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Journal of Photochemistry and Photobiology A: Chemistry 108 (1997) 45–49

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photocatalytic transformation of aromatic compounds in aqueous zinc oxide suspensions: effect of substrate concentration on the distribution of products

C. Richard *, F. Bosquet, J.-F. Pilichowski

Laboratoire de Photochimie, URA CNRS no. 433, Ensemble Universitaire des Cézeaux, 63177 Aubière, France

Received 26 February 1996; accepted 10 June 1996

Abstract

The photocatalytic transformations of 4-methoxybenzyl alcohol and 4-hydroxybenzyl alcohol were studied as a function of the substrate concentration in the presence or absence of a hydroxyl radical scavenger (isopropanol). In the absence of isopropanol, hydroxylated derivatives and aldehydic products are formed. The formation of aldehydic products is clearly favoured at high substrate concentrations. In the presence of isopropanol, the formation of hydroxylated derivatives is suppressed, whereas the formation of aldehydic products is only partially reduced. These results show that hydroxyl radicals and positive holes are both involved in the transformation of these compounds. Direct oxidation by positive holes, yielding the aldehydic products, is the main process at high substrate concentrations. The photocatalytic transformation of 4-hydroxyphenethyl alcohol yields many products. In the presence of isopropanol, only one product is observed. Its formation rate is clearly enhanced in the presence of the hydroxyl radical scavenger. © 1997 Elsevier Science S.A.

Keywords: Aqueous suspension; Distribution of products; Photocatalysis; Positive holes; ZnO

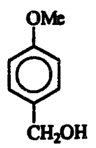
1. Introduction

Photocatalysis is an efficient tool for the degradation and complete mineralization of organic compounds [1,2]. It has been the subject of numerous studies to obtain a better understanding of the mechanisms of the reactions involved [3–7]. The absorption of light by a photoactive oxide creates pairs of electrons and holes (h^+). Water is oxidized by h^+ into hydroxyl radicals. These highly oxidizing species are involved in the photocatalytic degradation of many organic pollutants. However, the role of h^+ remains unclear.

It has been reported previously that the distribution of products in the photocatalytic transformation of 4-hydroxybenzyl alcohol (HBA) on ZnO is clearly modified when a hydroxyl radical scavenger, such as isopropanol (iPrOH), is added to the suspension [8]. The formation of 3,4-dihydroxybenzyl alcohol (DHBA) is completely inhibited by the alcohol, whereas the formation of 4-hydroxybenzaldehyde (HBZ) is only partially reduced and that of hydroquinone (QH_2) is slightly reduced. These findings suggest that two types of oxidizing species are involved in the transformation of HBA: hydroxyl radicals and positive holes. The production of the *ortho*-hydroxylated product only results from the oxidation of HBA by the former, whereas the latter is the main species responsible for the formation of QH_2.

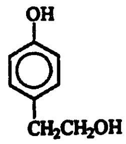
Golstein et al. [9] measured the yields and distribution of the hydroxylation products of phenol under several conditions. They compared results obtained by γ-radiolysis, reaction with $SO_4^{\cdot -}$ and photolysis in deaerated suspensions of TiO_2. They concluded that direct hole oxidation occurs, especially at high substrate concentration.

In this paper, we report the photocatalytic transformation of several aromatic compounds in oxygenated ZnO suspensions. We focused on the influence of the substrate concentration on the distribution of products in the absence or presence of iPrOH (hydroxyl radical scavenger). The behaviour of HBA and its methoxylated homologue (MBA) was compared. The photocatalytic oxidation of 4-hydroxyphenethyl alcohol (HPA) was also studied in order to obtain a better understanding of the influence of the OH function on the substituent.



MBA

HBA



HPA

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* Corresponding author.

PII S1010-6030(96)04431-0

2. Experimental details

2.1. Materials

All chemicals were commercially obtained and were of the highest purity available. Zinc oxide was supplied by Vieille Montagne SA (France). Its specific area (Brunauer–Emmett–Teller (BET) method) was 9.4 m^2 g^{-1}. Solutions were prepared with water purified using a Milli-Q system.

2.2. Irradiations

Aqueous suspensions of ZnO were irradiated by a fluorescent lamp (Philips TLAD 15 W/05) emitting in the range 300–450 nm with an emission maximum at 365 nm. The irradiation apparatus has been described previously [10]. Solutions were stirred under oxygen 20 min prior to irradiation.

