluminium cell block, whose temperature was regulated by a Peltier thermoelectric element. The light source was a Coherent Innova 70-3 argon-ion laser operating at 4880 \AA . Light scattered at 90° was collected from approximately one coherence area and imaged onto the slit of a photo-

multiplier tube (Products for Research, Inc.). A 64-channel Nicomp Model 370 computing autocorrelator was used to calculate and display the diffusion coefficient, D , and the associated derived parameters from cumulants analysis [11]. The hydrodynamic radius, R_h , was estimated by applying the Stokes–Einstein relation (for stick-boundary conditions, Eq. (12)) [12]

$$D = \frac{kT}{6\pi\eta R_h} \quad (12)$$

where η is the solvent viscosity.

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