Titanium dioxide photocatalyzed oxygenation of naphthalene and some of its derivatives

Federica Soana, Michela Sturini, Laura Cermenati and Angelo Albini

Department of Organic Chemistry, The University, v. Taramelli 10, 27100 Pavia, Italy.
E-mail: albini@chifis.unipv.it

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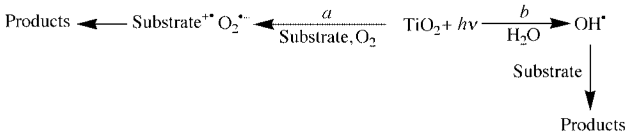
The titanium dioxide photocatalyzed oxygenation of naphthalene in water gives (*E*,*Z*)-2-formylcinnamaldehydes and 1,4-naphthoquinone besides traces of naphthols. 1-Substituted naphthalenes (both with an electron-withdrawing and -donating group) are likewise oxidised at about the same rate with a similar product distribution. The evidence obtained supports the hypothesis that the reaction involves transfer of a hydroxy group to naphthalene and reduction of oxygen to superoxide followed by coupling of the two species. In organic solvents the reaction is slower, more selective (a cyano group inhibits the reaction) and leads to phthalic anhydride and 1,4-naphthoquinone. The relation with the solvent-dependent course of the ozonation of the same substrates is commented upon.

Irradiation in the presence of a semiconductor powder (most commonly of the inexpensive titanium dioxide)[1] is an appealing method for the oxidation of organic molecules. Such heterogeneous photocatalysis has been carried out both in organic solvents (usually acetonitrile)[2] and in aqueous solution.[1] In the former case the reaction is initiated by electron transfer at the interface leading to the radical cation of the substrate and superoxide anion (Scheme 1, path *a*),[2] while in the latter one the actual active species are assumed to be hydroxy radicals formed by oxidation of the solvent (Scheme 1, path *b*).[3] Charge recombination in the semiconductor is extremely fast[4] and thus electron transfer from the solute is thought not to compete in aqueous solution.



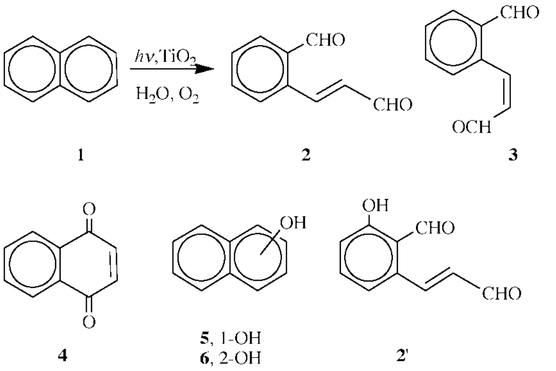
Scheme 1

There is, however, some evidence that, with good donors as the substrate, path *a* has a role also in water.[3b,5] This is a relevant issue for the evaluation of this oxidation procedure, in view of the application of photocatalytic oxidation both for the degradation of pollutants and for synthetic purposes. Polycyclic aromatic hydrocarbons (PAH) are significant examples in both respects, being representative of pollutants resistant to biodegradation and amenable to photocatalytic oxidation on one hand[6] and reasonably easily oxidised substrates for which ET initiation may be expected to lead to useful synthetic procedures on the other.[7] Presently, we report some data about naphthalene derivatives.

Results

Naphthalene photo-oxidation in water

Irradiation of a TiO_2 suspension in an aqueous naphthalene (**1**) solution (either 0.8 or 4×10^{-5} M solutions in water containing 1% MeCN at pH 6 were used, with no significant difference) led to consumption (and finally mineralisation) of the substrate (the photo-oxidation of **1** in water has been previously studied).[6a–c] Analysis of the extract from the solution showed that three intermediates were formed in significant amounts during the reaction. These could be separated and directly identified when the reaction was carried out on a preparative scale. These were the isomeric 2-formylcinnamaldehydes **2** and **3** and 1,4-naphthoquinone (**4**) (see Scheme 2, Table 1). This is in accord with the GC-MS identification by Theurich *et al.*,[6c] while disagreeing with the results by Das,[6a] who reported that 2-formyl-3-hydroxycinnamaldehyde (**2′**) was the product in TiO_2 oxidation. The present evidence, based on isolation and comparison of NMR data with an authentic sample (see Experimental section) left no doubt that the non-hydroxylated aldehydes are formed. As it appears from Fig. 1, in 4×10^{-5} M solutions such oxidation intermediates reached a maximal concentration of about 6% each with respect to the starting substrate as shown by GC. Minor products were the isomeric naphthols (**5**, **6**). Further products were present in a small amounts and were not identified, but no other aromatic derivative was a main product. In particular, 5-hydroxy-1,4-naphthoquinone was not detected and phthalic acid was present in a low amount (<1%, the aqueous phase after initial extraction was evaporated and the residue analysed). Several other products have been identified by GC-MS by other workers. In particular, in their detailed study Theurich *et al.*[6c] detected coumarin and 2,3-dihydro-2,3-epoxy-1,4-naphthoquinone as significant decomposition intermediates. We had no positive evidence for



