

# Early stages in the TiO<sub>2</sub>-photocatalyzed degradation of simple phenolic and non-phenolic lignin model compounds

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## Abstract

The TiO<sub>2</sub>-photocatalyzed degradation of phenolic and non-phenolic benzyl alcohols, which can be considered simple lignin model compounds has been studied in aqueous solution under a variety of conditions, with the aim of acquiring fundamental information on the early stages of the degradation process. The role of the electron scavengers O<sub>2</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and N<sub>2</sub>O on the degradation process as well as the influence of pH have been investigated. A major role in the degradation process is played by •OH and O<sub>2</sub>•<sup>-</sup>, while SO<sub>4</sub>•<sup>-</sup> plays a minor role. •OH plays a fundamental role in the conversion of non-phenolic substrates into phenolic ones, while O<sub>2</sub>•<sup>-</sup> exerts its role mainly by reacting with phenoxyl radicals to give aromatic ring-opening products. Addition of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as electron scavenger allows substantial substrate degradation also in the absence of O<sub>2</sub>, while N<sub>2</sub>O which is an excellent scavenger for the hydrated electron seems to be a very poor electron scavenger under the heterogeneous conditions employed. A general mechanistic scheme which proceeds through the formation of aromatic radical cations via one-electron oxidation of the neutral substrates by TiO<sub>2</sub>(h<sup>+</sup>), accounting for all the experimental observations has been proposed.

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## 1. Introduction

Lignin, a tridimensional amorphous phenolic polymer built from phenylpropane units linked together by different bonds, is amongst the most abundant biopolymers on earth, constituting approximately 30% of the dry weight of softwoods and 20% of hardwoods [1]. The chemical separation of lignin from cellulose is one of the key-processes of the pulp and paper industry, the aim being selective lignin degradation without damaging the carbohydrate components [2]. However, an ideal pulping process does not exist and all the current pulping methods represent a compromise between lignin removal and carbohydrate integrity (pulp yield versus pulp quality). Pulps as well as the effluents from the pulp processes require bleaching for many end uses: in fact the dark colour of pulps and waste waters is due to the presence of residual lignin and of its degradation products. Strong oxidants are required for the decomposition of these organic molecules: chlorine and compounds of chlorine have been the most widely used bleaching agents.

However, these reagents are toxic and since attention to cheap and environmentally friendly processes is growing, chlorine-free reagents such as oxygen, UV-illuminated hydrogen peroxide or a combination of ozone and peroxides have also been used [3,4].

An alternative approach to the degradation of residual lignin in pulps and pulp treatment effluents is based on heterogeneous photocatalysis, which seems to be more appealing than the conventional chemical oxidation methods because several semiconductors are inexpensive, non-toxic and capable of extended use without substantial loss of photocatalytic activity [5]. Semiconductors are characterized by a series of closely spaced energy levels associated with covalent bonding between atoms (the valence band) and a second series of spatially diffuse, energetically similar levels lying at higher energy and associated with conduction (the conduction band). The magnitude of the fixed energy gap between the electronically populated valence band and the vacant conduction band governs the extent of thermal population of the conduction band and also defines the wavelength sensitivity of the semiconductor to irradiation. Photoexcitation with light of energy greater than the band gap promotes an electron from the valence band to the conduction band, creating an electronic vacancy or "hole" (h<sup>+</sup>) at

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the valence band edge, a process which can be simply represented as described in Eq. (1) for TiO<sub>2</sub>, the most widely used semiconductor.



In order for photocatalysis to be productive, electron–hole pair recombination (the reverse of Eq. (1)) must be suppressed. This can be accomplished by trapping either the photogenerated electron or the photogenerated hole. Since the position of the valence band of TiO<sub>2</sub> is very high (3.1 V/SCE) [6], the photogenerated hole can oxidize a wide variety of organic substrates (S) to the corresponding radical cations (Eq. (2)).



The photogenerated electron is instead trapped by suitable acceptors (electron scavengers) A (Eq. (3)), the most widely used being O<sub>2</sub>, which forms the superoxide radical anion O<sub>2</sub><sup>•-</sup> [6].



Semiconductor photocatalysis has been widely employed for the degradation of organic compounds. Extensive work has shown that many organic pollutants or waste products can be completely decomposed (mineralized) on irradiated semiconductor suspensions [7]. In this context, semiconductor photocatalysis has also been successfully applied for the removal of residual lignin in pulp treatment effluents [8–17]. However, detailed mechanistic information on these processes is very limited. Since the complexity of the lignin polymer only seldom allows detailed mechanistic studies of these processes, the knowledge of lignin structural motifs makes possible the study of its reactivity by using suitable lignin model compounds, relatively simple molecules containing isolated functional groups and/or typical lignin bonding patterns [4]. Since amongst the bonding patterns present in lignin particularly abundant are the benzyl alcohol structures, constituting about 30% of the phenylpropane units [1], in this study the attention has been focused on phenolic and non-phenolic benzyl alcohols such as 1-(3,4-dimethoxyphenyl)ethanol (**1**), 3,4-dimethoxybenzyl alcohol (**2**), 3-hydroxy-4-methoxybenzyl alcohol (**3**) and 4-hydroxy-3-methoxybenzyl alcohol (**4**) (Plate 1), which can be considered very simple lignin model compounds.

The TiO<sub>2</sub>-photocatalyzed oxidation of substrates **1–4** has been studied under a variety of experimental conditions, with the aim of acquiring fundamental information on the early stages of the degradation process, the goal of this study being the development of a set of experimental conditions which allow the modulation of the lignin model compound degradation: from extreme conditions to milder ones, which, at least in principle, may be exploited for the selective degradation of lignin model compounds in the presence of carbohydrate molecules.

