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Photooxidation of Benzyl Alcohols Sensitized by TiO_2 in CH_3CN in the Presence of Ag_2SO_4. Kinetic Evidence for the Involvement of Adsorption Phenomena†

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X-Ring substituted benzyl alcohols are photooxidized to the corresponding aldehydes by TiO_2 in CH_3CN in the presence of Ag_2SO_4 and kinetic evidence suggests a changeover of the electron abstraction site from the aromatic moiety (X = 4-CH_3O, 4-CH_3, 4-Cl, H, 3-Cl) to the hydroxylic group (X = 3-CF_3, 4-CF_3), probably owing to the preferential adsorption of OH on TiO_2.

It is known that the TiO_2 photosensitized oxidation of organic compounds in aqueous media, in the presence of oxygen as the electron acceptor, can proceed through a 'direct' process (single electron transfer from the substrate to the photogenerated hole, h^+) or an 'indirect' one (substrate attack by $OH^•$ generated from the water oxidation).[1] In this respect, we have observed that deaerated CH_3CN, when used in the presence of Ag^+ as the electron acceptor, is an oxidatively inert medium suitable for mechanistic studies of the first process.[2] In particular, it has been possible to study, through reaction product analysis, some chemical properties of alkylaromatic radical cations [eqns. (1)–(3)].[2]

$$TiO_2 \xrightarrow{h\nu} (TiO_2)_{h^+} + (TiO_2)_{e^-} \quad (1)$$

$$(TiO_2)_{h^+} + ArCH_2Y \longrightarrow ArCH_2\overline{Y}^{+•} \longrightarrow \text{Products} \quad (2)$$

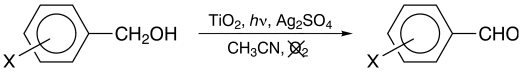
$$(TiO_2)_{e^-} + Ag^+ \longrightarrow Ag \quad (3)$$

An interesting result was the presence, within the reaction products from 1-phenylpropan-2-ol and its corresponding methyl ether,[2b] of a compound (benzyl methyl ketone) derived from oxidation of the OH group, a thermodynamically very unfavoured site with respect to the π system towards electron abstraction. One of the suggested explanations of this unexpected behaviour has been the increased oxidizability of the hydroxy group due to its preferential adsorption at the TiO_2 surface.[2b,3] Accordingly, this hypothesis was already formulated to explain the better oxidizability of OH with respect to phenyl in 5-phenylpentan-1-ol (5-phenylpentanal and 5-phenylpentanoic acid were the predominant reaction products).[4]

With the aim of providing more quantitative information on this argument we have undertaken a systematic study of the TiO_2 photosensitized oxidation of a series of benzyl alcohol derivatives [X-$C_6H_4CH_2OH$, with X = H (**1**), 4-CH_3O (**2**), 4-CH_3 (**3**), 3-Cl (**4**), 4-Cl (**5**), 3-CF_3 (**6**), 4-CF_3 (**7**)].

The reactions were carried out by external irradiation of a deaerated acetonitrile solution of the benzyl alcohol derivative in the presence of TiO_2 and Ag_2SO_4. Under these mild conditions a quite efficient process occurs leading to the corresponding benzaldehyde (Table 1) in fair to good yield (34–73%) and with satisfactory material balance (generally ⩾95%). At high substrate conversion (see entry 5 from **1**) the benzaldehyde selectivity is not significantly reduced (a small amount of benzoic acid is also formed). No reaction takes place if the substrate solution is irradiated in the absence of either TiO_2 or Ag_2SO_4. With oxygen as the electron acceptor a lower substrate conversion is observed (compare entry 2 with entry 1). The unexpected efficiency of the process even with scarcely oxidizable alcohols (with electron-withdrawing substituents) is noteworthy. For example the TiO_2 induced photooxidation of the 4-CF_3 derivative yields in 2 h a conversion in aldehyde (47%, entry 8) not much lower than that of unsubstituted alcohol (73%, entry 5).

