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Involvement of adsorption effects in the TiO_2-sensitized photooxidation rate of benzylic derivatives in CH_3CN

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ABSTRACT: Competitive kinetic experiments in the TiO_2-sensitized photooxidation of some series of differently ring-substituted benzylic derivatives (ArCHROR′) in aerated and/or deaerated CH_3CN and in the presence of Ag_2SO_4 were carried out. From $\log k_{rel}$ vs E_p plots it was hypothesized that a changeover of the electron abstraction site occurs on going from electron-donating to electron-withdrawing groups on the ring, from the aromatic moiety to the OCH_3 group of benzyl methyl ethers, probably owing to the preferential adsorption of this group on TiO_2 with respect to the aromatic ring. This phenomenon is not observed with benzyltrimethylsilanes because the orbital resulting from the overlap between the C— Si bond and the aromatic π system is the only adsorption site. The steric hindrance of an α-methyl group (in benzylic alcohols) or a *tert*-butyl group (in benzyl *tert*-butyl ethers) reduces the degree of adsorption but does not influence the shape of the plot because OR′ should still be the preferential adsorption group. This also provides useful information about the surface structure of TiO_2 suspended in CH_3CN.

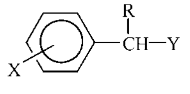
KEYWORDS: titanium dioxide; adsorption; photooxidation; benzylic derivatives

INTRODUCTION

The importance of substrate adsorption in the TiO_2-photosensitized oxidation of polluting organic compounds in waste water is known.[1] In previous papers we reported some of the implications of the substrate adsorption in a mechanistic study of the above-mentioned heterogeneous photooxidation of alkylaromatic compounds, in both CH_3CN[2–4] and water.[5]

Based on a competitive kinetic study, we recently reported[6] that the reactivity of ring-substituted benzyl alcohols in CH_3CN can be drastically influenced by the known[7] preferential adsorption of an OH group, with respect to the aromatic ring, on TiO_2. In particular, this phenomenon could be responsible for the changeover of the electron abstraction (by the photogenerated hole) site from the aromatic ring, in the presence of electron-donating groups, to the hydroxyl moiety, in the presence of electron-withdrawing groups.

Kinetic studies were conducted to acquire further information about the involvement of the adsorption phenomena on substrate reactivity in the TiO_2-sensitized photooxidation of some series of benzylic derivatives **1–4** in aerated or deaerated CH_3CN. Through this study, further information was obtained about the surface of this heterogeneous catalyst in the above-mentioned non-aqueous solvent.



Substrate	Y	R	X
1	OCH_3	H	**a**:4-CH_3O; **b**:4-CH_3; **c**:H; **d**:3-Cl; **e**:3-CF_3; **f**:4-CF_3
2	OH	CH_3	**a**:4-CH_3O; **b**:4-CH_3; **c**:H; **d**:4-CF_3
3	$Si(CH_3)_3$	H	**a**:4-CH_3; **b**:H; **c**:3-Cl; **d**:3-CF_3
4	$OC(CH_3)_3$	H	**a**:4-CH_3O; **b**:4-CH_3; **c**:H; **d**:4-CF_3

RESULTS AND DISCUSSION

The only product obtained from the TiO_2-photosensitized oxidation of benzyl methyl ethers **1a–f**, in deaerated CH_3CN, was the corresponding benzaldehyde (Table 1). After 2 h, the observed yield decreased on going from electron-donating ring-substituted compounds (lower E_p values) to benzyl methyl ether, whereas in the presence of electron-withdrawing groups (higher E_p values) the yield was practically unchanged. To evaluate this behavior

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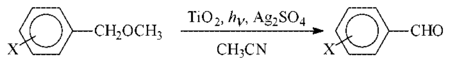
Table 1. Products yields in the photooxidation of benzyl methyl ethers sensitized by TiO_2 in deaerated CH_3CN and in the presence of Ag_2SO_4 (reaction time 2 h)



X	Benzaldehyde (%)	E_p (V vs SCE)
4-OCH_3	62	1.55
4-CH_3	19	1.98
H	8	2.22
3-Cl	9	2.30
3-CF_3	9	2.70
4-CF_3	10	2.80