## 2. Experimental

Water was obtained from a Millipore Milli-Q system. TiO<sub>2</sub> was Degussa P-25, which consists of 75% anatase and 25% rutile. Commercial samples of the highest purity available of 3,4-dimethoxybenzyl alcohol (**2**), 3-hydroxy-4-methoxybenzyl alcohol (**3**), 4-hydroxy-3-methoxybenzyl alcohol (**4**), 3,4-dimethoxyacetophenone (**5**), 3,4-dimethoxybenzaldehyde (**10**), HClO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10 H<sub>2</sub>O and Ba(OH)<sub>2</sub> were used as received.

1-(3,4-dimethoxyphenyl)ethanol (**1**) was prepared by reduction of the corresponding ketone with NaBH<sub>4</sub> in 2-propanol, purified by column chromatography (silica gel, eluent hexane/ethyl acetate 3:1) and identified by GC/MS. GC/MS *m/z* (relative abundance): M<sup>+</sup> 182, 167, 164, 149, 139 (100), 124, 108, 103, 91, 77, 65, 51.

GC analyses were performed on a Varian 3800 gas chromatograph (CP-Sil 5 CB capillary column, 30 m × 0.25 mm). GC–MS analyses were performed on a Shimadzu GC-17A gas chromatograph (Supelco MDN-5S capillary column 30 m × 0.25 mm) coupled with a QP-5000 mass spectrometer.

Steady-state photolysis was carried out employing a Photochemical Multirays Reactor (Helios Italquartz) equipped with 10 × 15 W lamps with emission maximum at λ = 365 nm. The reactor was a cylindrical glass flask equipped with a water cooling jacket thermostatted at 25 °C, which ensured cut off of the UV radiation at λ < 320 nm. In a typical experiment, the heterogeneous mixture containing the substrate (0.03 mmol), TiO<sub>2</sub> (13 mg) in H<sub>2</sub>O (5 ml, pH 3, 7 or 10 employing 0.001 M HClO<sub>4</sub>, 0.001 M phosphate buffer or 0.01 M borate buffer, respectively) was stirred for 30 min in the dark before irradiation to achieve complete adsorp-

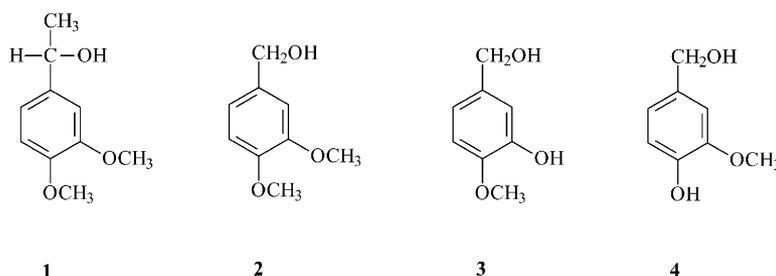


Plate 1.

tion of the substrate on the catalyst's surface. Irradiation was then performed at  $\lambda = 365$  nm ( $10 \times 15$  W lamps) under  $O_2$ ,  $N_2$  or  $N_2O$  bubbling. Irradiation times were varied between 15 and 90 min. After paper filtration of  $TiO_2$ , the reaction mixture was acidified, poured into water and extracted with ether ( $3 \times 10$  ml portions). Reaction products were identified by GC and by GC–MS (comparison with authentic specimens). The unreacted substrate and the reaction products were quantitatively determined by GC analysis in the presence of an internal standard (1,2,4-trimethoxybenzene or 3,4-methylenedioxybenzyl alcohol). Blank experiments were carried out under every condition showing negligible substrate consumption.

Evidence for  $CO_2$  formation was obtained by bubbling the gas stream passing through the solution under irradiation into a saturated  $Ba(OH)_2$  aqueous solution, through the formation of a white  $Ba(CO_3)_2$  suspension.

### 3. Results

As mentioned above, electron–hole pair recombination must be avoided in order for photocatalysis to be productive. An efficient trapping of the electron (Eq. (3)) makes possible the reaction of  $TiO_2$  ( $h^+$ ) with the substrate (Eq. (2)). Accordingly, experiments carried out for **1** and **2** at pH 7 under  $N_2$ , in the absence of an electron scavenger, showed that after 90 min negligible substrate consumption had occurred, indicating that under these conditions substrate oxidation does not compete significantly with electron–hole pair recombination. An observation that also suggests that hydroxyl radical formation by electron–hole oxidation of water is likely to play a minor role in substrate degradation [3,18]. Oxygen ( $O_2$ ), potassium peroxydisulfate ( $K_2S_2O_8$ ) or nitrous oxide ( $N_2O$ ) have thus been used as electron scavengers, all of them leading, after reaction with the electron, to reactive species which may be involved in the degradation process.

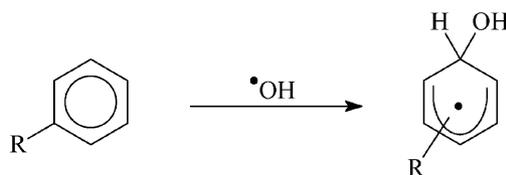
Reaction of the electron with oxygen leads to the formation of the superoxide radical anion  $O_2^{\bullet-}$  (Eq. (4)), an oxidizing agent [19,20], which is known to promote aromatic ring-opening of phenols via addition to intermediate phenoxyl radicals [4,21].