2.3. Analyses

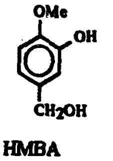
Samples were analysed by high performance liquid chromatography (HPLC) (Merck-Hitachi L6200) using an L3000 photodiode array detector and a Lichrospher RP 18 column (5 μm, 25 mm×4 mm). Calibrations were performed with standards. ZnO was removed prior to analysis by filtration on a Millipore filter (0.45 μm).

Nuclear magnetic resonance (NMR) spectra were obtained on samples dissolved in dimethylsulphoxide-d_6 (DMSO-d_6) (internal reference) with a Bruker AC400 spectrometer. For ^{1}H-NMR, classical sequences were used. For ^{13}C-NMR (at 100 MHz), distortionless enhancement by polarization transfer (DEPT) pulse frequency (with the variable pulse set to 45° and a delay time $\tau = 1/2J$, J being an average ^{1}H–^{13}C coupling constant set to 135 Hz) was necessary, this technique being one of the most sensitive.

2.4. Identification of the reaction products

2.4.1. Photocatalytic transformation of MBA

A typical chromatogram of a solution of MBA (5×10^{-4} M) irradiated for 5 min in the presence of ZnO (2 g l^{-1}) is given in Fig. 1. Three main products are formed. 3-hydroxy-4-methoxybenzyl alcohol (HMBA), HBA and 4-methoxybenzaldehyde (MBZ) were identified by comparing their HPLC retention times (see Fig. 1) and UV spectra with those of commercially available authentic samples. The ^{1}H-NMR spectrum of the reaction mixture after removal of the volatile products and a large amount of MBA confirmed the presence of HMBA and HBA and indicated that a fourth product is only present in traces (see Fig. 2).



HMBA

MBZ

HBA

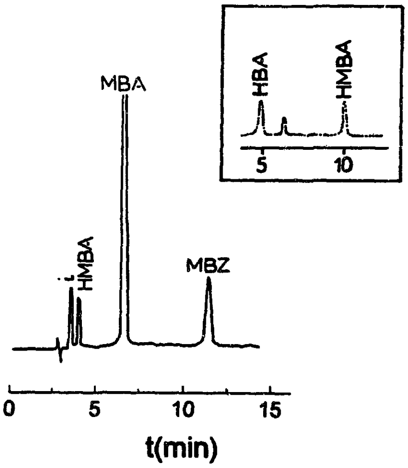
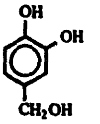


Fig. 1. High performance liquid chromatogram of a suspension containing ZnO (2 g l^{-1}) and MBA (5×10^{-4} M) irradiated for 5 min. Mobile phase, water–methanol (50 : 50, v/v). Detection set at 220 nm. Inset: mobile phase, water–methanol (85 : 15, v/v).

2.4.2. Photocatalytic transformation of HBA

HBZ and QH$_2$ were identified by comparing their HPLC retention times and UV spectra with those of commercially available authentic samples. DHBA was identified as described previously [8].



DHBA

HBZ

QH$_2$

2.4.3. Photocatalytic transformation of HPA

Many attempts were made to isolate the main product formed in the presence of iPrOH (λ_{max} = 232 nm). However, we were unsuccessful, because of its instability. After careful lyophilization of the crude reaction mixture, it was possible to obtain ^{1}H-NMR and ^{13}C-DEPT-NMR spectra in DMSO-d_6 solution. In addition to the resonance of HPA and aliphatic peaks, the proton spectrum shows a doublet ($\delta = 6.2$ and $J = 10$ Hz) corresponding to the A part of an AX two-proton system spin coupling and attributed to an α,β-unsaturated ketone (the X part is overlapped by one of the resonances of HPA). More relevant information can be obtained from ^{13}C-DEPT analysis. The observed vs. calculated resonances for a semi-quinoid structure are shown in Table 1. The two series of data are in very good agreement and are indicative of the product illustrated. Such a compound will present a high instability with a tendency to internal dehydration and oxidation.