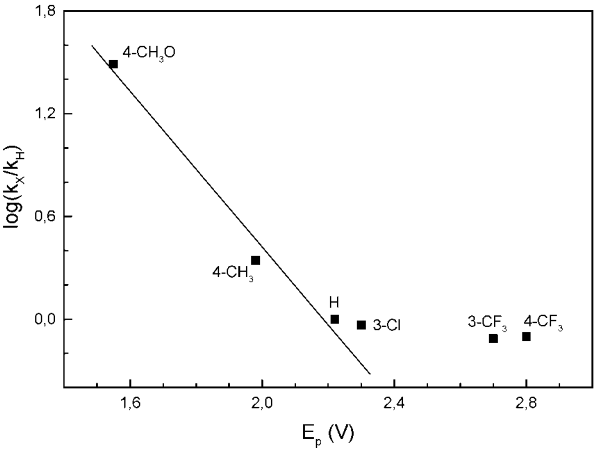


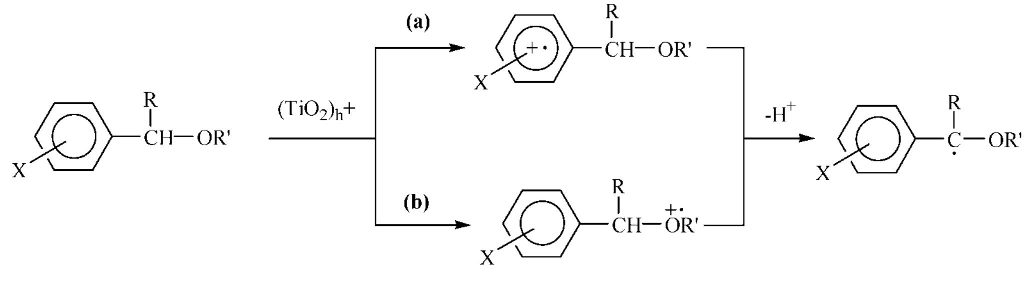
Figure 1. Plot of log(k_X/k_H) vs E_p for TiO_2-photosensitized oxidation of X ring-substituted benzyl methyl ethers ($XPhCH_2OCH_3$) to the corresponding benzaldehydes in deaerated CH_3CN and in the presence of Ag_2SO_4

more precisely, the relative reaction rates were determined by the competitive method. In the plot of logk_{rel} ($k_{rel} = k_X/k_H$) vs E_p (Fig. 1), ethers **1a**–**c** are linearly correlated and show a rate decrease as the redox potential increases, which indicates a rate-determining electron-transfer step from the aromatic ring to the photogenerated hole, $(TiO_2)_{h+}$, of the semiconductor (via **a** in Scheme 1). The slope ($-2.2\ V^{-1}$) is characteristic of a substrate-like transition state in a slightly exoergonic electron-transfer step.[8] In contrast, the ethers with higher reduction potentials (**1d**–**f**) had similar reactivity that was higher than expected based on the correlation. This behavior could be due to the involvement of an alternative electron-transfer process from the OCH_3 group (via **b** in Scheme 1), in which the substituent would have much less kinetic effect. The changeover of the electron abstraction site cannot be justified on a thermodynamic basis. In fact, the reduction potential of an aliphatic ether such as diethyl ether, $E_p > 3$ V vs SCE (only the solvent/electrolyte signal is observed up to 3 V in the voltammogram), is higher than that of the least oxidizable benzyl methyl ether **1f**, $E_p = 2.80$ V. Therefore, this behavior should be in line with the increased oxidizability of the OCH_3 group due to the adsorption of the molecule by this moiety, as reported for the OH group of benzyl alcohols.[3,6,7] A recent study, based on oxidation peak current measurements, supports this hypothesis, indicating that adsorbed species are consistently characterized by less positive potentials (are therefore more oxidizable) than those attributed to solution free species.[9] The increased oxidizability of the OCH_3 group would favor competition for electron abstraction with respect to the aromatic site when deactivated by substituents having a sufficiently high electron-withdrawing effect (such as 3-Cl, 3-CF_3 and 4-CF_3).