Reaction of the electron with  $K_2S_2O_8$  leads to the formation of  $SO_4^{\bullet-}$  (Eq. (5)), a very strong one-electron oxidant which is known to react with aromatic compounds to give the corresponding radical cations (Eq. (6)) [22–25].



Reaction of the electron with  $N_2O$  leads to the formation of  $N_2$  and of a hydroxyl radical ( $\bullet OH$ ) (Eq. (7)) [26].



Scheme 1.

$\bullet OH$  is a strong oxidizing species ( $E = 2.32$  V/NHE at pH 7), but in spite of its high oxidizing power, it reacts preferentially by addition to electron-rich aromatic moieties [27].  $\bullet OH$  addition leads to the formation of hydroxycyclohexadienyl radicals (Scheme 1), which may then undergo a variety of reactions, the most important being hydroxylation and, with ring-methoxylated substrates, demethoxylation.

It is thus possible, at least in the early stages of the photocatalyzed degradation<sup>1</sup> to modulate the reaction conditions in order to selectively generate one or more of these reactive species ( $O_2^{\bullet-}$ ,  $SO_4^{\bullet-}$ ,  $\bullet OH$ ), and thus try to establish their relative role in the degradation process.

#### 3.1. Photocatalyzed degradation of non-phenolic substrates

##### 3.1.1. 1-(3,4-Dimethoxyphenyl)ethanol (**1**) and 3,4-dimethoxybenzyl alcohol (**2**)

The  $TiO_2$ -photocatalyzed oxidation of substrates **1** and **2** was initially studied in the presence of  $O_2$  at pH 3 and 7. Under these conditions, the oxidation of **1** led to the formation of 3,4-dimethoxyacetophenone (**5**) as the major product accompanied by smaller amounts of phenolic benzyl alcohols (1-(3-hydroxy-4-methoxyphenyl)ethanol (**6**) and 1-(4-hydroxy-3-methoxyphenyl)ethanol (**7**)) and ketones (3-hydroxy-4-methoxyacetophenone (**8**) and 4-hydroxy-3-methoxyacetophenone (**9**)). The results are summarized in Table 1.

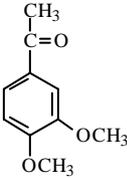
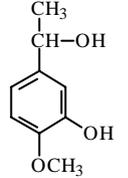
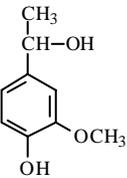
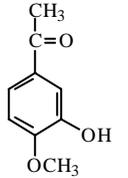
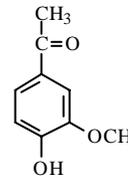
Similar results were obtained when **2** was irradiated under analogous experimental conditions: 3,4-dimethoxybenzaldehyde (**10**) was formed as the major product together with smaller amounts of the phenolic alcohols (3-hydroxy-4-methoxybenzyl alcohol (**3**) and 4-hydroxy-3-methoxybenzyl alcohol (**4**)) and aldehydes (3-hydroxy-4-methoxybenzaldehyde (**11**) and 4-hydroxy-3-methoxybenzaldehyde (**12**)).

Interestingly, the results of Table 1 show that significant material loss was observed in all experiments, the mass balance being around 10% after 90 min of irradiation at pH 7.

Experiments carried out bubbling the stream of oxygen passing through the solution under irradiation into a saturated  $Ba(OH)_2$  aqueous solution showed the formation of  $Ba(CO_3)_2$  (indicative of  $CO_2$  formation) after approximately

<sup>1</sup> Sufficiently long irradiation times may increase the importance of additional pathways for the generation of reactive oxygen species leading to a more complex mechanistic picture. See ref [18].

Table 1  
TiO<sub>2</sub>-photocatalyzed oxidation of **1** in the presence of O<sub>2</sub> at T = 25 °C<sup>a</sup>

Irradiation time (min)	pH	Recovered substrate (μmol)	Mass balance (%)	Reaction products <sup>b</sup>				
				 ( <b>5</b> ) (μmol)	 ( <b>6</b> ) (μmol)	 ( <b>7</b> ) (μmol)	 ( <b>8</b> ) (μmol)	 ( <b>9</b> ) (μmol)
30	7	7.3 (24%)	33	1.8	–	0.4	–	0.3
90	7	1.2 (4%)	11	1.6	0.1	0.2	0.1	0.2
90	3	4.5 (15%)	23	1.7	–	0.4	–	0.4
90 <sup>c</sup>	7	1.3 (4%)	7	0.5	0.1	0.1	0.1	0.1

<sup>a</sup> [Substrate] = 0.006 M, [TiO<sub>2</sub>] = 2.6 g l<sup>-1</sup>, λ<sub>irr</sub> = 365 nm.

<sup>b</sup> Error ≤ 10%.

<sup>c</sup> In the presence of 0.006 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

30 min of irradiation. No attempt was, however, made to quantitatively determine CO<sub>2</sub>.

O<sub>2</sub> was then replaced by N<sub>2</sub>, and the TiO<sub>2</sub>-photocatalyzed oxidation of substrates **1** and **2** was studied at pH 3, 7 and 10. In all these experiments 0.006 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added since, as mentioned above, no reaction takes place in the absence of a suitable electron scavenger. Under these conditions, the photocatalyzed oxidation of **1** led to the formation of the same products observed under an O<sub>2</sub> atmosphere (**5–9**, see Table 1) but significantly lower substrate consumptions and higher mass balances were observed (Table 2). Interestingly, a slight decrease in mass balance was observed as the pH was increased, changing, for example, after 30 min of irradiation, from 81% (pH 3) to 71% (pH 10).

Similar results were obtained when **2** was irradiated under analogous experimental conditions (see above).