Scheme 2

Table 1 Titanium dioxide sensitised photodecomposition of naphthalene and 1-naphthonitrile in water[a]

Substrate	Conditions[a]	Relative decomp. rate	Products, Yields (%)[b] Quinone	Dialdehydes		Naphthols	
1		1	**4**, 5.2	**2**, 6.2	**3**, 5.6	**5**, 0.1	**6**, 0.1
1	pH 3	1	3	4.3	6	0.3	0.2
1	SOD, 5 equiv.	0.05	4.5	≤0.5	≤0.5		
1	SOD, 1 equiv.	0.6	5	3.2	2.8	0.3	0.2
1	*i*-PrOH, 0.1%	0.01	3	4.3	3	0.2	0.1
1	*i*-PrOH, 0.01%	0.5	7	6.5	6.5	0.2	0.1
7b, X = CN		1		**10**–**11** (4 products)	3.2		
7b, X = CN	pH 3	0.75			4		
7b, X = CN	SOD, 5 equiv.	0.21			1.7		
1	H_2O_2/Fe^{3+}(dark)		**4**, 4	**2**, 0.5	**3**, 0.1		**6**, 0.5

[a] Solutions of the naphthalenes (**1**, **7b**) in water containing 1% MeCN were used. No buffer was added and the observed pH was close to 6 (except for experiments at pH 3, as noted). [b] At *ca.* 50% conversion.

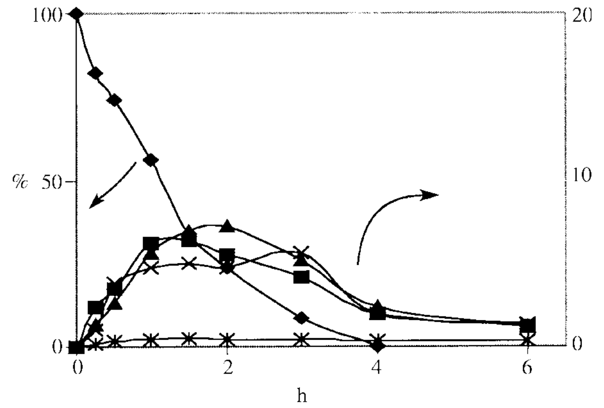
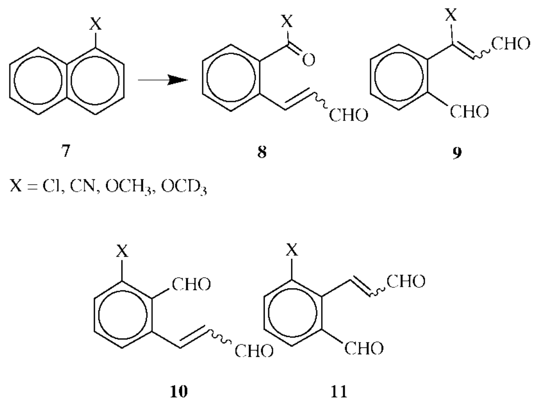


Fig. 1 Product distribution upon photo-oxidation of naphthalene in water. Starting material **1** (◆, left-hand scale). Products (right-hand scale): **2** (■), **3** (▲), **4** (×), sum of **5** + **6** (*).



Scheme 3

such compounds, at least for 50% conversion of the starting material.†

By comparison, naphthalene was fairly rapidly consumed when treated with hydrogen peroxide and iron ions in the dark (Fenton reaction). Naphthoquinone was again a significant intermediate—and probably arose from stepwise oxidation *via* dihydroxynaphthalene—but the above aldehydes were formed only in traces (Table 1).

