SHORT PAPER

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"Dark" adsorption equilibrium constants of benzylic derivatives on TiO_2 and their implications in the sensitised heterogeneous photooxidation[†]

Marta Bettoni[a], Tiziana Del Giacco[b], Cesare Rol[b]*, and Giovanni V. Sebastiani[a]*

[a]Dipartimento di Ingegneria Civile ed Ambientale (Sez. Tecnologie Chimiche), Università di Perugia, Via G. Duranti, 06125 Perugia, Italy

[b]Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 06123 Perugia, Italy

The "dark" adsorption equilibrium constants of different series of benzylic derivatives on TiO_2 suspended in CH_3CN were determined through a Langmuir-type adsorption isotherm. In particular, the similarity of the K values of differently ring substituted α-OH derivatives within the same series confirms the previously suggested preferential adsorption of the hydroxyl group (at the oxygen atom) with respect to the aromatic moiety.

Keywords: titanium dioxide, adsorption constants, sensitised photooxidation

It is known that pollutant adsorption on the semiconductor surface is crucial for an efficient mineralization through TiO_2-photosensitised oxidation in aqueous phase[1]. In this context, in order to evaluate substrate adsorption, equilibrium constants in the "light" have frequently been determined in water using an indirect method (from the rate or quantum yield of the photosensitised oxidation treated according to a Langmuir-Hinshelwood type isotherm[2]). These constants have only been obtained directly in a few cases, that is by treating the substrate concentration values, determined in the absence of irradiation (in the "dark"), according to the Hiemens equation where the competition between the substrate and solvent adsorption on the semiconductor is considered.[3]

The dark measurements were also previously performed in CH_3CN[4] and the observed values were higher (and then determined with greater precision) than in water, probably due to less solvent competition with the substrate towards adsorption on TiO_2.

We studied the mechanism of the TiO_2-photosensitised oxidation of benzylic derivatives in CH_3CN where the primary process, with all the considered substrates, involves an electron transfer from the preadsorbed substrate to the photogenerated hole.[5]

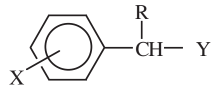
Recently, we observed that X-ring substituted α-OR (R = H or alkyl group) benzylic derivatives have an anomalous reactivity pattern as shown in the plot $\log(k_X/k_H)$ *vs* E_p. This behaviour was ascribed to the preferential adsorption of the OR group with respect to the aromatic ring on the semiconductor surface.[6] To test this hypothesis, we have determined in this work the "dark" adsorption constants in CH_3CN for the series of substrates **1–4**.

Moreover, this study also evaluated how substrate structural modifications influence the extent of adsorption at the TiO_2 surface.

Results and discussion

The "dark" adsorption constants on TiO_2 of benzylic derivatives **1-4** in CH_3CN are reported in the Table. The constants were determined by a Langmuir type treatment using an equation (Eqn. 1) suggested by Hiemens[3,7] which assumes the formation of a monolayer at the TiO_2 surface by the competitive adsorption of CH_3CN and the considered benzylic derivative.

$$\frac{C}{n} = \frac{1}{K\ n_{sat}} + \frac{C}{n_{sat}} \qquad (1)$$



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

Table 1 "Dark" adsorption equilibrium constants (K) of benzylic derivatives on TiO_2 as powder suspended in CH_3CN.

Entry		$K \times 10^{-2}$, M^{-1}
1	$Ph\text{-}CH_2OH$	6.9 ± 0.8
2	$4\text{-}CH_3O\text{-}Ph\text{-}CH_2OH$	6.9 ± 1.0
3	$3\text{-}CH_3O\text{-}Ph\text{-}CH_2OH$	7.2 ± 1.0
4	$4\text{-}CF_3\text{-}Ph\text{-}CH_2OH$	7.4 ± 1.0
5	$Ph\text{-}CH(CH_3)OH$	4.9 ± 0.6
6	$4\text{-}CH_3O\text{-}Ph\text{-}CH(CH_3)OH$	5.4 ± 0.9
7	$4\text{-}CH_3\text{-}Ph\text{-}CH(CH_3)OH$	5.1 ± 0.8
8	$4\text{-}CF_3\text{-}Ph\text{-}CH(CH_3)OH$	4.7 ± 0.5
9	$4\text{-}CH_3\text{-}Ph\text{-}CH_2OCH_3$	< 1
10	$Ph\text{-}CH_2OCH_3$	< 1
11	$4\text{-}CF_3\text{-}Ph\text{-}CH_2OCH_3$	< 1
12	$Ph\text{-}CH_2Si(CH_3)_3$	< 1

In particular, C is the equilibrium bulk donor concentration, $n = V(C_o - C)/W$ is the number of moles of the substrate adsorbed per gram of TiO_2 (in the expression, C_o is the substrate concentration, V is the volume of the solution and W is the weight of TiO_2) and n_{sat} is the maximum number of solute moles that can be adsorbed per gram of TiO_2.

