Influence of the substituent on selective photocatalytic oxidation of aromatic compounds in aqueous TiO_2 suspensions†

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Received (in Cambridge, UK) 9th November 2005, Accepted 4th January 2006
First published as an Advance Article on the web 23rd January 2006
DOI: 10.1039/b515853b

Experimental results are reported showing that the photocatalytic oxidation of aromatic compounds containing an electron-donor group (EDG) gives rise mainly to *ortho*- and *para*-monohydroxy derivatives while in the presence of an electron-withdrawing group (EWG) all the monohydroxy derivatives are obtained.

Photocatalytic oxidation of aromatic compounds has been widely studied,[1–10] while photocatalytic syntheses represent an incoming research field.[11] In this work a systematic attempt was made to understand the influence of the substituent group on the selectivity of photo-oxidation of the aromatic molecules to hydroxylated compounds, in the presence of polycrystalline TiO_2.

Photocatalytic runs were performed in liquid–solid regime to oxidise aromatic compounds containing an EDG (phenol, phenylamine, and *N*-phenylacetamide) or an EWG (nitrobenzene, cyanobenzene and 1-phenylethanone). The photocatalyst used was commercial anatase TiO_2 (Merck) with an amount of 0.4 g l^{-1} and the pH was the natural one (*ca.* 6.5). The experiments lasted 1.5 h and were performed in a batch photoreactor of cylindrical shape, containing 0.5 l of aqueous suspension, with pure O_2 continuously bubbling. A 125 W medium-pressure Hg lamp (Helios Italquartz, Italy) was axially immersed within the photoreactor and it was cooled by water circulating through a Pyrex thimble. The temperature of the suspension was about 300 K. The radiation energy impinging on the suspension had an average value of 10 mW cm^{-2}. The initial concentration of the substrates was *ca.* 500 μM. The extent of adsorption in the dark was measured by monitoring the concentration of the substrates before adding the catalyst and after 1 h of contact with it, when the physical equilibrium was achieved. During the photocatalytic runs, samples for analyses were withdrawn at fixed intervals of time and the catalyst was immediately separated from the aqueous solution by filtering through 45 μm Millex Millipore filters.

All the monohydroxylated species produced during the reactions were analyzed with a HPLC Beckman Coulter (System Gold 126 Solvent Module and 168 Diode Array Detector), equipped with a Luna 5 μ Phenyl-Hexyl column (250 mm long × 2 mm i.d.); the flow rate was 0.2 ml min^{-1} and the identification was made by comparison with authentic samples. TOC (total organic carbon) measurements were carried out by using a TOC Shimadzu 5000 A analyser.

It is important to point out that two competing pathways were present from the starting of irradiation: substrate degradation that produced CO_2 and formation of monohydroxylated species released into the bulk of the solution. Particular care was devoted to determine the concentrations in the liquid phase of each hydroxylation product (*ortho*, *meta* and *para*).

The alternative oxidation route to complete mineralization was reported in literature for toluene[6] and it should be stressed that it occurs at various extents from the beginning of irradiation when the molecules of substrates are not very big, as in our case. The evolution to CO_2 occurs through various oxidation steps involving unknown intermediates species strongly (photo)adsorbed onto TiO_2 surface without their release into the bulk of solution. An experimental evidence of the occurrence of this parallel and kinetically very fast process derives from the observation of TOC results showing a decrease from the very beginning of irradiation (see, for example, Fig. S1 in ESI†).

The results obtained with an aromatic compound containing an EDG and an EWG are reported in Fig. 1(a) and (b), respectively. Fig. 1(a) reports the concentration values of nitrobenzene and its monohydroxylated products *vs.* irradiation time, while Fig. 1(b) reports the results obtained with *N*-phenylacetamide.

It may be observed that the aromatic molecules were oxidised in both cases and the concentrations of their oxidation products increased with irradiation time. The whole molar yields of the three hydroxylated species (OH-derivatives produced divided by the reacted substrate) were *ca.* 20% and *ca.* 60% for nitrobenzene and *N*-phenylacetamide, respectively.