Substituted naphthalenes

Extension of the study to some substituted naphthalenes could document the scope of the method for PAH degradation as well as give some indication about the mechanism of the process. The identification of the main products from **1** encouraged us to carry out such a study, since, although the isolation of the individual products was expected to be unpractical in this case due to their number, comparison of the GC-MS spectra with that of the oxidation products from parent **1** could give sufficient information for structure attribution.

The 1-substituted naphthalenes **7a**–**c** (X = chloro, cyano, methoxy) were similarly photo-oxidised. All of them reacted under these conditions and gave several intermediates, most of which could be recognised as the analogues of formylcinnamaldehydes **2** and **3**, being formed in the course of the decomposition in yields not exceeding 2% individually and 8–10% overall. As it appears in Scheme 3, four regioisomers (**8**–**11**) might be formed from these derivatives, each of them as both the *E* and the *Z* isomer.

Six isomers could be detected from 1-chloronaphthalene, four involving attack at the unsubstituted ring (formulae **10**, **11**), two at the substituted ones. The other two may have escaped detection since the pair of isomers arising from **8** were acyl chlorides, and thus hydrolysed to the corresponding acids, to which our analysis was less sensitive. Naphthalene-1-carbonitrile gave cleanly four dialdehydes, and analysis of the mass spectra (see Experimental section) showed that these had formulae **10** and **11** (see Table 1). 1-Methoxynaphthalene also gave several products. Apart from some 1,4-benzoquinone, most of the other ones could be recognised as dialdehydes (six isomers detected) and analysis of the mass spectra (supplemented by examination of the photo-oxidation products from the *O*-d_3 derivative) supported that three of these arose from attack to the substituted and three to the unsubstituted rings (see Experimental section).

The decomposition of the four naphthalenes **1**, **7a**–**c** followed a first order law and the relative rate of oxidation changed only marginally along the series (see Table 2).

Medium effects

Lowering the pH to 3 caused no significant change in the TiO_2 sensitised oxidations (Table 1). On the other hand, addition of Cu–Zn superoxide dismutase (SOD) quenched both the naphthalene oxidation and product formation, with a stronger effect on the dialdehydes **2** and **3**. Formation of these products was virtually suppressed when SOD was used in a 5 equivalent excess (Table 1). Addition of isopropanol slowed down the reaction (strongly when present at a 0.1% concentration, moderately at 0.01%), but did not significantly affect the product distribution. The results were similar with 1-naphthonitrile: acidic condition had little effect, while SOD again quenched the oxidation, though to a lesser extent.

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† The fact that we fail to detect some of the products identified in the study by Theurich *et al.*[6c] is not completely surprising in view of the somewhat different experimental conditions and, probably more importantly, of the more extensive conversion in that case. In fact, products arising from further oxidation steps, such as phthalic acid, quinone epoxide or coumarin are more important in that case.

Table 2 Rate constants for the titanium dioxide photosensitised decomposition of naphthalene and some of its derivatives (4×10^{-5} M)

	$k_{decomp.}/min^{-1}$	
Naphthalene	(H_2O)	(Solvent)
1, X = H	1.3×10^{-2}	1.5×10^{-3} (MeCN), 2.1×10^{-3} (MeCN with Ag_2SO_4)
7, X = Cl	1.4	2.2×10^{-3} (CH_2Cl_2)
7, X = CN	1.8	
7, X = OMe	1.9	

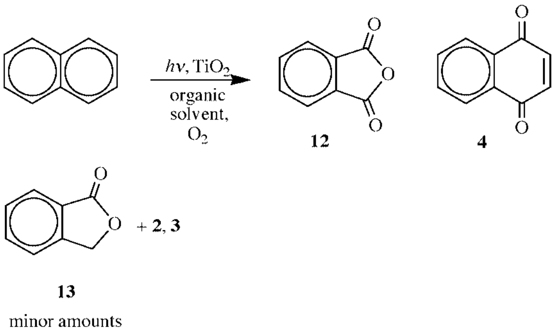
Table 3 Titanium dioxide photosensitised oxidation of naphthalene in organic solvents

Conditions	Products, Yield (%)[a]				
TiO_2,MeCN	**12**, 8	**4**, 2	**2**, <0.5	**3**, <0.5	**13**, <0.5
TiO_2/Ag_2SO_4, MeCN	**12**, 22	**4**, 20	**2**, 0.5		**5**, 1
TiO_2,CH_2Cl_2	**12**, 20				

[a] At *ca.* 50% conversion.