3. Results

3.1. Photocatalytic oxidation of MBA

The initial rates of MBA disappearance and photoproduct formation were measured for various initial MBA concentra-

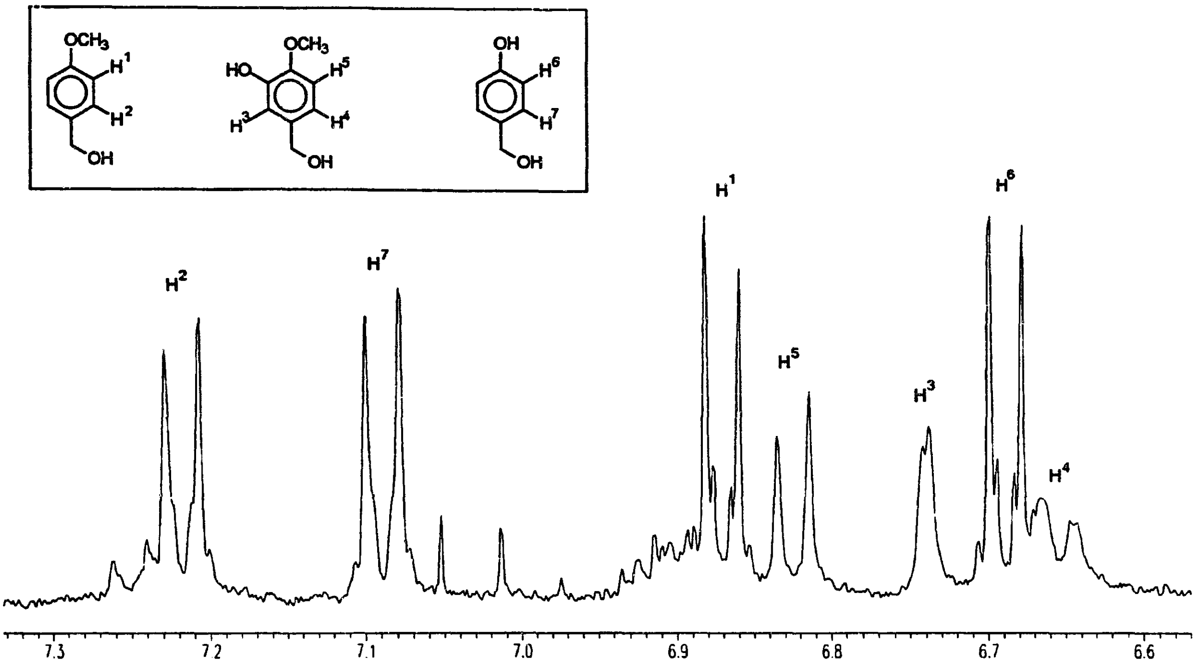
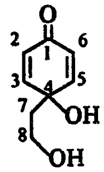


Fig. 2. ^{1}H-NMR (DMSO-d_6, internal reference) spectrum of the reaction mixture obtained after irradiation of MBA and ZnO (see text).

Table 1
Observed vs. calculated resonances for a semi-quinoid structure

	Carbon	1	2	3	4	7	8
							
	Measured	[a]	149	126	[a]	44	54
	Calculated[b]	187	147	126	70	42	55

[a] These carbons are not visible with the DEPT 45 sequence used.
[b] Obtained from ChemWindow software and calculated with data from Refs. [11,12].

tions in the range 10^{-4}–10^{-2} M. The irradiation times were chosen in order to obtain a conversion of MBA close to 20%. The results are summarized in Table 2 and Fig. 3.

The initial rate of MBA transformation increases with increasing initial concentration of MBA, gradually approaching a constant value. The rate of HMBA formation is independent of the MBA concentration in the range 2.5×10^{-4}–10^{-2} M, and the chemical yield of HMBA formation is about 2.5 times lower at 10^{-2} M than at 2.5×10^{-4} M. In contrast, the rate of MBZ formation increases linearly with increasing MBA concentration, and the chemical yield of MBZ increases by about twofold as the MBA concentration is increased from 2.5×10^{-4} to 10^{-2} M. Thus the distribution of the products depends on the concentration of MBA.

In the presence of iPrOH at concentrations corresponding to the ratio [iPrOH] / [MBA] = 170, the formation of HMBA is completely inhibited, whereas that of MBZ is reduced by only 66% (see Table 2). The rate of MBA consumption is reduced by 92%. Hence the chemical yield of MBZ formation is much higher in the presence of iPrOH than in its absence. Based on a rate constant for the reaction between hydroxyl radicals and MBA of 2×10^{10} M^{-1} s^{-1} and on a rate constant for the reaction between hydroxyl radicals and iPrOH of 2.3×10^{9} M^{-1} s^{-1} [13], the concentration of iPrOH added is sufficient to scavenge more than 95% of OH$^{\cdot}$. As a consequence, it can be concluded that reactive species other than hydroxyl radicals are responsible for the formation of MBZ.