Table 1 Product yields in TiO_2 photosensitized oxidation of ring substituted benzyl alcohols in deaerated CH_3CN and in the presence of Ag_2SO_4[a]



Entry	X	*t*/min	Unreacted substrate (%)[b]	Aldehyde (%)[b]
1	4-CH_3O (**2**)	15	54	41
2[c]		15	68	19
3	4-CH_3 (**3**)	30	63	34
4	H (**1**)	60	52	43
5		120	14	73[d]
6	3-Cl (**4**)	120	50	48
7	3-CF_3 (**6**)	120	47	52
8	4-CF_3 (**7**)	120	51	47

[a]No reaction takes place in the absence of TiO_2 or Ag_2SO_4. [b]With respect to starting material. [c]In the absence of Ag_2SO_4 and in aerated medium. [d]Benzoic acid (3%) is also formed.

For comparison, we have carried out the photooxidation of the same substrates in the homogeneous phase (CH_3CN, O_2, at room temperature) sensitized by 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$), an electron transfer oxidant whose redox potential at the excited state ($E^*_{red} = E_{red} + \Delta E_{oo} = 2.53$ V *vs.* SCE)[5] is similar to that of the TiO_2 valence band edge ($E \cong 2.4$ V).[6] Under these conditions benzyl alcohol was much more efficiently converted (after 4 h) into products (benzaldehyde, 39%, and benzoic acid, 41%) than the 4-CF_3 derivative (4-trifluoromethylbenzaldehyde was obtained in 8% yield).

The relative photooxidation rates have also been determined by means of competition kinetics. An initial observation is that, in line with the behaviour observed in Table 1, the rate of the reaction is significantly increased by the

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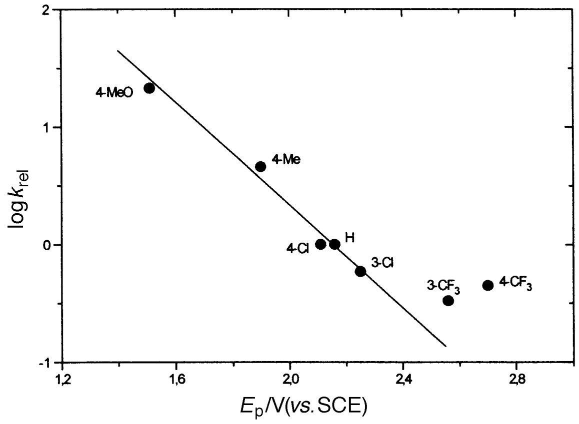
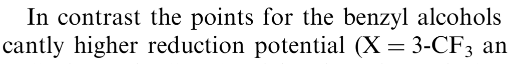


Fig. 1 Plot of log k_{rel} *vs.* E_p for TiO_2 photosensitized oxidation of X-ring substituted benzyl alcohols in deaerated CH_3CN and in the presence of Ag_2SO_4

electron-donating groups 4-CH_3O and 4-CH_3 while a much lower reactivity is observed with the electron-withdrawing substituents 3-CF_3 and 4-CF_3. A quantitative assessment of the phenomenon is provided by the log k_{rel}/E_p plot[7] (Fig. 1). In particular a good linear correlation ($r = 0.992$) is observed for benzyl alcohols with X = 4-CH_3O, 4-CH_3, 4-Cl, H, 3-Cl. This behaviour is in line with a single electron transfer (SET) rate determining step to $(TiO_2)_{h^+}$ where the electron is removed from the aromatic moiety [eqn. (4)]. The low value of the slope (–2.1 V^{-1}) could be related to a substrate like transition state, as expected for a slightly exoergonic step.[7]

(4)

8



(5)