Photo-oxidation in organic solvents

We explored the course of the naphthalene photoreaction in organic solvents under otherwise identical conditions. The oxidation of naphthalene (4×10^{-5} M) in MeCN was almost an order of magnitude slower than in water. It gave only traces of dialdehydes **2** and **3** as well as of phthalide (**13**), while a significant amount of naphthoquinone (**4**) was formed and the main product was phthalic anhydride (**12**, see Table 3, Scheme 4). In the presence of equimolecular silver sulfate the reaction was faster and cleaner, giving the quinone and the anhydride, along with a trace of 1-naphthol. Under these conditions the reaction occurred up to 50% conversion, in close to quantitative transformation into characterised products. The oxidation took place conveniently also in dichloromethane and gave phthalic anhydride as by far the main product. In accord with a previous report by Fox and associates,[7] 1-methoxynaphthalene was likewise oxidised in MeCN, while 1-naphthonitrile was practically unreactive under these conditions.



Scheme 4

Discussion

The detailed mechanism of the chemical process occurring in titanium dioxide photocatalytic oxidation has been relatively little investigated, despite the fact that the clarification of mechanistic issues may help to assess the scope and the effectiveness of the method. In particular, little support has been offered for the postulated mechanisms. Due to the above mentioned importance of the topic, several studies have been devoted to the photodegradation paths of PAH in water. In this, as in other cases, it is generally assumed that the reactions involve photoproduced hydroxy radicals. However, a study of the oxidation of a heteroaromatic compound, quinoline, in water showed that the TiO_2 process can not be satisfactorily explained as occurring *via* hydroxy radicals, since some of the main products are different from those obtained in authentic $OH^{\bullet}$ oxidations and the attack shows different regioselectivity. The crucial role of the superoxide anion was demonstrated.[5] Furthermore, the relation between the TiO_2 photoinduced reactions in aqueous and non aqueous media needs to be addressed.

Quinoline has unique properties as a mechanistic probe, *viz.* its solubility in water and its different rings, which give more hints about the type of attack occurring. However, the solubility of naphthalene in water—at least with 1% MeCN—is sufficient for a detailed product study. Therefore we decided to perform a study on this aromatic carbocycle and some of its derivatives, as well as carrying out specific mechanistic tests and comparing the results in organic solvents.

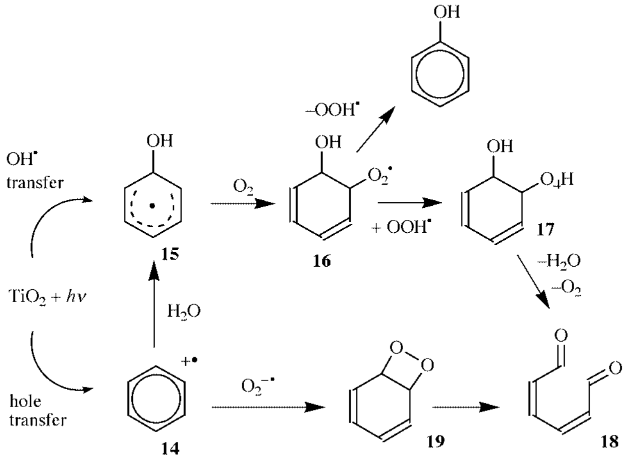
In our hands, the photosensitised oxidation of naphthalene in water up to 50% consumption gives the formylcinnamaldehydes **2** and **3** and naphthoquinone **4** as the main products, besides minor amounts of the naphthols and traces of phthalic acid (see Table 1). This is in accord with the GC-MS study by Theurich *et al.*[6c] (who also detected several other oxidation intermediates) and corrects a previous structure assignment for the aldehydes.[6a]

As for the mechanistic indication that a product study may give, the quinone seemed to us ill-suited, since there are several possibilities for the formation of this compound and it seems difficult to track unambiguously the path involved. As an example, Theurich *et al.*[6c] suggest that **4** (and isomeric 1,2-naphthoquinone) are formed from the naphthols *via* dihydroxynaphthalenes and, although there is little evidence for the latter type of intermediates in this and in other cases, it is certainly true that naphthols are easily oxidized to naphthoquinones. On the other hand, the aldehydes are more characteristic and possibly arise *via* a more direct path (see below). Therefore, attention was centred on these products as mechanistic probes. Their formation is a general reaction and the analogues of dialdehydes **2** and **3** are also important products of the 1-substituted naphthalenes investigated. The oxidative cleavage occurs at about the same rate with all of these compounds and is not regioselective. It is possible to detect most of the expected isomers, except for the case of 1-naphthonitrile where attack takes place only at the unsubstituted ring.