Inside the investigated irradiation time, the monohydroxylated isomers were the main reaction products, with yields in the 50–75% range when the photocatalytic reaction was carried out by using an aromatic compound containing an EDG. On the contrary, the yields in monohydroxylated isomers were in the 20–30% range for the aromatic compounds containing an EWG. It is worth noting that oxidation of the $-COCH_3$ and $-NHCOCH_3$ substituents (although in lesser extent) could also take place during the photocatalytic process as unidentified peaks were observed in the chromatograms.

Table 1 summarizes the obtained results for all of the studied compounds; it reports the amounts of substrates adsorbed in the dark, the conversions and yields in monohydroxylated isomers along with the HPLC-eluents appropriately chosen.

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† Electronic supplementary information (ESI) available: TOC trend during **4** (see Table 1) photo-oxidation; graphics with the concentrations of compounds **1**, **2**, **5**, **6** (see Table 1) and intermediates during their photocatalytic oxidations. See DOI: 10.1039/b515853b

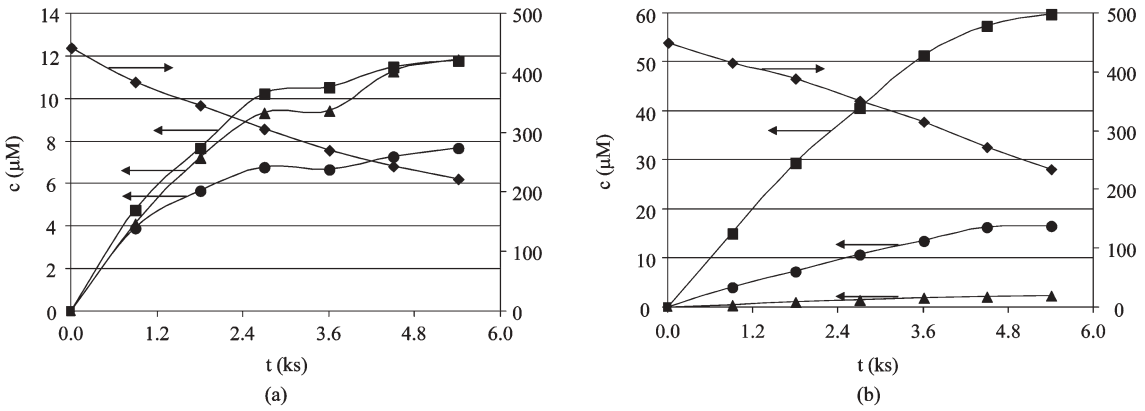


Fig. 1 (a) Photocatalytic oxidation of nitrobenzene: (◆) nitrobenzene, (●) 2-nitrophenol, (▲) 3-nitrophenol, (■) 4-nitrophenol. (b) Photocatalytic oxidation of *N*-phenylacetamide: (◆) *N*-phenylacetamide, (●) *N*-(2-hydroxyphenyl)acetamide, (▲) *N*-(3-hydroxyphenyl)acetamide, (■) *N*-(4-hydroxyphenyl)acetamide.

The data of Table 1 clearly indicate that the substituent nature strongly influences: (i) the adsorption of the aromatic substrates onto the surface of the catalyst, and (ii) the position of the hydroxyl group entering the aromatic ring, giving rise to a regioselectivity in the monohydroxylated reaction products.

The adsorption of aromatic compounds containing an EDG is negligible in all cases. A notable adsorption, instead, was observed with a strongly EWG. The behaviour of 1-phenylethanone, that showed a negligible adsorption, can be explained by considering that this substituent has only a slight electron withdrawing effect. The above findings indicate that the presence of a certain additional electron density, induced in the aromatic ring by the presence of an EDG, is not beneficial for the molecule adsorption. On the contrary, the presence of a strongly EWG induces a delocalized electron density in the aromatic ring, lower with respect to that of benzene, that promotes the adsorption of the molecule onto the surface. This effect could support the reaction pathway to complete mineralization onto TiO_2 surface with consequent lower yields in monohydroxylated species (see Table 1), observed for the substrates containing an EWG.