From the linear plot C/n *vs* C (see, for example, Fig. 1 relative to **2c**) it is possible to determine the "dark" adsorption constant as the slope/intercept ratio. It is noteworthy that the K value obtained for benzyl alcohol (see Table, entry 1), similar to that reported in the literature,[4] is not influenced by the introduction of substituents on the ring (entries 1-4 in the Table). In fact, the same K value in the benzylic alcohols

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* To receive any correspondence. E-mail: gseb@tech.ing.unipg.it and rol@unipg.it

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

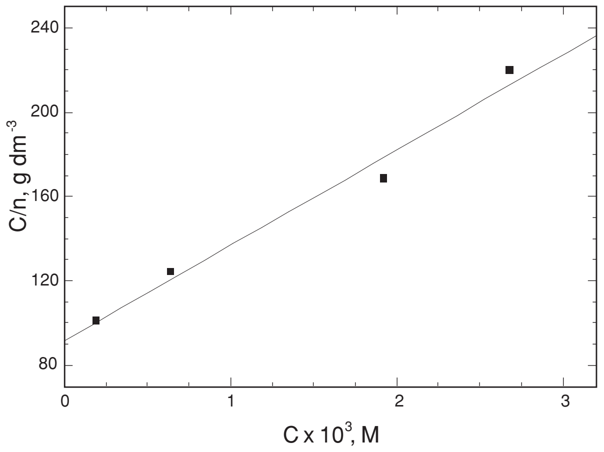
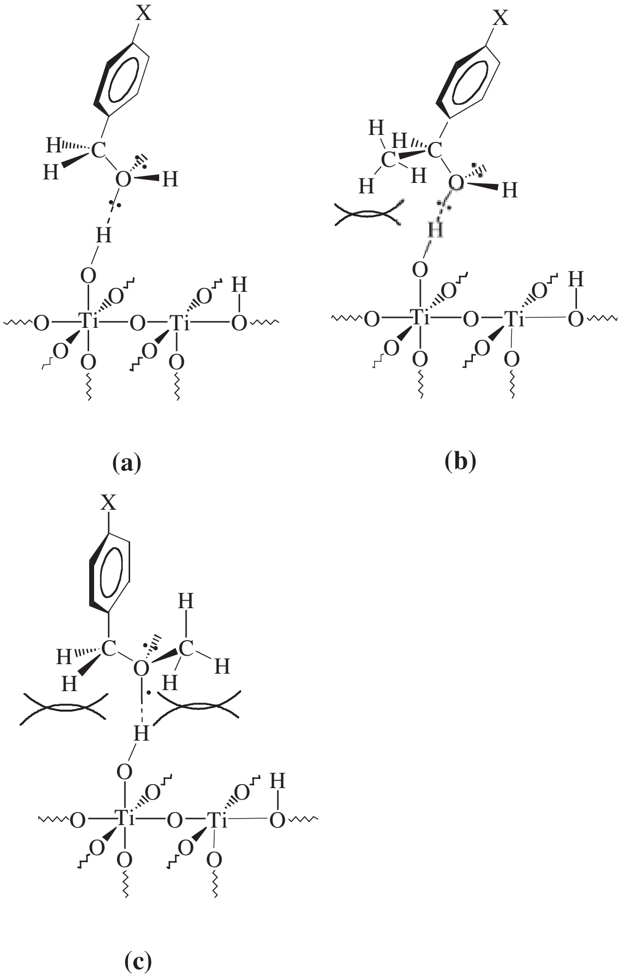


Fig. 1 Isotherm for "dark" adsorption of α-methylbenzyl alcohol (2c) onto TiO2 from CH_3CN solution



(a) **(b)**

(c)

Fig. 2 Possible interactions between TiO_2 surface and (**a**) benzyl alcohols, (**b**) α-methylbenzyl alcohols and (**c**) methyl benzyl ethers.

series **1a-d** is in line with the previously suggested (on the basis of photooxidation reactivity data[6a]) preferential adsorption, with respect to the aromatic ring, of the OH group, a moiety that should not interact electronically with the far ring substituent. Moreover, the adsorption on TiO_2 probably occurs (via hydrogen bond [6b]) with the most stable substrate conformation in which the ring is far from the TiO_2 surface. The substituent therefore should not sterically interact with the semiconductor surface (Fig. 2a).

In a previous work the adsorption constants of alcohols **1a** and **1b** were determined in an indirect way (under irradiation);[8] the K values for the two alcohols were similar. It must be noted that the two different absolute values of K, *ca* 7×10^2 M^{-1} for each alcohol in the "dark" (see Table) and *ca* 1.5×10^2 M^{-1} under irradiation, can be ascribed to the different experimental conditions used with powdered and colloidal TiO_2, respectively. The fact that the K values determined in colloidal TiO_2 were always smaller than those found in the presence of TiO_2 powder could depend on the competitive adsorption of isopropanol, the co-solvent used in the preparation of the colloid.[8]

