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Titanium dioxide photosensitised oxidation of α,β-dihydroxybenzyl derivatives in CH_3CN☆

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Abstract

The TiO_2-photosensitised oxidation in CH_3CN of a series of 1-(X-phenyl)-1,2-ethanediols (**1**) and of 2-(X-phenyl)-1,2-propanediols (**2**) gives the corresponding benzaldehyde and acetophenone, respectively, accompanied by formaldehyde, whereas a series of symmetrically X-ring-substituted 1,2-diphenyl-1,2-ethanediols (**3**) yields the corresponding benzaldehyde (substrate/product molar ratio = 0.5). The adsorption constant values (2400–3900 M^{-1}) are significantly higher than those of benzylic alcohols and can be explained by assuming that the TiO_2 surface adsorption occurs through both OH groups (chelation effect). The relative rates, determined for each series from competitive kinetic experiments, remained nearly constant when the oxidation potential increased, instead of decreasing as observed in homogeneous phase. This behaviour has been attributed to the preferential adsorption of the OH groups, that increases their oxidizability until they favourably compete, as regards electron abstraction, with the aromatic site. The reaction rate thereby becomes much less sensitive to the ring substituent effect. Based on the comparison of true quantum yield values (obtained in the photo-oxidation in the presence of colloidal TiO_2) of ring unsubstituted **1** and **2**, the deprotonation pathway of the cation radical was excluded. Analogous to what happens with 2-aminoalcohol radical cations, the most probable path is a heterolytic, concerted and base-catalysed (by basic sites at the TiO_2 surface) C_α–C_β fragmentation that produces a radical and a final product (carbonyl compound).

Keywords: TiO_2; Photo-oxidation; 1,2-Diols

1. Introduction

Useful information about the TiO_2-sensitised photodegradation pathways involved in the mineralization of organic pollutants in waste water can be obtained by a mechanistic investigation of the primary oxidation steps of the substrate preadsorbed onto the semiconductor surface [1].

A suitable approach that we have considered in the case of benzylic derivatives [2] (arenes, alcohols, ethers, silanes and sulfides) as pollutant models, has involved the use of CH_3CN as reaction medium because this solvent, unlike water, (i) is suitable for dissolving organic substrates, (ii) is inert under the experimental organic conditions used and (iii) allows more reliable data to be obtained from some analytical methods (substrate adsorption constant measurements, quantum yield determinations and current yield measurements). This approach is justified because we have observed [3] that, at least for benzylic derivatives, the products and the mechanism relative to the primary oxidation steps (electron transfer from the substrate to the photogenerated positive hole and fragmentation of the radical cation intermediate) are the same as in water.

In this paper, we perform a mechanistic study on the TiO_2 sensitised photo-oxidation in CH_3CN of three series of benzylic diols (1-aryl-1,2-ethanediols, **1a**–**c**, 2-aryl-1,2-propanediols, **2a**–**c**, and 1,2-diaryl-1,2-ethanediols, **3a**–**d**) that gives the corresponding carbonyl compounds as fragmentation products.

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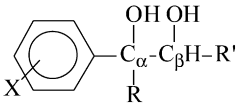


	X	R	R'
1a	H	H	H
1b	3-CH_3O	H	H
1c	4-CF_3	H	H
2a	H	CH_3	H
2b	3-CH_3O	CH_3	H
2c	4-CF_3	CH_3	H
3a	H	H	Ph
3b	4-CH_3O	H	4-CH_3OPh
3c	3-CH_3O	H	3-CH_3OPh
3d	4-CF_3	H	4-CF_3Ph

The objective of this paper is to systematically investigate, in this organic medium, the mechanism of C_α–C_β breaking of benzylic 1,2-diols in relation to the heterogeneous phase. To achieve this purpose, the products were analyzed, the adsorption equilibrium constants of the substrates on TiO_2 were determined and the relative reactivity (competitive kinetic experiments) and absolute rates (quantum yield determinations) of the photo-oxidation reaction were measured.