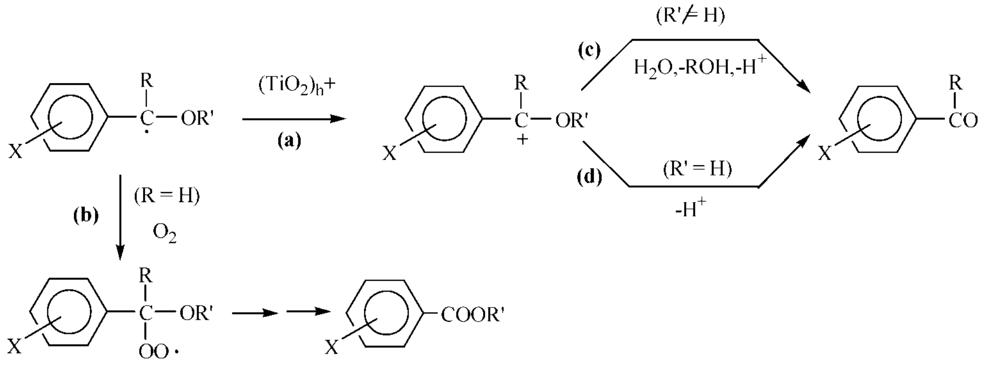
Similar results obtained with benzylic alcohols[6] support the hypothesis that preferential adsorption (with respect to the aromatic ring) on the semiconductor surface occurs at the OR′ (R′ = H, CH_3) group. Whereas in our previous study[6] it was not possible to establish whether the preferential OH adsorption occurred through the H or O atom, it is now plausible to suggest that only the oxygen atom of the OR′ group is involved. This interaction probably involves the oxygen lone pair which facilitates the abstraction of the electron by the corresponding orbital.[9]

The final product, aldehyde, is probably derived from the benzylic cation (path **c** in Scheme 2) obtained from the oxidation, probably by $(TiO_2)_{h+}$,[10] of the corresponding benzylic radical (path **a**).

The logk_{rel} vs E_p profile, relative to the heterogeneous photooxidation of ethers **1a**–**f** in aerated medium (in this case the aldehyde is accompanied by the corresponding methyl benzoate, Table 2), maintained the same shape as that in the deaerated medium. This behavior is expected



Scheme 1

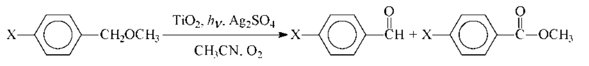


Scheme 2

since oxygen should not be involved in the kinetically significant steps (Scheme 1) but rather could participate in the subsequent steps.[11–13] In fact, the benzylic radical can be captured by oxygen (path **b** in Scheme 2) or oxidized by the hole (path **a**); the rate ratio of the two competitive paths depends on the reduction potential of this intermediate radical (the relative amount of ester increases on going from the electron-donating to the electron-withdrawing ring-substituted substrates, Table 2).[11] To confirm that the anomalous relationship between the log k and E_p values is due to the presence of two electron abstraction sites on the same molecule (benzyl alcohols[6] or ethers), the reactivity behavior of a series of ring-substituted benzyltrimethylsilanes was evaluated. These compounds have only one adsorption site, the orbital resulting from the overlap between the C—Si bond and the π system, from which the electron is abstracted through a process kinetically influenced by the substituent effect. In the photooxidation of silanes **3a**–**d** sensitized by TiO_2 in deaerated medium to the corresponding 1,2-diarylethanes[2] the diagram of $\log k_{rel}$ (from a previous study[2]) vs E_p values [determined in this work: E_p = 1.49 (**3a**), 1.69 (**3b**), 1.89 (**3c**) and 2.22 V (vs SCE) (**3d**)] shows that the rate decreases linearly as the reduction potential increases (Fig. 2).

A confirmation that the observed anomalous reactivity pattern in the heterogeneous photooxidation of methyl ethers **1a**–**f** should be due to the involvement of adsorption phenomena is represented by the reactivity behavior of the ethers in homogeneous oxidation in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate,[11] a photosensitizer with a reduction potential in the excited state similar to that of the valence band edge of TiO_2 (ca 2.4 V in CH_3CN[14]). In contrast to what happens in the heterogeneous oxidation with TiO_2, substrates with high E_p, such as 3- and 4-CF_3 ring-substituted ethers, are less reactive than the unsubstituted ether. Moreover, the reactivities of the two substrates are linearly correlated in the endoergonic zone of the plot of $\log k_q$(fluorescence quenching) vs ΔG_{et}(electron transfer) derived from Marcus–Rehm–Weller treatment (see Fig. 4 in Ref. 11). This behavior is expected in the homogeneous phase (absence of adsorption phenomena) because the ring is the electron abstraction site for all the substrates. [It is also interesting to observe that, unlike the heterogeneous phase, 4-MeO and 4-Me substituted ethers appear in the plateau of the $\log k_q$ vs ΔG_{et} diagram, where the rate-determining step is the diffusion process. This step is not kinetically influential in the heterogeneous phase since the pre-adsorption of the substrate is required for its