The presently observed oxidative cleavage to aldehydes **2** and **3** is analogous to the TiO_2 photocatalyzed oxidation of other aromatic and heteroaromatic substrates in water: 2-formylphenyliminoethanal is the main product from quinoline[5] and polymeric aldehydes thought to arise from muconic aldehyde (hexadienedial) are formed from benzene[8a] (this substrate gives also hydroquinone and benzoquinone, but no phenol).[8b] It is also important to notice that the dialdehydes are minor products in organic solvents, in which the photoxidation of naphthalene rather gives phthalic anhydride. Furthermore, in these media the photo-oxidation is inhibited by an electron-withdrawing group such as cyano, contrary to what happens in water.

The two paths of oxidation by TiO_2 photocatalysis in aqueous or, respectively, organic medium have a close analogy with other oxygenation procedures. Thus dialdehydes **2** and **3** are the main products of the ozonolysis of naphthalene in water,[9] while phthalic anhydride is produced by its air oxidation over vanadium pentoxide[10,11] as well as (along with other phthalic acid derivatives) by its ozonolysis in an organic solvent.[12–14]

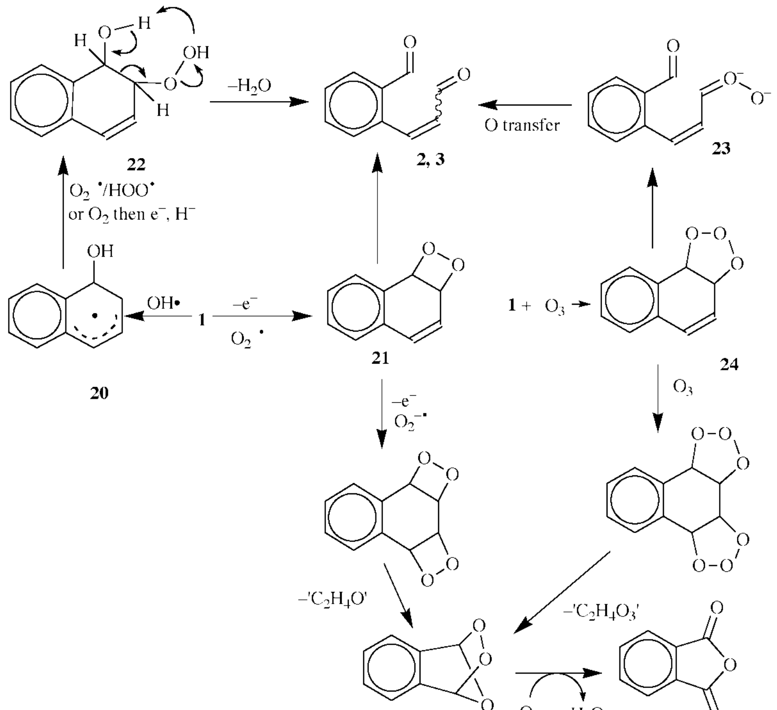
As mentioned in the introduction, the alternatives in water are that the excited semiconductor acts as a source of hydroxy radicals or that the organic substrate undergoes electron transfer (path *a* and *b* in Scheme 1). This is shown in Scheme 5 for the case of the simplest aromatic derivative, benzene. Electronic excitation promotes an electron to the conduction band and this reduces oxygen to superoxide anion (or its conjugated acid, the hydroperoxyl radical, pK_a 4.7 in water).[15a] The oxidation path may involve formation of $OH^\bullet$ and addition to give the hydroxycyclohexadienyl radical **15**. Such radicals are known to be efficiently trapped by dioxygen to give peroxyl radicals such as **16**.[15b,c] In radiolytic experiments, it has been demonstrated that the main fate of the last species is loss of a hydroperoxyl radical and rearomatisation to give a phenol.[15b] Polyhydroxylated compounds are formed also in the Fenton reaction, known to occur *via* hydroxy radicals.[15d] However, very little phenol (or dihydroxybenzenes) has been obtained from benzene with TiO_2.[8a] In that case it has been proposed that **16** rather adds a $HOO^\bullet$ radical giving the hydrotetraoxide **17** and this in turn gives the dialdehyde by loss of oxygen and water[8a] (a sequence reminiscent of the Russell's mechanism operating in the oxidation of aliphatic derivatives).[15e] A recent theoretical study points in the same direction, showing that in the presence of a sufficiently high NO_x concentration radical **16** is intercepted and finally gives muconaldehyde **18**, while at a low concentration of NO_x **16** rather gives phenol.[15f] In the alternative mechanism, hole transfer, the aromatic radical cation **14** may either add water (and in this case the distinction from $OH^\bullet$ transfer is purely semantic) or add superoxide leading to peroxide **19** that in turn cleaves to the aldehyde.