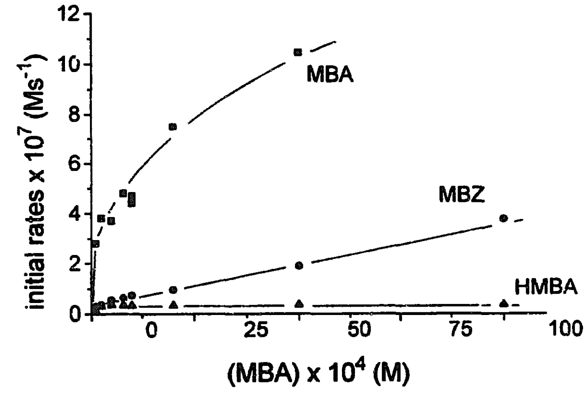


Fig. 3. Initial rates of MBA consumption (■) and MBZ (●) and HMBA (▲) formation vs. MBA concentration.

3.2. *Photocatalytic oxidation of HBA*

Quantitative results are given in Table 3. The initial rate of HBA disappearance increases with increasing initial concentration of HBA and reaches a plateau value. The rate of DHBA formation is independent of the HBA concentration in the range 2.5×10^{-4}–2.0×10^{-3} M, and the chemical yield of

Table 2
Influence of MBA concentration and of iPrOH on the photocatalytic transformation of MBA

[MBA] ($\times 10^4$ M)	Irradiation time (s)	$-d[MBA]/dt$ ($\times 10^7$ M s^{-1})	$d[HMBA]/dt$ ($\times 10^8$ M s^{-1})	$d[MBZ]/dt$ ($\times 10^8$ M s^{-1})	Yield of HMBA	Yield of MBZ
1.0	90	2.8	1.2	2.9	0.04	0.10
2.5	150	3.8	3.0	3.6	0.08	0.095
2.5 (iPrOH, 0.04 M)	450	0.3	0	1.3	0	0.43
5.0	300	3.7	3.5	5.4	0.09	0.14
5.0 (iPrOH, 0.08 M)	900	0.46	0	1.8	0	0.39
8.0	300	4.8	3.4	6.3	0.07	0.13
10.0	400	4.7	3.2	7.2	0.07	0.14
10.0 (iPrOH, 0.16 M)	900	0.63	0	2.9	0	0.46
20.0	480	7.5	3.3	9.6	0.04	0.13
50.0	600	10.5	3.5	19	0.03	0.18
100	600		3.6	38		

Table 3
Influence of HBA concentration and of iPrOH on the photocatalytic transformation of HBA

[HBA] ($\times 10^4$ M)	$-d[HBA]/dt$ ($\times 10^7$ M s^{-1})	$d[DHBA]/dt$ ($\times 10^8$ M s^{-1})	$d[HBZ]/dt$ ($\times 10^8$ M s^{-1})	$d[QH_2]/dt$ ($\times 10^8$ M s^{-1})	Yield of DHBA	Yield of HBZ	Yield of QH_2
2.5	1.8	7.5	2.1	2.5	0.42	0.11	0.14
2.5 (iPrOH, 0.04 M)	0.9	0	1.1	2.2	0	0.12	0.24
5.0	4.2	7.0	5.2	6.4	0.16	0.12	0.13
5.0 (iPrOH, 0.08 M)	1.2	0	2.1	3.3	0	0.18	0.24
10.0	4.6	7.9	8.4	6.2	0.17	0.18	0.13
10.0 (iPrOH, 0.16 M)	1.2	0	3.1	4.7	0	0.26	0.39
20.0	5.7	5.7	8.9	6.2	0.10	0.16	0.11
20.0 (iPrOH, 0.32 M)	1.6	0	5.4	5.6	0	0.33	0.43

DHBA is drastically reduced by an increase in HBA concentration. The formation of DHBA is completely inhibited by iPrOH. The rate of HBZ formation increases with increasing HBA concentration. In the presence of iPrOH, it is reduced by about twofold. The rate of QH_2 formation also increases with increasing HBA concentration, but reaches a limiting value for $[HBA] = 5 \times 10^{-4}$ M. The inhibiting effect of iPrOH on the formation of QH_2 is weak. Thus, as previously observed with MBA, the distribution of the products depends on the substrate concentration. Moreover, it is not the same in the absence and presence of a hydroxyl radical scavenger.