It must be observed that this C_α–C_β fragmentation reaction could be a crucial and favorable pathway towards the mineralization of benzylic 1,2-diols, as pollutant models in waste water. Therefore, the data collected in this work can give useful suggestions for mechanistic studies performed with these substrates in aqueous medium.

2. Experimental

^1H NMR spectra were run on a Bruker AC 200 (200 MHz) spectrometer, with solutions in $CDCl_3$ with TMS as internal standard. GC–MS analyses were performed on a Hewlett Packard 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 5890 gas-chromatograph using a HP-Innovax capillary column, 15 m. UV–vis 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). HPLC analyses were performed with a liquid chromatograph HP 1100.

2.1. Starting materials

TiO_2 (P25, 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), were commercial samples. $LiClO_4$ was an analytical grade commercial product. 1-Phenyl-1,2-ethanediol (**1a**), 2-phenyl-1,2-propanediol (**2a**), 1,2-diphenyl-1,2-ethanediol (**3a**), (*S*,*S*)-(−)-1,2-diphenyl-1,2-ethanediol (*S*,*S*-**3a**), *meso*-1,2-diphenyl-1,2-ethanediol (*meso*-**3a**) were commercial samples. 1-[4-(Trifluoromethyl)phenyl]-1,2-ethanediol [4], 1-(3-methoxyphenyl)-1,2-ethanediol [4a,5], 2-[4-(trifluoromethyl)phenyl]-1,2-propanediol [4a,6], 2-(3-metoxyphenyl)-1,2-propanediol [4a,6], 1,2-bis(3-metoxyphenyl)-1,2-ethanediol [6], 1,2-bis(4-metoxyphenyl)-1,2-ethanediol [6], 1,2-bis[4-(trifluoromethyl)phenyl]-1,2-ethanediol [7] were prepared and characterised as described in the literature.

2.2. Adsorption equilibrium constants

Equilibrium constants (*K*) of benzylic derivatives on 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, see Eq. (3)) at room temperature (temperature was not controlled because it is reported [8] that *K* value is not significantly influenced in the range 22–40 °C). The equilibrium concentration values (*C*, see Eq. (3)) were obtained (by HPLC) after overnight equilibration of the shaken suspensions and filtration (through Millipore filters) as reported [9]. Each *K* value corresponds to the average of two or three determinations.

2.3. Photochemical oxidation

For the heterogeneous TiO_2 sensitised photo-oxidation, a solution of the substrate (1.0×10^{-2} M) in 10 ml of the reaction medium (CH_3CN) containing 11 mg of TiO_2 (P25) was stirred for ca. 1 h at room temperature in the dark; at this time, as previously reported for benzyl alcohol [9], the adsorption equilibrium for the considered diols was reached within the experimental error (10%). The mixture was 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 organic extract was concentrated under vacuum giving an oil (crude).

For the homogeneous DCA sensitized photo-oxidation, the substrate (0.10 mmoles) was dissolved in 10 ml of a solution containing DCA in CH_3CN (4×10^{-4} M). The resulting solution was irradiated and the reaction mixture was worked up as above.

2.4. Reaction product analysis

The reaction products were identified directly from the crude by comparison of ^1H NMR and GC analysis data with those of the commercial samples (acetophenone, 3-methoxyacetophenone, 4-trifluoromethylacetophenone, 4-methoxybenzaldehyde, 3-methoxybenzaldehyde, benzaldehyde, and 4-trifluoromethylbenzaldehyde). Formaldehyde was recognized as dimedone adduct [MS *m*/*z* (rel intensity) 292 M^+, 191, 165(100), 124, 97, 83, 69, 55].