Table 2. Product yields in the photooxidation of benzyl methyl ethers sensitized by TiO_2 in aerated CH_3CN and in the presence of Ag_2SO_4



X	Reaction time (h)	Benzaldehyde (%)	Ester (%)
CH_3O	1	30	41
CH_3	2.5	12	23
H	2.5	2	28
CF_3	3	—	20

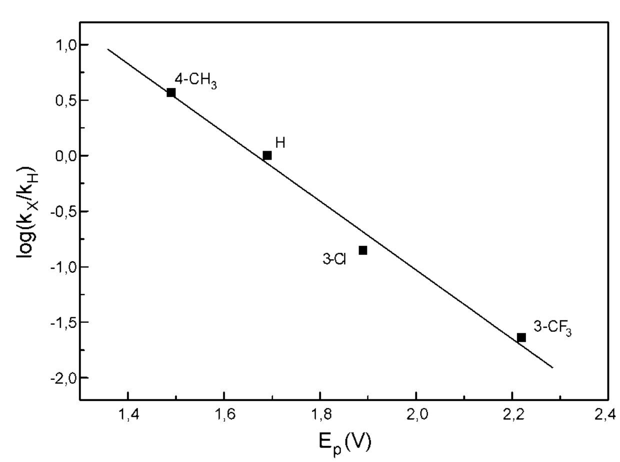
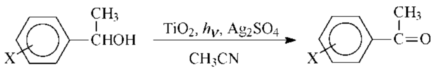


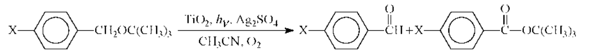
Figure 2. Plot of $\log(k_X/k_H)$ vs E_p for TiO_2-photosensitized oxidation of X ring-substituted benzyltrimethylsilanes [$XPhCH_2Si(CH_3)_3$] to the corresponding 1,2-diarylethanes in deaerated CH_3CN and in the presence of Ag_2SO_4

Table 3. Product yields in the photooxidation of α-methylbenzyl alcohols sensitized by TiO_2 in deaerated CH_3CN and in the presence of Ag_2SO_4



X	Reaction time (min)	Acetophenone (%)	E_p (V vs SCE)
4-OCH_3	30	97	1.60
4-CH_3	10	40	2.00
H	30	20	2.28
4-CF_3	30	50	2.73

Table 4. Product yields in the photooxidation of benzyl *tert*-butyl ethers sensitized by TiO_2 in aerated CH_3CN and in the presence of Ag_2SO_4



X	Reaction time (h)	Benzaldehyde (%)	Ester (%)	E_p (V vs SCE)
CH_3O	0.5	30	2	1.53
CH_3	2	2	38	1.98
H	3	2	55	2.25
CF_3	3	—	31	2.65

photooxidation[1,7a,b] and, therefore, the rate for the two ethers is correlated with that for the unsubstituted ether in the plot of $\log k_{rel}$ vs E_p.]

It must be noted that the introduction of a methyl group in place of a hydrogen atom linked to the adsorption site (oxygen) generates steric hindrance. In fact, it has been shown that the adsorption constant of 4-methoxybenzyl alcohol is higher than that of the corresponding methyl ether **1a**.[15] Therefore, the analogous reactivity behavior observed for alcohols and ethers leads to the hypothesis that the steric effect of the methyl group is not high enough to avoid the preferential adsorption of the oxygen of the OCH_3 group with respect to the aromatic ring.