Scheme 5

The present investigation with naphthalene and some of its derivatives makes evident the following characteristics of the process: in water the typical products are dialdehydes **2** and **3**, not obtained with authentic $OH^\bullet$ methods (exactly the same result has been previously obtained with quinoline).[5] Naphthols are not main products. The reaction is quenched both by isopropanol (at a 0.01% concentration, *viz.* when it is in a fourfold excess with respect to the aromatic, it halves the rate of oxidation) and, more efficiently, by SOD (it reduces the rate of oxidation to 60% when used at equimolecular concentration and to 5% when in a fivefold excess); the product distribution changes from water to organic solvents, but in both cases it is similar to that obtained by ozonation under the same conditions; the photo-oxidation is quite indiscriminate in water, but it is chemoselective in organic solvents. Most of these pieces of evidence are in conflict with a process where reaction with $OH^\bullet$ radical is the main path, or at least differ significantly from hydroxy radical degradation of PAHs in homogeneous solution or in the gas-phase (see above).

Scheme 6 rationalises the formation of the observed products in water either *via* the hydroxycyclohexadienyl radical **20** or *via* the cyclic peroxide **21**. If radical **20** is the intermediate, superoxide is also involved as shown, by SOD quenching. Thus, either **20** couples with $O_2^{-\bullet}/OOH^\bullet$ (either of which, since there is little difference above and below the pK_a) as soon as it is formed, or it first adds oxygen and the peroxyl radical is then rapidly reduced by $O_2^{-\bullet}$. This justifies the difference in the course of the reaction with other sources of $OH^\bullet$ radicals. The resulting adduct **22** may directly eliminate water to give dialdehydes **2**, **3**. Alternatively, this product may be formed through the electron transfer path through retro-cycloaddition from dioxetane **21** (as well as by ozonation *via* carbonyl oxide **23**, explaining the similar results of the two methods of oxidation in water). In either way, it is appears viable that these products, which are in fact naphthalene–oxygen adducts, are formed directly from the components *via* TiO_2 photoactivation and there is no indication that they are



Scheme 6

formed from some other intermediate.‡ Formation of $O_2^{-\bullet}$ is relevant, not only for the mechanism of the TiO_2 photo-oxidation, but also for its efficiency, since *simultaneous* electron transfer to oxygen is a condition for successful $OH^\bullet$ (or hole) transfer to naphthalene, as one might expect, since this process must compete with the extremely fast e_{cb}^-/h_{vb}^+ recombination (bet) at the semiconductor surface (see Scheme 6).[4]

As for the choice between the two possible mechanisms, the non selectivity of the oxidation (note in particular that nitrile **7b** is oxidised at a rate somewhat higher than parent **1** in water, while it remains almost un-oxidised in organic solvents) supports the former one (unless excited TiO_2 is a much stronger oxidant in water than it is in organic media). Intervention of $OH^\bullet$ is in accord with the quenching by hydrogen donating isopropanol and, due to its electrophilicity, with the fact that a strong electron-withdrawing substituent such as a cyano group directs the attack towards the unsubstituted rings, although in all the other cases there is no regioselectivity.

Oxidation in organic solvents necessarily involves the electron transfer path. The oxidation of some dimethylnaphthalene and of 1-methoxynaphthalene in acetonitrile has been previously studied by Fox and associates[7] and shown to give phthalic acid derivatives. Table 3 shows that the same process occurs also with parent **1**.