2.5. Competitive experiments

For the heterogeneous TiO_2 sensitised photo-oxidation, the kinetic experiments were performed at 25 °C by irradiating (as above) the mixtures containing 11 mg of TiO_2, and 0.10 mmoles of the two substrates (equimolar amounts) in 10 ml of the reaction medium (CH_3CN).

For the homogeneous DCA sensitized photo-oxidation, the two substrates (0.10 mmoles, equimolar amounts) were dissolved in 10 ml of a solution containing DCA in CH_3CN (4×10^{-4} M). The resulting solution was irradiated as above.

The amounts of the products (benzaldehydes or acetophenones) 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.

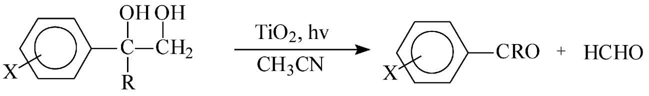
2.6. Quantum yield determinations

To prepare 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.

A spectrophotometric cuvette (optical path = 4.00 cm) containing a suitable substrate ($2–50 \times 10^{-3}$ M) in a colloidal solution of TiO_2 in CH_3CN, 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). The mixture was irradiated under magnetic stirring until ≤5% substrate conversion (up to ca. 20 min). The product formation was determined by GC analysis (bibenzyl as an internal standard). Light intensity was measured by ferrioxalate actinometry (15×10^{-9} einstein s^{-1}). Only the experiments with quantitative material recovery were considered.

3. Results and discussion

The TiO_2-photosensitised oxidation of 1,2-diols **1a–c** and **2a–c** gave C_α–C_β fragmentation products, the corresponding benzaldehyde and acetophenone, respectively, accompanied by formaldehyde in all cases (Eq. (1)). The presence of formaldehyde was proved by the formation of its dimedone adduct.



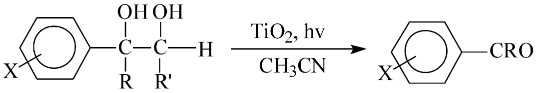
X= H, 3-OCH_3, 4-CF_3; R= H, CH_3

(1)

As reported in Table 1, the material recovery (substrate + benzylic carbonyl compound) was nearly quantitative (~90%).

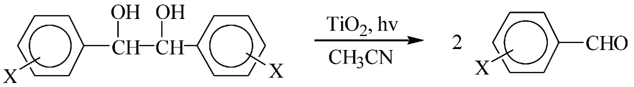
The corresponding benzaldehyde was obtained from 1,2-diaryl-1,2-ethanediols **3a–d** with a nearly quantitative material recovery (~90%, Table 1) when the reaction stoichiometry in Eq. (2) was considered.

Table 1
X-PhCRO yield in the TiO_2-sensitised photo-oxidation of 1,2-diols in CH_3CN



Substrate	*t* (min)	Unreacted substrate (%)	X-PhCRO yield (%)
1a	15	70	28
1b	25	70	22
1c	10	87	6
2a	15	72	17
2b	25	75	25
2c	35	54	36
3a	30	74	15[a]
3b	15	77	11[a]
3c	30	34	55[a]
3d	15	72	20[a]

[a] According to the X-Ph-CRO/substrate stoichiometry (2/1) the reported yield is half of the measured one.



(2)

3.1. Adsorption equilibrium constants

The adsorption constants (*K*) of **1a–c**, **2a**, *S*,*S*-**3a** and *meso*-**3a** on TiO_2 as powder dispersed in CH_3CN are reported in Table 2. The *K* values were determined by a Langmuir-type treatment, using an equation (Eq. (3)) suggested by Hiemens [11] which assumes the formation of a monolayer at the TiO_2 surface by the competitive adsorption of CH_3CN and the considered diol.

$$\frac{C}{n} = \frac{1}{K n_{\text{sat}}} + \frac{C}{n_{\text{sat}}} \qquad (3)$$