An analogous study on the TiO_2-sensitized photooxidation of α-methylbenzyl alcohols in deaerated CH_3CN evaluated the steric hindrance induced by introducing an α-methyl group. In all cases, the reaction product was the corresponding acetophenone (Table 3), which was probably formed by the oxidation of the benzylic radical (paths **a** and **d** in Scheme 2). The plot of $\log k_{rel}$ vs E_p (Fig. 3) is similar to the plots for benzyl alcohols[6] and ethers (Fig. 1), showing that an α-methyl group on the benzylic carbon is not bulky enough to avoid the preferential adsorption of oxygen with respect to the aromatic ring. However, this structural change would generate steric hindrance to the adsorption of alcohols **2a–d** on TiO_2 with respect to the corresponding α-unsubstituted alcohols **1**. In fact, we have observed that the adsorption constant of **2a** is nearly 1.5 times higher than that of 4-methoxybenzyl alcohol.[16]

Steric hindrance to the OR′ adsorption could be increased if benzyl *tert*-butyl ethers were the starting material. The photooxidation reaction products of these substrates in aerated CH_3CN are again the corresponding aldehydes and esters (see Table 4) in relative amounts depending on the reduction potential of the intermediate benzylic radicals, as observed for methyl benzyl ethers. The plot in Fig. 4, similar to those obtained for the above α-OR′ benzyl derivatives, also shows that the introduction of a very bulky *tert*-butyl group directly linked to the oxygen atom furnishes greater steric hindrance than the methyl group bound to oxygen (as shown above comparing the adsorption constants of **1a** with that of 4-methoxybenzyl alcohol); the steric hindrance, how-

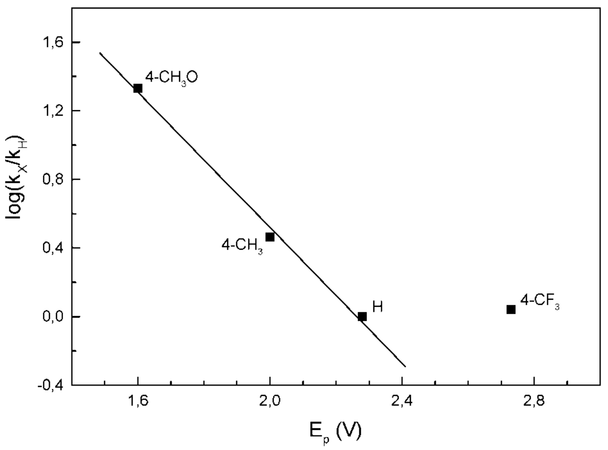


Figure 3. Plot of $\log(k_X/k_H)$ vs E_p for TiO_2-photosensitized oxidation of X ring-substituted α-methylbenzyl alcohols ($XPhCH(CH_3)OH$) to the corresponding acetophenones in deaerated CH_3CN and in the presence of Ag_2SO_4

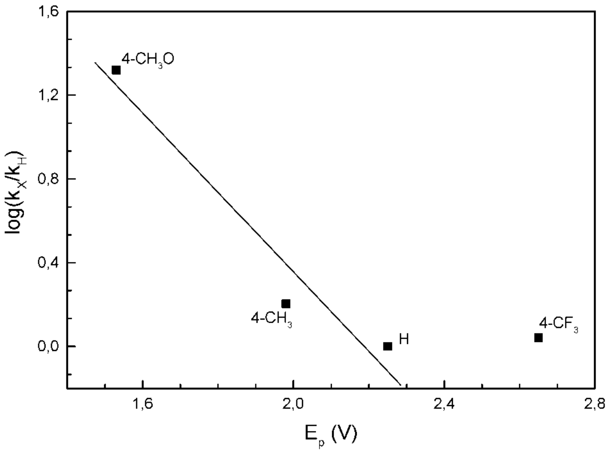


Figure 4. Plot of $\log(k_X/k_H)$ vs E_p for TiO_2-photosensitized oxidation of X ring-substituted benzyl tert-butyl ethers to the corresponding benzaldehydes and *tert*-butyl benzoates in aerated CH_3CN and in the presence of Ag_2SO_4

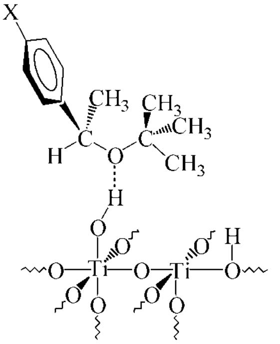


Figure 5. Possible interaction (via hydrogen bonding) between benzyl *tert*-butyl ethers **4a–d** and TiO_2 hydroxylated surface

ever, is not high enough to limit the interaction between the oxygen lone pairs of the OR′ group and TiO_2 with respect to the interaction through the π-system of the aromatic ring.