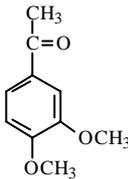
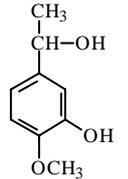
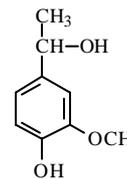
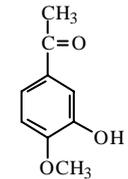
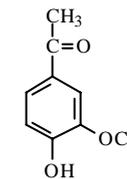
Also under these conditions some experiments were carried out bubbling the stream of nitrogen passing through the

solution under irradiation into a saturated Ba(OH)<sub>2</sub> aqueous solution. Formation of Ba(CO<sub>3</sub>)<sub>2</sub> (indicative of CO<sub>2</sub> formation) was observed after approximately 90 min of irradiation. Again, no attempt was made to quantitatively determine CO<sub>2</sub>.

Under these conditions, the effect of the concentration of electron scavenger (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) was also studied. The results of the TiO<sub>2</sub>-photocatalyzed oxidation of **1** under N<sub>2</sub> at pH 3 and 7, in the presence of different K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentrations (between 0.006 and 0.06 M) are collected in Table 3. Interestingly, a decrease in mass balance is observed, both at pH 3 and 7, by increasing K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration.

In order to investigate the possible role played by •OH in the degradation process, some experiments were carried out in the presence of N<sub>2</sub>O (see Eq. (7)). The TiO<sub>2</sub>-photocatalyzed oxidation of **1** was thus studied at pH 3 and 7, in the absence or presence of added K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.006 M). The results are collected in

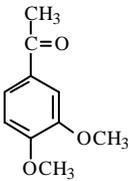
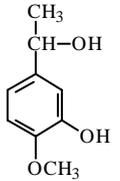
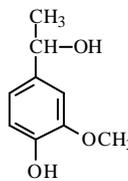
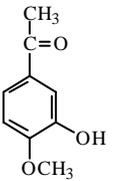
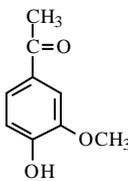
Table 2  
TiO<sub>2</sub>-photocatalyzed oxidation of **1** in the presence of N<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, at different pH values<sup>a</sup>

pH	Irradiation time (min)	Recovered substrate (μmol)	Mass balance (%)	Reaction products <sup>b</sup>				
				 ( <b>5</b> ) (μmol)	 ( <b>6</b> ) (μmol)	 ( <b>7</b> ) (μmol)	 ( <b>8</b> ) (μmol)	 ( <b>9</b> ) (μmol)
10	30	19.3 (64%)	71	0.9	0.4	0.4	0.1	–
10	90	15.2 (51%)	63	1.5	1.0	0.9	0.3	–
7	30	21.3 (71%)	77	0.7	0.5	0.5	Traces	Traces
7	90	16.3 (54%)	69	1.5	1.2	1.2	0.2	0.2
3	30	20.2 (67%)	81	1.9	1.0	0.9	0.2	0.2
3	90	14.0 (47%)	74	2.4	1.7	1.9	0.4	0.4

<sup>a</sup> [Substrate] = 0.006 M, [TiO<sub>2</sub>] = 2.6 g l<sup>-1</sup>, [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 0.006 M, λ<sub>irr</sub> = 365 nm, T = 25 °C.

<sup>b</sup> Error ≤ 10%.

Table 3  
Effect of  $K_2S_2O_8$  concentration on the  $TiO_2$ -photocatalyzed oxidation of **1** in the presence of  $N_2$ , at pH 3 and 7<sup>a</sup>

pH	[ $K_2S_2O_8$ ] (M)	Recovered substrate ( $\mu\text{mol}$ )	Mass balance (%)	Reaction products <sup>b</sup>				
				 ( <b>5</b> ) ( $\mu\text{mol}$ )	 ( <b>6</b> ) ( $\mu\text{mol}$ )	 ( <b>7</b> ) ( $\mu\text{mol}$ )	 ( <b>8</b> ) ( $\mu\text{mol}$ )	 ( <b>9</b> ) ( $\mu\text{mol}$ )
7	0.006	16.3 (54%)	69	1.5	1.2	1.2	0.2	0.2
7	0.03	13.1 (44%)	61	2.3	1.2	1.2	0.3	0.3
7	0.06	11.7 (39%)	51	2.2	0.6	0.6	0.2	0.2
3	0.006	14.0 (47%)	74	2.4	1.7	1.9	0.4	0.4
3	0.06	11.5 (38%)	62	2.3	1.8	2.0	0.5	0.5

<sup>a</sup> [Substrate] = 0.006 M, [ $TiO_2$ ] =  $2.6\text{ g l}^{-1}$ , irradiation time = 90 min,  $\lambda_{\text{irr}}$  = 365 nm,  $T$  = 25 °C.

<sup>b</sup> Error  $\leq 10\%$ .

Table 4, and are directly compared with the results obtained in the corresponding experiments carried out in the presence of  $N_2$ , previously described in Tables 2 and 3.

### 3.1.2. 3,4-Dimethoxyacetophenone (**5**) and 3,4-dimethoxybenzaldehyde (**10**)

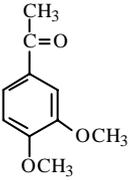
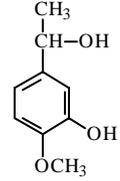
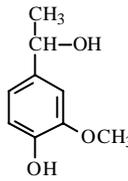
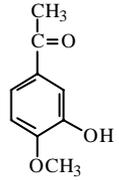
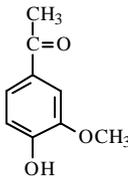
Since under all conditions the oxidation of **1** and **2** led to 3,4-dimethoxyacetophenone (**5**) and 3,4-dimethoxybenzaldehyde (**10**), respectively, as major products (see Tables 1–4), the oxidation of **5** and **10** was also studied. The results of the  $TiO_2$ -photocatalyzed oxidation of **5** and **10** under a variety of conditions are collected in Table 5.