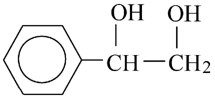
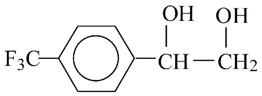
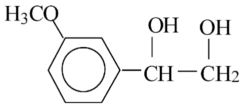
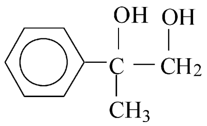
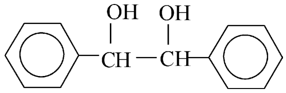
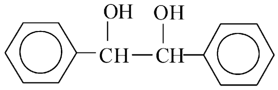
In Eq. (3), *C* is the equilibrium bulk donor concentration, $n = V(C_o - C)/W$ is the number of moles of the substrate adsorbed per gram of TiO_2 (in the expression, C_o is the substrate concentration, *V* the volume of the solution and *W* is the weight of TiO_2) and n_{sat} is the maximum number of substrate moles that can be adsorbed per gram of TiO_2.

From the linear plot *C*/*n* versus *C* (see, for example, Fig. 1 relative to **1a**) it is possible to determine the “dark” adsorption constant as the slope/intercept ratio.

The *K* values of the diols (2400–3900 M^{-1}) are higher than those observed [12] for benzyl alcohols (500–700 M^{-1}). This behaviour can be explained by assuming that the preferential adsorption of these 1,2-diols onto the semiconductor surface occurs, as for alcohols, through the lone pair of the oxygen atom of the OH group [2g,12], but it is stronger because both vicinal OH groups are involved (chelation effect, Fig. 2).

As observed for benzyl alcohols [12], the *K* value is not influenced by the introduction of the substituents on the ring (entries 1–3 in Table 2) because the adsorption efficiency (through the OH groups) does not depend on the electronic effect of the far

Table 2
Adsorption equilibrum constants (K) of some 1,2-diols on TiO_2 in CH_3CN

Entry	Substrate	$K \times 10^3$ (M^{-1})
1		3.9 ± 0.3
2		3.5 ± 0.3
3		3.3 ± 0.3
4		2.5 ± 0.2
5	 (S,S)	2.4 ± 0.2
6	 (meso)	2.7 ± 0.2

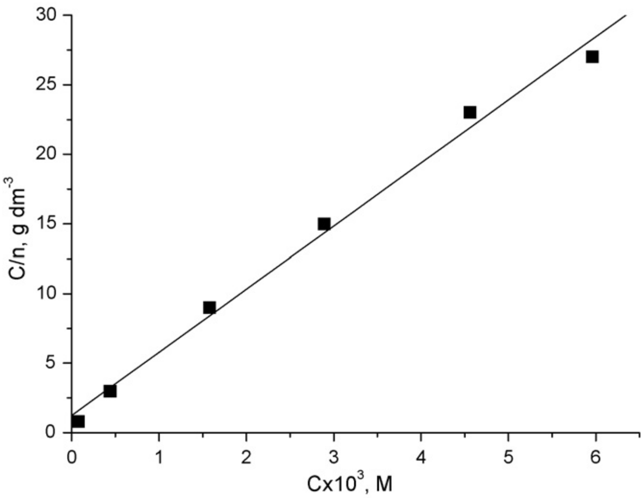


Fig. 1. Isotherm for adsorption of 1-phenyl-1,2-ethanediol (**1a**) onto TiO_2 from CH_3CN solution.

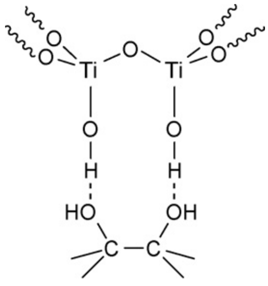


Fig. 2. Chelation effect in the adsorption of 1,2-diols onto the TiO_2 surface.

ring substituent. On the contrary, the introduction of another group (methyl or phenyl) at the carbon linked to the OH lowers the K value (compare entry 1 with entries 4, 5 and 6), due to the steric hindrance of this group near the adsorption site. It must be noted that *S,S*-**3a** and *meso*-**3a** have the same K values and, therefore, the stereoisomerism does not influence the adsorption.