The reaction is slower than in water (see Table 2). This may be due to a less favoured adsorption on the semiconductor as well as to less efficient electron transfer, in view of the above-mentioned fast charge recombination on a surface. Thus, the beneficial effect of silver sulfate in MeCN is due to the fact that Ag^+ ions deposited on the surface, and thus at a high local concentration, participate in the redox equilibrium and increase the overall chance of e_{cb}^-/h_{vb}^+ transfer *vs.* bet. However, the reaction occurs conveniently also in dichloromethane with no added silver salt (thus also excluding the role of Ag^+ is the catalysis of the decomposition of peroxides, which would otherwise decay to **1** and singlet oxygen).[16] In the last solvent a good yield of isolated products is obtained (see Tables 2, 3), likely due to the fact that a less polar solvent further differentiates the rate of oxidation of **1** and of the poorer donors **4** and **12**, causing an enhanced accumulation of these products, that would otherwise be only intermediates in the path leading to the complete mineralisation of **1**.

As for the medium effect onto the product distribution, it should be noted that C–C bond fragmentation in intermediates such as **21**, **22** and **24** likely involves considerable charge separation. This is probably the cause of the predominance of ring-opened aldehydes in water both in the TiO_2 photocatalysis and in ozonation. These are products that, as mentioned above, may result from the addition of a single molecule of oxygen or, respectively, ozone. In organic solvents, in contrast, only products necessarily requiring a further addition process are isolated. This may be because ring closed peroxides and ozonides do not cleave and the reaction proceeds with further oxidation and elimination of carbon atoms in positions 2 and 3 to give phthalic anhydride, *e.g. via* ozonide **25**; there is some evidence for the intermediacy of **25** in the ozonation of **1** in chloroform.[14]§ Naphthoquinone may likewise result from a further oxidation step *via* this mechanism by $OH^\bullet$ addition *via* dihydroxynaphthalenes.

In conclusion, TiO_2 photocatalysis is a powerful method for the oxidation of aromatics, and in particular of naphthalene. The efficient process in water differs from other oxidations in the same medium, *e.g.* radiolysis or Fenton reaction, involving free hydroxy radicals. Even if a hydroxycyclohexadienyl radical may be the intermediate also in this case, this occurs at the catalyst surface and coupling with the simultaneously formed superoxide anion predominates over addition to dioxygen. The reaction is neither chemo- nor regioselective and leads to cleaved dialdehydes or to 1,4-naphthoquinone. In contrast to the rather unspecific oxidation in water, the slower oxidation in organic media is inhibited by electron-withdrawing substituents on the naphthalene ring and is regiospecific toward the electron rich ring, as previously shown by Fox *et al.*[7] This is due to the lower efficiency of the redox step at the semiconductor surface in this case, but this limitation can be at least in part overcome by the appropriate choice of solvent or by additives (Ag^+), and there is the advantage that the oxidation can be driven to a >50% yield of identified products, rather than *ca.* 15% as in water, where subsequent oxidation of the first formed intermediates is less easily controlled. Progress toward the use of this oxidation for synthetic methods appears feasible.

Experimental

Naphthalenes **1**, **7a–c** were commercial products. 1-[α,α,α-$^2H_3$]-Methoxynaphthalene was prepared from 1-naphthol and [$^2H_3$]methyl iodide. Titanium dioxide (Degussa P25), a known mixture of 80% anatase and 20% rutile with an average particle size of 30 nm and a reactive surface area of approximately 50 $m^2\ g^{-1}$, was used as received.

Irradiations were carried out on mechanically stirred, air equilibrated solutions contained in 4.5 cm diameter cylindrical reactors. Samples (10 ml) containing 5 mg TiO_2 were used. For experiments in water, 0.1 ml of the appropriate stock solution of the naphthalene in MeCN was added. The suspension was stirred for 20 min and then irradiated using two 15 W phosphor-coated lamps (centre of emission, 360 nm). For aqueous solution, the photolyte was extracted with 2 × 3 ml dichloromethane, filtered with a 0.2 µm porosity filter under vacuum and rotary evaporated. The residue was dissolved in MeCN (0.5 ml total volume, containing an appropriate internal standard). The aqueous solution was filtered with a water-compatible 0.2 µm porosity filter under vacuum and rotary evaporated. The residue was also in this case dissolved in MeCN (0.5 ml total volume, containing an appropriate internal standard) for the determination of more polar products such as phthalic acid. Gas chromatography analyses were carried out using an HP 5890 apparatus with a 0.3 mm × 30 m capillary column with a flame ionisation detector. Gas chromatography-mass spectrometry determination was performed using an HP 5970B instrument operating at a ionizing voltage of 70 eV, connected to an HP 5890 instrument equipped with the same column as above. In the case of **1**, calibration curves for the determination of the photo-oxidation products were constructed by adding appropriate amounts of the authentic materials to samples which were taken in the dark and treated as the irradiated samples. In the case of substituted naphthalenes **7** it was assumed that the sensitivity of the method was similar to that for the products obtained with **1**.