The absence of a ring-substituent effect on the "dark" adsorption constants of the series of α-methylbenzyl alcohols **2a-d** (entries 5-8 in the Table) is also in line with the preferential OH adsorption with these substrates, as previously hypothesized on the basis of photooxidation reactivity data.[6b] The K values (*ca* 5×10^2 M^{-1}) are lower than those (*ca* 7×10^2 M^{-1}) observed for benzyl alcohols. This is probably related to the conformations of adsorbed derivatives **2a-d**, in which the phenyl and methyl group are both present at the same carbon linked to the OH group (Fig. 2b). In any case the steric hindrance should be higher than that of alcohols **1a-d** (Fig. 2a). It must be observed that the K value under irradiation previously measured for 4-methoxy derivative **2a** (1.0×10^2 M^{-1})[8] is again lower than that measured in the "dark"; in particular, the fact that the ratio K("dark")/K("light") for **2a** (*ca* 5) is the same observed for **1a** and **1b** should confirm that the changes in the K value depend on the experimental conditions, apart from the substrate structure.

Many attempts were also made to measure K values for the ethers **3a-c**, but the amount of adsorbed material in all the cases was so low that it was impossible to evaluate the adsorption constants ($K < 10^2$ M^{-1}). This result suggests that in the case of the OR group ($R=CH_3$), the steric hindrance of the methyl group linked to the adsorption site (oxygen) reduces the interaction between the substrate and TiO_2 (Fig. 2c), proposed for the alcohols **1a-d** (Fig. 2a), more significantly than that of an α-methyl group in alcohols **2a-d** (Fig. 2b). However, as suggested on the basis of kinetic data reported in a previous work,[6b] the steric hindrance of the methyl group in the ethers **3a-c** should not be strong enough to change the adsorption site from OCH_3 to the aromatic π system.

A further confirmation that the OR group is a preferential adsorption site with respect to the aromatic ring was obtained by determining the K of benzyltrimethylsilane (**4**) a benzylic derivative in which the π system is the only absorption site. In effect, the K of this substrate is too low to be evaluated and therefore it is significantly smaller than that of benzyl alcohol.

Finally it must be noted that the Langmuir treatment equation for heterogeneous rate[3,2a] can assume the simplified expression of Eqn. (2), where k is the pseudo first order rate constant (as the monolayer surface concentration of oxidant sites should be high and nearly constant) and C is the equilibrium concentration of the substrate in the solution, that can be approximated to the starting substrate concentration (C_o) if the conversion is low.

$$\text{Rate} = kKC/(1+KC) \qquad (2)$$

The fact that the K values are not changed by the ring substituent in these two series of benzyl derivatives (alcohols and α-methyl alcohols) indicates that the contribution of K can be removed from the rate comparison of two alcohols of the same series in equimolar amounts. The determined k_{rel} values[6] can therefore be interpreted as an intrinsic reactivity comparison ($k_{rel}=k_H/k_X$). A confirmation of the reliability of our hypothesis can be obtained by comparing the limit quantum yield (intrinsic reactivity) ratio (2.3) relative to the colloidal TiO_2-sensitised photooxidation of alcohols **1a** and **1b**[8] and k_{rel} (2.6) obtained in this paper by a competitive experiment relative to the oxidation of the two alcohols photosensitised by powdered TiO_2.

Experimental

^{1}H-NMR spectra were measured on a Bruker AC 200 (200 MHz) spectrometer. GC analyses were carried out on a HP 5890 gas-chromatograph. HPLC analyses were performed with a liquid chromatograph HP 1100.

"Dark" adsorption equilibrium constants. Equilibrium constants (K) of benzylic derivatives onto TiO_2 (Degussa P-25, particle concentration 20 g dm^{-3}) in CH_3CN (HPLC grade) were evaluated using different initial substrate concentrations (C_o) at room temperature (temperature was not controlled because it is reported[9] that K value is not significantly influenced in the range 22-40°C). The equilibrium concentrations values (C) were obtained (by HPLC) after overnight equilibration of the shaken suspensions and filtration (through Millipore filters) as reported.[4] Each K value corresponds to the average of two or three determinations.

Photochemical oxidation. A solution of alcohol **1a** or **1b** (1.0×10^{-2} M) in CH_3CN (20 ml) containing 22 mg of TiO_2 (P25) was stirred for *ca* 1h at room temperature in the dark and then externally irradiated using a Helios Italquartz 500 W high pressure mercury lamp (through Pyrex filter). The semiconductor 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 ether. The exclusive reaction products, 4- or 3-methoxybenzaldehyde respectively, were observed by ^{1}H NMR and GC analysis of the crude.

Competitive experiments. The kinetic experiments were performed at 25°C by irradiating (Applied Photophysics multilamp photochemical reactor, $\lambda=355\pm20$ nm) the mixtures containing 11 mg of TiO_2 and 0.10 mmoles of **1a** + **1b** (equimolar amounts) in CH_3CN (10 ml, HPLC grade). The amounts of the two benzaldehydes were determined by GC with respect to an internal standard at different times and the values were inserted into a suitable kinetic equation.[10] The reported k_{rel} value is the average of three determinations.

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