3.2. Competitive kinetic experiments

The relative rates of the diols **1a–c**, **2a–c** and **3a–d** (diastereoisomeric mixtures), determined through the kinetic competitive method, are reported in Table 3. The k_X/k_H values do not change with time within the experimental error (see note a, Table 3). To determine the k_X/k_H value of **3a–d**, it was not necessary to prepare pure diastereoisomers of **3b–d** because the relative reactivity of *meso*-**3a**, *S,S*-**3a** and **3a** (commercial samples) versus **3b** was the same, within the experimental error (see Table 3). The E_p values of the above substrates, determined by cyclic voltammetry measurements, are also reported in Table 3. It must be noted that the relative reaction rate for the three series does not significantly change when the oxidation potential of the substrates increases. This behaviour does not seem to be in line with a kinetically significant single electron transfer step, where the rate decreases linearly as the oxidation potential increases (endothermic zone of the Marcus–Rhem Weller equation) [13]. The rate independence from the oxidation potential was already observed in the TiO_2-photosensitised oxidation of benzyl alcohols [2f] and ethers [2g], but only for substrates having ring substituents with a sufficiently high electron-withdrawing effect (X = 3- or 4-CF_3). This behaviour has been attributed to the preferential adsorption of the OH group at the semiconductor surface, that increases the oxidizability of this group [2c,2f,14]. In this way, OH can favourably compete, as regards electron abstraction, with scarcely oxidizable aromatic sites (X = 3- or 4-CF_3) and, therefore, the reaction rate becomes much less sensitive to the ring substituent effect.

In the case of diols, this behaviour was observed for all of the X-substituents within the three series of substrates and can be

Table 3
Relative rate (k_X/k_H) of 1,2-diols **1**, **2** and **3** (diastereoisomeric mixture) in the TiO_2-sensitised photo-oxidation in CH_3CN

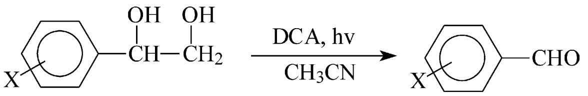
Substrate	k_X/k_H[a]	E_p (vs. SCE)[b]
1a	1.0	2.12
1b	0.9	1.65
1c	0.9	2.64
2a	1.0	2.15
2b	1.0	1.63
2c	1.3	2.60
3a	1.0	2.10
3b	1.7[c]	1.30
3c	1.3	1.52
3d	0.8	2.55

[a] As the medium value (maximum error ± 10%) among the determinations at different times (10, 20 and 30 min).

[b] Determined by cyclic voltammetry measurements in $CH_3CN/LiClO_4$.

[c] This value is also obtained from the comparison of **3b** with *S,S*-**3a** or *meso*-**3a**.

Table 4
X-PhCHO yield in the photo-oxidation of 1-aryl-1,2-ethanediols sensitised by 9,10-dicyanoanthracene (DCA), in CH_3CN



Substrate	*t* (min)	Unreacted substrate (%)	X-PhCHO yield (%)
1a	20	76	14
1b	20	5	91
1c	180	86	3

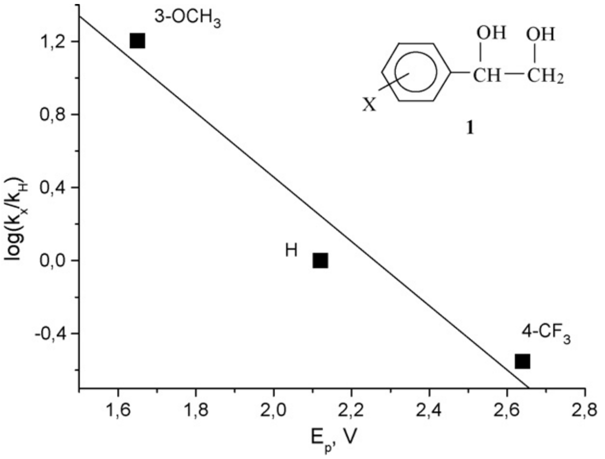
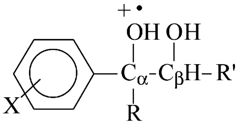