The latter result confirms the hypothesis[4,5] that, in CH_3CN, the TiO_2 surface structure has hydroxyl groups that are derived from water physiadsorption or dissociative chemiadsorption, as in aqueous medium.[17] If a hydroxylated surface structure derived from dissociative chemiadsorption is considered, the *tert*-butyl group does not significantly hinder the interaction between the oxygen lone pair and the hydroxyl group on TiO_2 via hydrogen bonding, allowing a greater distance between the substrate and the TiO_2 surface (Fig. 5). In contrast, if the interaction involves the oxygen lone pairs and the superficial Ti atoms (Lewis acid sites), the *tert*-butyl steric hindrance would become so important as to move the adsorption site from the oxygen atom to the ring and, in this case, the $\log k_{rel}$ vs E_p profile would be linear, as observed for silanes.

EXPERIMENTAL

Instrumentation. ^1H 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 Model 6890A gas chromatograph (HP-Innovax capillary column, 15 m) coupled with a MSD-HP 5973 mass-selective detector (70 eV). GC analyses were carried out on a HP Model 5890 gas chromatograph (HP-Innovax capillary column, 15 m).

Materials. TiO_2 (anatase) (Aldrich, 99.9%, dried at 110 °C), CH_3CN (HPLC grade, water content 0.02% from Karl Fischer coulometry), Ag_2SO_4 and α-methyl benzyl alcohols **2a–d** were commercial samples. Benzyltrimethylsilanes **3a–d** were available from previous studies.[2] Benzyl methyl ethers **1a–f** were prepared as described[18] by methylation (with CH_3I in DMSO) of the sodium alkoxide obtained from the reaction of the corresponding benzyl alcohol with NaH in the same solvent. The crude material obtained from the usual work-up was purified by column chromatography on silica gel, eluting with n-hexane. **1a–c** and **f** were characterized by ^1H NMR[18,19] and GC–MS. **1d**, b.p. (15 mmHg) = 74 °C; δ_H 7.4–7.2 (4H, m, ArH), 4.42 (2H, s, CH_2), 3.38 (3H, s, OCH_3); *m/z* 156 (M^+), 155, 127, 125, 121 (100%), 91, 89, 77. **1e**, b.p. (15 mmHg) = 52 °C; δ_H 7.6–7.4 (4H, m, ArH), 4.51 (2H, s, CH_2), 3.42 (3H, s, OCH_3); *m/z* 136 (M^+), 135, 121, 105 (100%), 104, 91, 77, 65, 51. Benzyl *tert*-butyl ethers **4a**, **b** and **d** were prepared by mixing the corresponding alcohols with *tert*-butyl alcohol and concentrated sulfuric acid as described,[20] whereas **4c** was prepared by silane reduction of benzaldehyde in acidic *tert*-butyl alcohol;[21] all the ethers were characterized by ^1H NMR[20,22–24] and GC–MS.

Photochemical oxidation. A solution of benzylic alcohol or ether (0.22–0.24 mmol) in N_2- or O_2-purged CH_3CN (20 ml, HPLC grade), in the presence of 130 mg of TiO_2 and 0.30 mmol of Ag_2SO_4, was externally irradiated using a Helios Italquartz 500 W high-pressure mercury lamp (through a Pyrex filter), with stirring at room temperature. The TiO_2 powder was then filtered through double paper and repeatedly washed with CH_3CN and diethyl ether; the reaction mixture was poured into water and extracted with diethyl ether. Quantitative analysis of the crude product was performed by ^1H NMR and/or GC with a suitable internal standard.

Reaction products. The products were identified directly from the crude material by comparison of the ^1H NMR and GC–MS data with those for commercial samples (aldehydes and ketones) or literature spectroscopic data (esters).

Competitive experiments. Kinetic experiments were performed at 25 °C by irradiating (Applied Photophysics multilamp photochemical reactor, $\lambda = 355 \pm 20$ nm) mixtures containing the same amounts of TiO_2, Ag_2SO_4, CH_3CN and substrate (corresponding to the sum of equimolar quantities of the two compounds) as reported in the above photooxidation procedure. The amounts of reaction products were determined by GC with respect to an internal standard at different times and the values were inserted in a suitable kinetic equation.[25]

Cyclic voltammetry. E_p values were obtained using an AMEL 552 potentiostat controlled by a programmable AMEL 568 function generator (at 100 mV s^{-1}, 1 mm diameter platinum disk anode) in CH_3CN–$LiClO_4$ (0.1 M).

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