The photocatalyzed oxidation of **5** was studied only in the presence of  $O_2$  at pH 7. Under these conditions, comparable amounts of 3-hydroxy-4-methoxyacetophenone

(**8**) and 4-hydroxy-3-methoxyacetophenone (**9**) were observed as exclusive products. Material loss was again observed, the mass balance decreasing from 78 to 61% by increasing irradiation time from 15 to 60 min, even though, as compared to the corresponding alcohol (**1**) the mass balance is now significantly higher (compare with Table 1).

The photocatalyzed oxidation of **10** was instead studied in the presence of  $O_2$  or  $N_2$  at pH 3 and 7. All experiments were carried out in the presence of 0.006 M  $K_2S_2O_8$ . Under all conditions 3-hydroxy-4-methoxybenzaldehyde (**11**) and 4-hydroxy-3-methoxybenzaldehyde (**12**), in comparable amounts, were observed as exclusive products. Significant material loss was observed also in these experiments, the mass balance decreasing by increasing pH and on going from  $N_2$  to  $O_2$ .

Table 4  
 $TiO_2$ -photocatalyzed oxidation of **1** at pH 3 and 7, in the presence of  $N_2$  or  $N_2O$ <sup>a</sup>

Gas	pH	Recovered substrate ( $\mu\text{mol}$ )	Mass balance (%)	Reaction products <sup>b</sup>				
				 ( <b>5</b> ) ( $\mu\text{mol}$ )	 ( <b>6</b> ) ( $\mu\text{mol}$ )	 ( <b>7</b> ) ( $\mu\text{mol}$ )	 ( <b>8</b> ) ( $\mu\text{mol}$ )	 ( <b>9</b> ) ( $\mu\text{mol}$ )
$N_2O$	3	26.9 (90%)	95	1.1	0.3	0.3	Traces	0.1
$N_2O^c$	3	15.5 (52%)	70	2.9	1.0	0.9	0.3	0.4
$N_2^c$	3	14.0 (47%)	74	2.4	1.7	1.9	0.4	0.4
$N_2O$	7	24.7 (82%)	94	2.2	0.6	0.5	Traces	Traces
$N_2O^c$	7	20.7 (69%)	78	0.8	0.9	0.9	0.1	Traces
$N_2^c$	7	16.3 (54%)	69	1.5	1.2	1.2	0.2	0.2

<sup>a</sup> [Substrate] = 0.006 M, [ $TiO_2$ ] =  $2.6\text{ g l}^{-1}$ , irradiation time = 90 min,  $\lambda_{\text{irr}}$  = 365 nm,  $T$  = 25 °C.

<sup>b</sup> Error  $\leq 10\%$ .

<sup>c</sup> In the presence of 0.006 M  $K_2S_2O_8$ .

Table 5

TiO<sub>2</sub>-photocatalyzed oxidation of 3,4-dimethoxyacetophenone (**5**) and 3,4-dimethoxybenzaldehyde (**10**) under a variety of conditions<sup>a</sup>

Substrate	Gas	[K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] (M)	pH	Irradiation time (min)	Recovered substrate (μmol)	Mass balance (%)	Reaction products <sup>b</sup>			
							( <b>8</b> ) (μmol)	( <b>9</b> ) (μmol)	( <b>11</b> ) (μmol)	( <b>12</b> ) (μmol)
<b>5</b>	O <sub>2</sub>	–	7	15	21.6 (72%)	78	0.8	0.9	–	–
<b>5</b>	O <sub>2</sub>	–	7	30	17.7 (59%)	66	1.0	1.1	–	–
<b>5</b>	O <sub>2</sub>	–	7	60	14.6 (49%)	61	1.8	1.8	–	–
<b>10</b>	N <sub>2</sub>	0.006	3	90	23.2 (77%)	85	–	–	1.0	1.9
<b>10</b>	N <sub>2</sub>	0.006	7	90	17.5 (58%)	61	–	–	0.4	0.4
<b>10</b>	O <sub>2</sub>	0.006	3	90	8.2 (27%)	37	–	–	0.9	1.9
<b>10</b>	O <sub>2</sub>	0.006	7	90	2.1 (7.0%)	10	–	–	0.4	0.5

<sup>a</sup> [Substrate] = 0.006 M, [TiO<sub>2</sub>] = 2.6 g l<sup>-1</sup>, λ<sub>irr</sub> = 365 nm, T = 25 °C.<sup>b</sup> Error ≤10%.