Fig. 3. Plot of log(k_X/k_H) vs. E_p for the photo-oxidation of 1-aryl-1,2-ethanediols sensitised by 9,10-dicyanoanthracene (DCA) in CH_3CN.

ascribed to the fact that the adsorption constant, higher than that of the alcohols (see Section 3.1), indicates a strong decrease in the oxidation potential of the OH group until it favourably competes, concerning the electron abstraction, even with aromatic sites with strong electron-donor substituents (the most oxidizable within the series).

The involvement of adsorption phenomena in this photo-oxidative process can be confirmed by comparing the kinetic results obtained in the photo-oxidation process sensitised in homogeneous phase by the electron transfer sensitizer 9,10-dicyanoanthracene (DCA) [15], with an excited state reduction potential (~2 V) [16] similar to that of $(TiO_2)_{h+}$ [17]. In particular, considering diols **1a–c** as substrates, it can be observed (Table 4) that the reaction quantitatively (material recovery ~90%) yields the same products as those obtained in heterogeneous phase, but with a relative reactivity (Fig. 3) that decreases, as expected, when the oxidation potential of the substrate increases. From these kinetic results, we can suggest that the TiO_2-sensitised oxidation involves the transfer of an electron from one of the two OH groups to the hole, $(TiO_2)_h$+, which produces cation radicals **4** and **5**.



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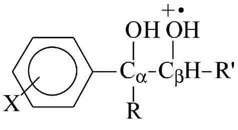

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3.3. Quantum yield measurements

While the radical cations from the diols **2a–c** should only react through C_α–C_β breaking, those from diols **1a–c** and **3a–c** (that have benzylic hydrogens) could undergo C_α–H or C_α–C_β fragmentation. However, in mechanistic studies of homogeneous electron transfer oxidations of benzylic 1,2-diols, it has been shown that only the second fragmentation path is operative [18]. To verify if this statement is also true in TiO_2 sensitised photo-oxidation, we compared the true quantum yields obtained from the reaction of **1a** and **2a**, in the presence of TiO_2 as transparent colloid. The observed quantum yield data (Φ) at different concentrations of **1a** or **2a** were treated using a Langmuir–Hinshelwood-type equation, from which a correlation between $1/\Phi$ and 1/[diol] was obtained [19]. From the relative plots, the true quantum yields (Φ_o, the reactivity at infinite substrate concentration, independent of the adsorption phenomena [19]) of the two diols were obtained (0.28 for **1a** and 0.12 for **2a**).

The Φ_o values were much higher than those of methoxybenzyl alcohols (0.08–0.04 [19a]). These results show that the benzylic diols are more reactive than the benzylic alcohols, not only because of the higher *K* value (see above), but also due to a higher intrinsic reactivity (Φ_o).