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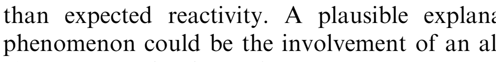
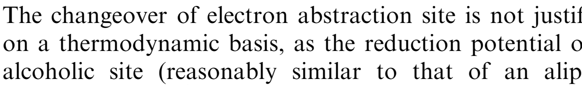


(6)

8 or 9



(7)

In contrast the points for the benzyl alcohols with significantly higher reduction potential (X = 3-CF_3 and 4-CF_3) lie well above the line fitted by the other substituents; in particular the last two compounds show a similar and higher than expected reactivity. A plausible explanation of this phenomenon could be the involvement of an alternative one electron transfer from the OH group [eqn. (5)], a process much less kinetically influenced by the substituent effect. The changeover of electron abstraction site is not justifiable on a thermodynamic basis, as the reduction potential of the alcoholic site (reasonably similar to that of an aliphatic alcohol, $E_p \approx 3$ V[8]) is higher than that of 4-trifluoromethylbenzyl alcohol ($E_p = 2.70$ V). This behaviour is in line with the increase of oxidizability of the OH group, explained on the basis of its preferential adsorption with respect to the phenyl ring;[2b,4] in our case OH could favourably compete, with electron abstraction, with an aromatic site deactivated by substituents with a sufficiently high electron-withdrawing effect (as 3- or 4-CF_3). Further kinetic evidence that the observed phenomenon is connected to the medium heterogeneity (probable involvement of preferential adsorption) could be the relative reactivity values obtained from the photooxidation of **1**, **3** and **6** in the homogeneous phase in the presence of $TPP^+BF_4^-$; in effect, the expected decreasing reactivity trend as a function of increasing reduction potential of substrate is observed [k(4-CH_3)/k(H) = 1.8 and k(3-CF_3)/k(H) = 0.024].

It should be noted that the high reduction potential of the two trifluoromethyl substituted derivatives could suggest the involvement of a mechanism different from electron transfer such as radical benzylic hydrogen transfer, not depending on reduction potential. Otherwise this hypothesis is not plausible in CH_3CN, even with scarcely oxidizable substrates; for example the observed higher reactivity of the primary *vs.* the secondary alcoholic site in the TiO_2 sensitized photooxidation of pentane-1,4-diol[9] (an aliphatic alcohol, a compound with an high reduction potential, see above) is opposite to the behaviour expected in a radical process. In effect, the observed trend has been justified through a preferential electron transfer to the less hindered and more efficiently adsorbed primary group with respect to the secondary one.

The benzylic radical obtained from deprotonation [eqn. (6)] of both cation radicals **8** and **9** should undergo a further oxidation (probably by Ag^+) giving the protonated form of the corresponding benzaldehyde [eqn. (7)].[2d]

Experimental

A solution of benzylic alcohol (0.22–0.24 mmol) in N_2 purged CH_3CN (20 ml, HPLC grade) was externally irradiated (through a Pyrex filter) by a 500 W high pressure mercury lamp, with stirring at room temperature, in the presence of 130 mg of TiO_2 (Aldrich, 99.9%, anatase, dried at 110 °C) and 0.30 mmol of Ag_2SO_4. 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. The quantitative analysis of the crude product was performed by ^1H NMR and/or by GC relative to a suitable internal standard. The same photochemical reactor was used to irradiate a solution of the alcohol (0.5 mmol) and $TPP^+BF_4^-$ (0.021 mmol) in O_2 purged CH_3CN (20 ml).

Competitive experiments were performed at 25 °C by irradiation (multilamp photochemical reactor, $\lambda = 350 \pm 30$ nm) of mixtures containing equimolar amounts of two substrates and determination (by GC with respect to an internal standard) of the amount of unreacted starting material at different times.

E_p values were obtained by cyclic voltammetry (100 mV s^{-1}, 1 mm diameter platinum disc anode) in $CH_3CN/LiClO_4$ (0.1 M).

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