Table 6

TiO<sub>2</sub>-photocatalyzed oxidation of 3,4-dimethoxybenzyl alcohol (**2**), 3-hydroxy-4-methoxybenzyl alcohol (**3**) and 4-hydroxy-3-methoxybenzyl alcohol (**4**) at pH = 3<sup>a</sup>

Substrate	Gas	Irradiation time (min)	Recovered substrate (μmol)	Mass balance (%)	Reaction products <sup>b</sup>				
					( <b>10</b> ) (μmol)	( <b>3</b> ) (μmol)	( <b>4</b> ) (μmol)	( <b>11</b> ) (μmol)	( <b>12</b> ) (μmol)
<b>2</b>	O <sub>2</sub>	30	16.4 (54%)	70	4.2	0.2	–	0.2	0.1
<b>3</b>	O <sub>2</sub>	30	6.9 (23%)	27	–	–	–	1.2	–
<b>4</b>	O <sub>2</sub>	30	4.5 (15%)	21	–	–	–	–	1.7
<b>2</b>	N <sub>2</sub> <sup>c</sup>	90	15.9 (53%)	76	3.4	1.3	0.2	1.5	0.4
<b>3</b>	N <sub>2</sub> <sup>c</sup>	90	9.1 (31%)	41	–	–	–	3.3	–
<b>4</b>	N <sub>2</sub> <sup>c</sup>	90	7.4 (25%)	38	–	–	–	–	3.9

<sup>a</sup> [Substrate] = 0.006 M, [TiO<sub>2</sub>] = 2.6 g l<sup>-1</sup>, λ<sub>irr</sub> = 365 nm, T = 25 °C.<sup>b</sup> Error ≤10%.<sup>c</sup> In the presence of 0.006 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

### 3.2. Photocatalyzed degradation of phenolic substrates

#### 3.2.1. 3-Hydroxy-4-methoxybenzyl alcohol (**3**) and 4-hydroxy-3-methoxybenzyl alcohol (**4**)

The reactivity of 3,4-dimethoxybenzyl alcohol (**2**) was also compared with that of the corresponding phenolic alcohols 3-hydroxy-4-methoxybenzyl alcohol (**3**) and 4-hydroxy-3-methoxybenzyl alcohol (**4**). The results of the TiO<sub>2</sub>-photocatalyzed oxidation of **2**, **3** and **4** at pH 3 in the presence of O<sub>2</sub> or N<sub>2</sub> are collected in Table 6.

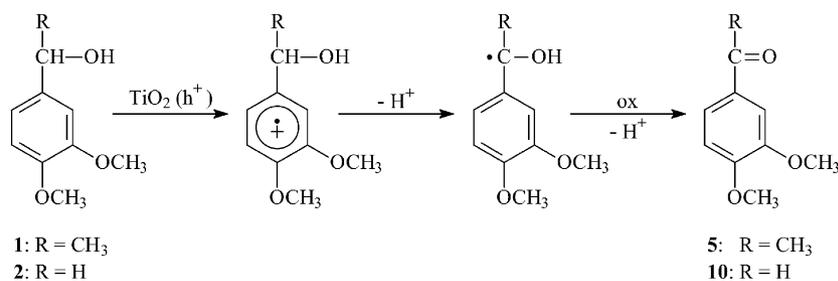
The results show that in the presence of both O<sub>2</sub> and N<sub>2</sub>, degradation of the phenolic alcohols **3** and **4** is significantly more pronounced than that of the non-phenolic alcohol **2**,

the mass balance being between 20 and 40% for **3** and **4** and around 70% for **2**.

## 4. Discussion

As clearly shown in Table 1, the photocatalyzed oxidation of **1** under an O<sub>2</sub> atmosphere both at pH 3 and 7 leads to the formation of 3,4-dimethoxyacetophenone (**5**) as the major product accompanied by 1-(3-hydroxy-4-methoxyphenyl)ethanol (**6**), 1-(4-hydroxy-3-methoxyphenyl)ethanol (**7**), 3-hydroxy-4-methoxyacetophenone (**8**) and 4-hydroxy-3-methoxyacetophenone (**9**).

3,4-Dimethoxyacetophenone (**5**) very likely derives from the deprotonation of an intermediate radical cation (**1**<sup>•+</sup>)



Scheme 2.

formed by oxidation of the substrate by  $\text{TiO}_2 (h^+)$  to give an  $\alpha$ -hydroxybenzyl-type radical which is then oxidized in the reaction medium to give ketone **5** (Scheme 2;  $\text{R} = \text{CH}_3$ ), in analogy with one-electron oxidations of arylalkanoles [28–33].

Similar results were obtained when **2** was irradiated under the same conditions: 3,4-dimethoxybenzaldehyde (**10**) was formed as the major product together with 3-hydroxy-4-methoxybenzyl alcohol (**3**), 4-hydroxy-3-methoxybenzyl alcohol (**4**), 3-hydroxy-4-methoxybenzaldehyde (**11**) and 4-hydroxy-3-methoxybenzaldehyde (**12**). Formation of 3,4-dimethoxybenzaldehyde (**10**) can be again rationalized on the basis of the involvement of an intermediate radical cation (Scheme 2;  $\text{R} = \text{H}$ ), as described above for **1** [23].

Formation of the phenolic products can be instead explained in terms of  $\cdot\text{OH}$  addition to the aromatic ring of the substrates (**1** or **2**), or of the primary oxidation products **5** and **10** [27], leading to the corresponding phenolic benzyl alcohols (**6** and **7** or **3** and **4**, respectively), acetophenones (**8** and **9**) and benzaldehydes (**11** and **12**). Accordingly, in the  $\text{TiO}_2$ -photocatalyzed oxidation of **5** and **10** described in Table 5, the only products observed were acetophenones **8** and **9** (from **5**) and benzaldehydes **11** and **12** (from **10**).

In the presence of  $\text{O}_2$ , significant material loss was observed for the oxidation reactions of both **1** and **2**, and clear evidence for the formation of  $\text{CO}_2$  (indicative of substrate mineralization) after 30 min of irradiation was obtained. On the basis of these observations and of the results of previous studies showing the formation of aromatic ring-opening products (aliphatic esters and acids) as degradation intermediates in the  $\text{TiO}_2$ -photocatalyzed degradation of dimethoxybenzenes in aqueous solution [34], compounds structurally related to **1** and **2**; the material loss observed after irradiation can be reasonably attributed to the formation of aromatic ring-opening products and, increasing irradiation time,  $\text{CO}_2$ .