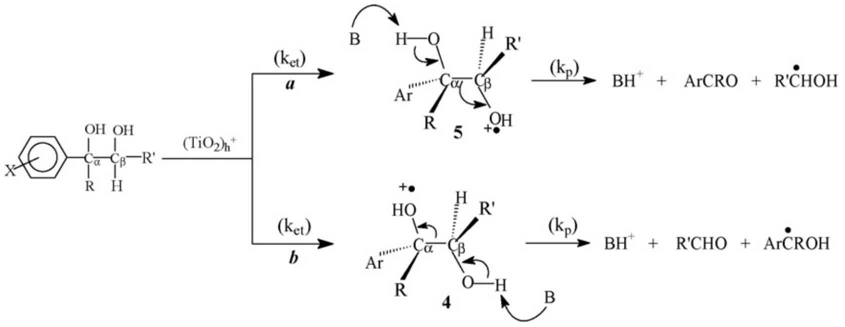
Considering that Φ_o can be expressed as a function of rate constants relative to a previously reported kinetic pattern [19], the Φ_o ratio of the two substrates can be expressed by Eq. (4). In this case, the $(\Phi_o)_{rel}$ value (0.4) is the k_p (cation radical fragmentation rate) ratio of the two compounds (**1a** and **2a**) because the k_{et} (electron transfer rate) and k_{-et} (back electron transfer rate) values should be similar due to a reasonably similar ionization potential of the OH group of the two adsorbed diols.

$$(\Phi_o)_{rel} = \frac{k_p^{CH_3} k_{et}^{CH_3} / k_{-et}^{CH_3}}{k_p^H k_{et}^H / k_{-et}^H} \qquad (4)$$

The determined $(\Phi_o)_{rel} \cong k_p^{CH_3}/k_p^H = 0.4$ suggests that k_p should be the rate of C_α–C_β cation radical fragmentation; in fact, a significant involvement of C_α–H fragmentation on the k_p for $\mathbf{1a}^{\bullet+}$ can be excluded because the $(\Phi_o)_{rel}$ value should be much lower than 0.4 ($\mathbf{2a}^{\bullet+}$ cannot undergo benzylic deprotonation).

3.4. Reaction mechanism

From the collected data, the suggested reaction mechanism (see Scheme 1) involves the formation of cation radical **4** and **5** with the positive charge and the unpaired electron located on an OH group. The most probable C_α–C_β fragmentation of these cation radicals should involve a heterolytic, concerted and base-catalysed (by basic sites at the TiO_2 surface [20]) process analogous to that of 2-aminoalcohol radical cations [21]. This step produces a radical fragment and a carbonyl compound as final product (Scheme 1). It must be observed that for asymmetric diols **1** and **2** (with R′ = H), the preferred path involves a radical cation **5** located at the β-OH group (via ***a*** in the Scheme 1), that yields a more stable carbonyl compound (the corresponding benzaldehyde and acetophenone, respectively).



Scheme 1.

Obviously, paths ***a*** and ***b*** are equivalent for the symmetric diols **3**.

The suitable conformation of C_α–C_β fragmentation of radical cation **5**, that results in the coplanarity of the two C–OH bonds in anti position, is reported in the Scheme 1.

This stereoelectronic requirement can also explain the slightly higher k_p value in the C_α–C_β fragmentation step for the reaction of **1a** with respect to that of **2a** ($k_p^{CH_3}/k_p^{H} = 0.4$). In fact, a methyl in the place of a hydrogen would make the conformation of the radical cation **5** from **2a** less stable than that from **1a**, thereby slowing the rate of C_α–C_β fragmentation and, consequently, slowing the whole process.

4. Conclusions

The mechanism of TiO_2 photosensitised oxidation of benzylic 1,2-diols in CH_3CN has been studied. From the collected data (product analysis, adsorption equilibrium constants, competitive kinetic experiments, quantum yields) we suggest that the reaction involves a SET process that is peculiar of heterogeneous medium. With all the considered substrates, the intermediate radical cation presents the positive charge and the unpaired electron located on an OH group rather than on the aromatic moiety, a thermodinamically more oxidizable site in homogeneous phase. Probably, the preferential adsorption of two OH groups at the TiO_2 surface (chelation effect) increases, with all the substrates, the oxidizability of this group in respect to the aromatic ring. The above radical cation should undergoe a heterolytic, concerted and base-catalysed (by basic sites at the TiO_2 surface) C_α–C_β fragmentation that directly produces a final product (benzylic carbonyl compound) together with a radical (from which the second carbonylic product is formed).

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