Literature[12–15] reports that aromatic molecules can adsorb through the formation of $Ti^{4+}_{(surface)}\cdots\pi$ electron or $OH_{(surface)}\cdots\pi$ electron type complexes,[12,13] and the latter should be related to the production of monohydroxylated species under irradiation before their release in the solution bulk. For both types of adsorption, the more or less significant basic nature of the substituents, related to their withdrawing or donor capacity, could play a major role. All types of Lewis and Brønsted–Lowry acid–base sites are generally present at various extent on the surface of polycrystalline TiO_2, as revealed by FTIR spectroscopy,[14,15] and consequently it is difficult to establish which of them are the most important for the measured adsorption in the dark.

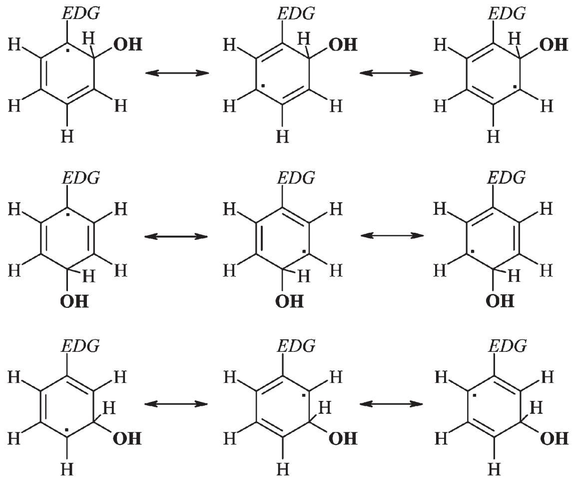
The conversion values (calculated after 1.5 h of irradiation) were not strongly influenced by the amount of adsorption in the dark nor from the nature of the substituent. The highest and the lowest conversions were those of phenol (∼70%) and phenylamine (∼40%), respectively.

Another aspect that may be stressed concerns the selectivity of the attack to the aromatic ring in positions *ortho*, *meta* and *para*: it can be seen that it is strongly dependent from the type of substituent (Table 1). It is worth noting that the yields and *o*:*m*:*p* values reported in Table 1 were calculated as average percentages, considering that during the first 45 min of irradiation time they did not change significantly. The yield data of monohydroxylated compounds obtained starting from aromatic substrates containing an EDG indicate that the main products were *ortho*- and *para*-isomers, while the *meta*-isomer was not present or it was present only in very small amounts. Completely different is the behaviour exhibited by the photocatalytic oxidation when an EWG is present in the aromatic ring: no influence on the orientation of the monohydroxy substituent was observed, given that *ortho*-, *meta*- and *para*-isomers were all present in significant amounts (>20%). This finding is confirmed by the intermediates found during photocatalytic oxidation of a large number of substituted aromatic compounds, using different kinds of TiO_2 under various experimental conditions.[1–10] It is furthermore reported[8] that the presence of both an ED and an EW group gives rise to a behaviour similar to that observed when only an EDG is present.

Table 1 Adsorption in the dark (after 1 h), average yields in hydroxylated species, *o*:*m*:*p* average ratios (during the first 45 min of irradiation), eluents used for HPLC-analyses of the substrates studied