In the  $\text{TiO}_2$ -photocatalyzed degradation of dimethoxybenzenes, it has been proposed that an important role in the formation of ring-opening products is played by  $\text{O}_2^{\bullet-}$  [35], formed according to Eq. (4), and a similar explanation can be reasonably extended also to the photocatalyzed oxidations of **1** and **2**.

The results of Table 1 also provide information on the effect of pH and of added  $\text{K}_2\text{S}_2\text{O}_8$  on the photocatalyzed degradation of **1**. Substrate consumption increases slightly by increasing pH (from 85 to 96% on going from pH 3 to 7). Since the amount of 3,4-dimethoxyacetophenone (**5**), formed by deprotonation of  $\text{1}^{\bullet+}$  (Scheme 2), appears to be pH independent (at least in the pH range between 3 and 7), the observed increase in substrate consumption can be tentatively interpreted in terms of the pH dependence of the reaction between  $\text{1}^{\bullet+}$  and  $\text{O}_2^{\bullet-}$  [35], which is favored on going from pH 3 to 7, based on the  $\text{pK}_a$  value of 4.7 for the equilibrium between  $\text{HO}_2^{\bullet}$  and  $\text{O}_2^{\bullet-}$  [19].

No significant difference was instead observed by addition of  $\text{K}_2\text{S}_2\text{O}_8$ , suggesting that under these conditions either  $\text{O}_2$  is a much better electron scavenger than  $\text{K}_2\text{S}_2\text{O}_8$  or that  $\text{SO}_4^{\bullet-}$  does not play a major role in the degradation process.

On the basis of these results, it appears that in the presence of  $\text{O}_2$  the  $\text{TiO}_2$ -photocatalyzed degradation of **1** and **2** is an extremely efficient process in line with previous studies where semiconductor photocatalysis was successfully applied for the mineralization of residual lignin in pulp treatment effluents [8–17]. However, due to this high reactivity, in pulp treatments selectivity is expected to be very low and thus lignin degradation is likely to be accompanied by extensive carbohydrate degradation, limiting the application of such system for the removal of lignin from pulp.

In order to find milder conditions for the degradation of substrates **1** and **2**, oxygen was replaced by nitrogen and  $\text{K}_2\text{S}_2\text{O}_8$  was added as electron scavenger. In the absence of oxygen, direct formation of  $\text{O}_2^{\bullet-}$ , according to Eq. (4), cannot occur and substrate degradation is expected to be less pronounced, even though, as mentioned above, indirect pathways for the formation of  $\text{O}_2^{\bullet-}$  cannot be excluded [18]. Under these conditions, the photocatalyzed oxidation of **1** and **2** led to the formation of the same products observed under an oxygen atmosphere (**5–9** from **1** and **3, 4, 10–12** from **2**); however, comparison between the results of Tables 1 and 2 shows that in the presence of  $\text{N}_2$  significantly higher mass balances and lower substrate consumptions were observed.

For what concerns the influence of pH on the oxidation products, their amount decreases by increasing pH, a result which may reflect the greater ease of oxidation of phenols as the pH increases [27].

The increase in  $K_2S_2O_8$  concentration (Table 3) influences both the amount of recovered substrate and, to a smaller extent, of oxidation products, suggesting that under these conditions the main role of  $K_2S_2O_8$  is to act as an electron scavenger (Eq. (5)), thus initiating the photocatalyzed oxidation process (Eq. (2)).  $SO_4^{\bullet-}$ , formed according to Eq. (5), plays an additional role through its action as a one-electron oxidant (Eq. (6)); however, it is not easy to establish the relative contribution of this pathway to the degradation process.

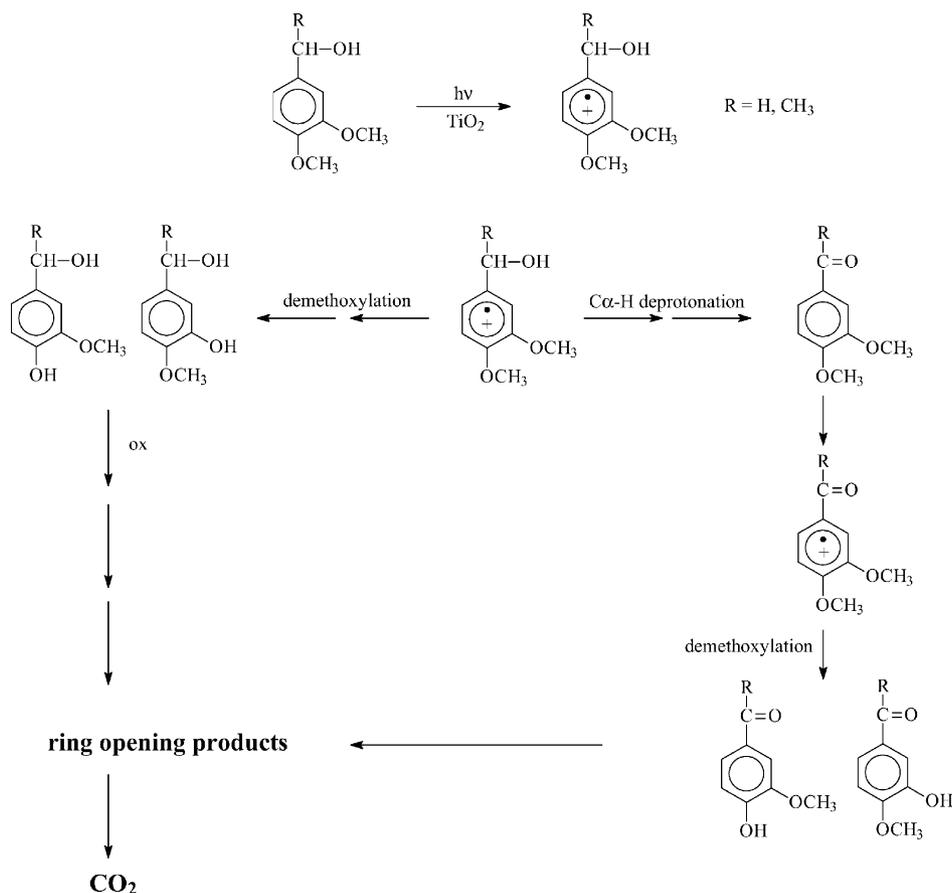
The fact that the mass balance is always significantly below 100%, points again towards the presence of products of aromatic ring-opening (see above) and  $CO_2$ , as clearly shown by the observation of  $Ba(CO_3)_2$  formation after approximately 90 min of irradiation.