3.3. Photocatalytic oxidation of HPA

Several products are formed on irradiation of aqueous suspensions of ZnO (2 g l^{-1}) and HPA (10^{-3} M). In the presence of iPrOH, these products are no longer formed, with the exception of one product whose formation is significantly enhanced (see Fig. 4). With hydroxyl radical scavengers other than iPrOH (e.g. azide or formate ions), the results are similar. The formation rate of this product increases slightly with increasing concentration of HPA. The NMR data suggest that this product has a semi-quinoid structure.

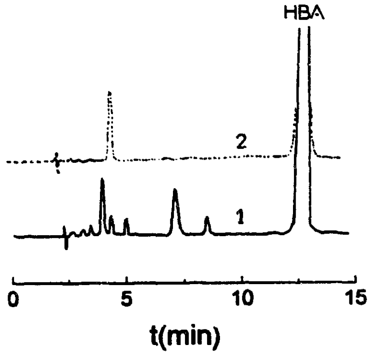


Fig. 4. High performance liquid chromatogram of a suspension containing ZnO (2 g l^{-1}) and HPA (1×10^{-3} M) irradiated for 15 min. Mobile phase, water–methanol (85 : 15, v/v). Detection set at 240 nm.

4. Discussion

The photocatalytic transformations of MBA and HBA lead to the same types of product. Hydroxylation of the molecules occurs at the ortho position with respect to OH or OMe, and oxidation of the CH_2OH group into COH takes place. With HBA, substitution of CH_2OH by OH also occurs. When hydroxyl radicals are scavenged, the formation of *ortho*-hydroxylated products is suppressed, whereas the formation of the other products is only partially reduced. From this, we can infer that reactive species other than hydroxyl radicals are involved in the transformation of the substrates.

The distribution of products clearly depends on the concentration of the substrate. The proportion of *ortho*-hydroxylated products is significantly lower at high than at low substrate concentrations. The most striking effect is obtained with HBA: the ratio $(d(DHBA)/dt)/(d(HBZ)/$

dt) decreases by a factor of five when the concentration of HBA is increased from 2.5×10^{-4} M to 2.0×10^{-3} M. Since hydroxyl radicals are responsible for the formation of *ortho*-hydroxylated products, it can be deduced that, at low concentration, the substrate is mainly oxidized by the hydroxyl radicals. However, at high substrate concentrations, direct oxidation by positive holes becomes the main process. The number of molecules adsorbed at the surface of ZnO increases with increasing concentration. As a consequence, the reaction between adsorbed substrate and positive holes is expected to be favoured at high substrate concentration. The results show that these reactions do not compete with the oxidation of water by positive holes. Otherwise, the formation rates of the *ortho*-hydroxylated products would decrease with increasing substrate concentration. The oxidation of the substrate by positive holes probably competes with electron–hole recombination.

The results obtained with HPA show that the presence of the substituent CH_2CH_2OH instead of CH_2OH increases the number of oxidation sites and thus the number of reaction products. Nevertheless, the oxidation by positive holes leads to a single product whose formation is enhanced in the presence of a hydroxyl radical scavenger. The primary step in the transformation is the attack of the substrate by hydroxyl radicals or positive holes. The resulting radicals can then disappear in several ways. They can react with oxygen, with another radical or with a hydroxyl radical. The latter process is suppressed in the presence of iPrOH and the reaction is thus much more specific.

5. Conclusions

The distribution of products in the photocatalytic transformation of 4-hydroxybenzyl and 4-methoxybenzyl alcohol depends on the concentration of the substrate. The oxidation of the substituent is favoured by an increase in concentration, whereas the hydroxylation of the aromatic ring at the ortho position of the hydroxy or methoxy function is unfavoured. These differences of stoichiometry are explained by the involvement of two oxidizing species: the oxidation by hydroxyl radicals is the main process at low substrate concentration, whereas the oxidation by positive holes is the main process at high substrate concentration. With 4-hydroxyphenethyl alcohol, the reaction with positive holes is very specific.

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