Species	Group	Orientation	Adsorption in the dark[a]	Conversion[a,b] (%)	Total yield (%) in OH-derivatives[a]	*o*:*m*:*p* Ratio[a]	HPLC-eluent A; B; C (%)[c]
Phenol (**1**)	–OH (EDG)	*ortho*, *para*	Negligible	∼70	∼75	54.5:0.5:45.0	65; 35; 0
Phenylamine (**2**)	$–NH_2$ (EDG)	*ortho*, *para*	Negligible	∼40	∼50	49.7:0.0:50.3	90; 5; 5
N-Phenylacetamide (**3**)	$–NHCOCH_3$ (slightly EDG)	*ortho*, *para*	Negligible	∼50	∼60	20.0:3.0:77.0	60; 40; 0
Nitrobenzene (**4**)	$–NO_2$ (EWG)	—	∼8%	∼50	∼20	29.0:34.0:37.0	60; 20; 20
Cyanobenzene (**5**)	–CN (EWG)	—	∼6%	∼60	∼30	45.0:30.0:25.0	70; 15; 15
1-Phenylethanone (**6**)	$–COCH_3$ (slightly EWG)	—	Negligible	∼55	∼30	38.5:21.0:40.5	65; 35; 0

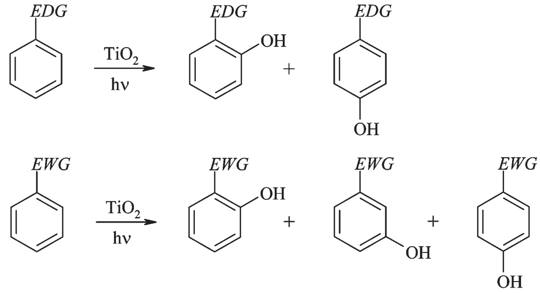
[a] Mol (%). [b] Values calculated after 1.5 h of irradiation. [c] A: 40 mM aqueous solution of KH_2PO_4; B: methanol, C: acetonitrile; vol. (%).



Scheme 1 Resonance structures of radical intermediates produced during the oxidation of a compound containing an EDG.

It is well known that heterogeneous photocatalytic oxidations can occur through a mechanism involving OH radicals during the first steps.[16] The reactivity of hydroxyl radical was a subject of intensive studies[17] and the correlation between the selectivity of the attack and the nature of the substituent in homogenous reactions was also recently studied with various experimental[18–22] and theoretical[23] methods. It is reported that the rate of addition of the OH radical to the aromatic rings (k = 10^9–10^{10} l mol^{-1} s^{-1}) is very high and this could mean that the attack should be rather unselective. It is, however, also reported that the ratio between the different regioisomers strongly depends on the oxidative power of the reaction medium. The oxidation of the radical intermediates arising from the addition of a hydroxyl radical to the aromatic ring of the substrates studied in this work could occur in different ways: (i) by means of another hydroxyl radical for hydrogen abstraction, (ii) by means of electron transfer followed by proton elimination. Consequently the further oxidation of the intermediates to the final products depends on the nature of the substituent: an easier process would take place in the case of an EDG, with larger difficulty when the electron withdrawing ability of the group increases.

Furthermore, by taking also into account the position of the attack, the different intermediates will show different abilities to be oxidized. In fact the behaviour of aromatic compounds containing an EDG can be explained by the stabilization of the radical intermediate, whose resonance structures are shown in Scheme 1. In particular the highest contribution to the stabilization is given by the formula with the unpaired electron on the carbon bonded to the EDG. This resonance structure can exist only when the hydroxyl radical enters *ortho*- and *para*-positions. On the other hand, a predominance of the *meta*-isomer would have been expected in the presence of an EWG for which the above reported resonance structure is particularly unstable. Nevertheless this behaviour was not observed and all the three isomers were found: this could be explained hypothesising that the further oxidation process of the radical intermediate is more difficult in this case, especially considering that in the whole mechanism the presence of TiO_2 plays an important role.



Scheme 2 Main hydroxylated products obtained during the photocatalytic oxidation of aromatic compounds containing either an electron donor or an electron withdrawing group.

In summary it was proved that the reaction of monohydroxylation of an aromatic ring occurs in all the three possible positions when an EWG group is present, while only the formation of *ortho*- and *para*-isomers virtually occurs when an EDG is present (see Table 1 and Scheme 2).

An interesting perspective is open not only to produce monohydroxylated compounds with high conversions and yields starting from aromatics with an EDG, but also to predict the intermediate products through which the photo-oxidation of aromatic compounds evolves.

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