The experiments carried out for substrate **1** in the presence of  $N_2O$  (Table 4) show that after 90 min of irradiation almost no oxidation has occurred both at pH 3 and 7. Addition of  $K_2S_2O_8$  significantly increases substrate consumption, which is now comparable to that observed in the presence of  $N_2/K_2S_2O_8$ . At a first sight, these results suggest that  $\bullet OH$  plays a minor role in the degradation process, an observation which however is in contrast with many studies indicating that in the  $TiO_2$ -photocatalyzed

degradation of organic compounds  $\bullet OH$  plays a major role [3,18].

This apparent discrepancy can, however, be reconciled if one considers that the observation of a very low reactivity for the oxidation of **1** in the presence of  $N_2O$  and of similar reactivities with the systems  $N_2O/K_2S_2O_8$  and  $N_2/K_2S_2O_8$  reflects the fact that  $N_2O$ , which is an excellent scavenger for the hydrated electron [26], becomes a very poor electron scavenger under the heterogeneous conditions employed, unable to compete significantly with electron-hole pair recombination. Accordingly, by addition of  $K_2S_2O_8$ , substantial substrate consumption is observed, quite independently from the nature of the gas used ( $N_2O$  or  $N_2$ ), in line with its role as electron scavenger. Unfortunately, these experiments did not add any new information on the role played by  $\bullet OH$  in the degradation process.

In order to compare the reactivity of non-phenolic substrates with that of phenolic ones, the  $TiO_2$ -photocatalyzed oxidation of 3,4-dimethoxybenzyl alcohol (**2**) was compared with that of 3-hydroxy-4-methoxybenzyl alcohol (**3**) and 4-hydroxy-3-methoxybenzyl alcohol (**4**) (Table 6). Under all conditions degradation of the phenolic alcohols **3** and **4** is significantly more pronounced than that of the non-phenolic alcohol **2**, the mass balance being between 20 and 40% for



Scheme 3.

**3** and **4** and around 70% for **2**. This result indicates that degradation is strongly favored by the presence of phenolic groups. In fact, it is well-known that one-electron oxidation of phenolic substrates leads to the formation of phenoxyl radicals [27], which are known to undergo ring-opening reactions in the presence of  $O_2^{\bullet-}$  [4,21].

On the basis of the results collected in Tables 1–6, it is thus possible to propose a general mechanism for the photocatalyzed degradation of **1** and **2**, which is able to account for all the experimental observations outlined above (Scheme 3).

The substrate is oxidized by  $TiO_2(h^+)$  to give the corresponding radical cation. The radical cation can then undergo two pathways: (a)  $C_\alpha-H$  deprotonation to give a carbon-centered radical, which is then oxidized in the reaction medium to give the corresponding carbonyl compound (Scheme 2); (b) demethoxylation via  $\bullet OH$  addition to give the corresponding phenolic compound. In the same way, oxidation of the non-methoxylated carbonyl compounds leads to the formation of the corresponding phenolic derivatives.

Oxidation of the phenolic compounds occurs more rapidly than that of the non-phenolic ones, leading to the formation of phenoxyl radicals which react with  $O_2^{\bullet-}$  to give products of aromatic ring-opening, precursors of  $CO_2$ . However, also the direct reaction between the radical cation and  $O_2^{\bullet-}$  is likely to play a role in substrate degradation. The smaller extent of substrate degradation observed in the presence of  $N_2$  as compared to  $O_2$ , can be thus ascribed to the fact that under these conditions a much lower concentration of  $O_2^{\bullet-}$  is present.

In conclusion, the  $TiO_2$ -photocatalyzed degradation of substrates **1–4** has been studied under a variety of conditions and it has been shown that substrate degradation can be strongly influenced by the experimental conditions employed. A general mechanistic scheme accounting for all the experimental observations has been proposed. A major role in the degradation process is played by  $\bullet OH$  and  $O_2^{\bullet-}$ , while  $SO_4^{\bullet-}$  appears to play a minor role.  $\bullet OH$  plays a fundamental role in the conversion of non-phenolic substrates into phenolic ones, while  $O_2^{\bullet-}$  exerts its role mainly by reacting with phenoxyl radicals to give aromatic ring-opening products, and, to a smaller extent, by direct reaction with the intermediate aromatic radical cations. Interestingly, addition of  $K_2S_2O_8$  as electron scavenger allows substantial substrate degradation also in the absence of  $O_2$ , while  $N_2O$  which is an excellent scavenger for the hydrated electron seems to be a very poor electron scavenger under the heterogeneous conditions employed.

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