Preparative experiments for the isolation of the photoproducts from **1** were carried out by using 100 ml samples containing 1 g naphthalene and irradiating for 20 h. The products were isolated by silica gel column chromatography eluting with cyclohexane–ethyl acetate mixtures. Aldehydes **2** and **3** are known compounds and were recognised on the basis of the comparison of the analytical and spectroscopic properties.[9,17,18]

The structure of the products from substituted naphthalenes was attributed on the basis of GC-MS data (see Table 4). The dialdehydes **2** and **3** are characterised by weak or undetectable

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‡ Theurich *et al.*[6c] suggest that the aldehydes are formed by secondary oxidation (apparently a typing mistake for reduction) of 1,2-naphthoquinone, in turn formed from the naphthols. It is known that quinones can be reduced under the conditions of photocatalysis,[19] but there is no indication of such a reductive ring-cleavage.

§ It may be noticed that products resulting from the addition of a single molecule of oxygen are also found in organic solvents when the peroxides are converted to stable end-products, as it is the case with alkenes.[20]

Table 4 Diagnostic peaks in the mass spectra of dialdehydes **2**, **3**, **8**–**11**[a]

X = H (M = 160), *m*/*z*	131(100)	131(100)				
	103(50)	103(50)				
	102(14)	102(14)				
X = Cl (M = 194), *m*/*z*	165(100)[b]	165(100)[b]	165(100)[b]	165(100)[b]	165(100)[b]	165(100)[b]
	129(16)	129(23)	137(20)[b]	137(14)[b]	137(13)[b]	137(15)[b]
	103(17)	103(20)	103(13)	103(13)	103(8)	103(12)
	102(31)	102(32)	102(33)	102(33)	102(28)	102(30)
X = CN (M = 185), *m*/*z*	156(100)	156(100)	156(100)	156(100)		
	128(20)	128(36)	128(36)	128(25)		
	102(20)	102(28)	102(26)	102(21)		
X = OMe (M = 192), *m*/*z*	161(100)[c]	161(100)[c]	161(100)[c]	161(100)[c]	161(100)[c]	161(100)[c]
	131(47)	131(32)	146(21)	146(24)	131(28)	146(25)
	118(19)	118(14)	118(17)	118(13)	118(19)	118(21)
	103(25)	103(16)	103(15)	103(5)	103(12)	103(4)

[a] The peaks attributed to the dialdehydes are reported in order of increasing GC retention time. [b] Contains one chlorine atom. [c] 164 *m*/*z* when the α,α,α-trideutero derivative is photo-oxidised.

M^+ (160 *m*/*z*) in the mass spectrum with base peak at 131 ($M^+ - 29$) and prominent peaks at 103 and 102 *m*/*z* corresponding to the sequential losses of the two formyl groups. In the case of 1-naphthonitrile, the cyano group is conserved in the corresponding ions (156, $M^+ - 29$ and 128 *m*/*z*), indicating that it is located on the intact ring. With 1-chloronaphthalene, six isomers are observed (base peak 165 *m*/*z*, $M^+ - 29$). Among these, four conserve the chlorine atom also after the loss of the second carbonyl, and thus arise from oxidation of the unsubstituted ring, two lose chlorine before CO and thus arise from oxidation at position 3 and 4. Attack at positions 1 and 2 leads to acyl chlorides, that are hydrolysed to the acids, poorly extracted with the present procedure. With 1-methoxynaphthalene, again six isomers are observed (base peak 161, $M^+ - 29$). In the subsequent fragmentation, losses of formyl and methyl groups compete to a various extent (rationalisation supported by experiments with the α,α,α-trideutero derivative), supporting that both rings are attacked.

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