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# Reaction paths in the titanium dioxide photocatalysed degradation of dodecane and some of its derivatives

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**Abstract**—The photocatalytic oxidation of dodecane and some of its derivatives ($C_{12}H_{26}$, **1**; $C_{10}H_{21}CH{=}CH_2$, **2**; $C_{12}H_{25}SH$, **3**; $C_{12}H_{25}OH$, **4**; $C_{12}H_{25}NH_2$, **5**; $C_{11}H_{23}CHO$, **6**) has been studied in air-equilibrated aqueous $TiO_2$ suspensions. The distribution of the intermediate products has been monitored during the degradation. $C_1$–$C_{12}$ Monocarboxylic acids are formed in all cases, though in a low yield with substrates **1**–**3**. With compounds **4**–**6**, acids are formed in a higher yield (>45%), initially including a large proportion of dodecanoic acid and are accompanied by significant amounts of aldehydes and alcohols. Relative efficiencies vary over a factor of 300 from **1** to **5** and a lower limit for the quantum yield is 1.18 for the latter compound, suggesting participation of a chain process. The data suggest that alkylperoxyl radicals are formed through initial hydrogen abstraction on the photocatalyst surface and oxygen addition and their reactivity with the starting reagent determines the course of the reaction. Activated substrates such as compounds **5** and **6**, and to a lesser degree **4**, easily transfer a hydrogen from position 1. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Photocatalytic degradation of organic compounds using semiconductor powders has been largely used for the purification of polluted water.[1] With respect to other abiotic degradation methods, this has the advantage that no further chemicals are added and quite often a complete mineralisation of the organic substrates is obtained. Commercial titanium dioxide produced as a pigment requires no treatment or activation and can be directly used as photocatalyst. This has fostered a large number of studies aiming to ascertain the applicability of this semiconductor for the elimination of a variety of pollutants. There is a general consensus that the chemistry occurring upon irradiation in air or oxygen equilibrated aqueous suspensions involves formation of hydroxyl radicals which are then the key active species in the oxidation of the organic substrates,[1] although there is evidence that good organic donors (in particular aromatics) can also be directly oxidised on the semiconductor surface.[1m]

However, differently from oxidation processes where the hydroxyl radical is produced in a homogeneous solution,[2] the intrinsically more complex photocatalysed degradation has not been characterized in depth and several intriguing points in the mechanism of the overall process leading to mineralisation of organic substrates remain. Some of these have been extensively addressed, but this mostly concerns the initial step, viz. charge transfer on the semiconductor surface, while chemical analysis of the degradation process of the organic molecule is generally limited either to the initial stage (by measuring the substrate reacted) or the

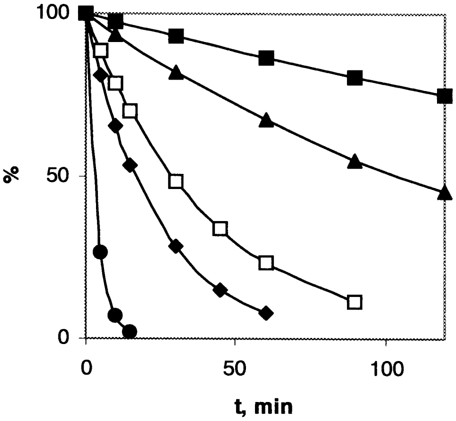

**Figure 1.** Photocatalytic degradation of $C_{12}H_{26}$, **1** (■); $C_{10}H_{21}CH{=}CH_2$, **2** (▲); $C_{12}H_{25}SH$, **3** (□); $C_{12}H_{25}OH$, **4** (◆); $C_{11}H_{23}CHO$, **6** (●).

**Table 1.** Apparent first order rate constants ($k_{ap}$) and quantum yield ($\Phi_{ap}$, moles per Einstein of *incident* light, see text) for reagent consumption in the $TiO_2$ photo-catalysed oxidation of dodecane and some of its derivatives

| | Compound | | | | | | |
|---|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | **5** | **6** | PhOH |
| $k_{ap}\times10^4\ s^{-1}$ | 0.4 | 1.1 | 4 | 7 | 130 | 44 | |
| $\Phi_{ap}$ | 0.0035 | 0.01 | 0.036 | 0.063 | 1.18 | 0.4 | 0.14 |

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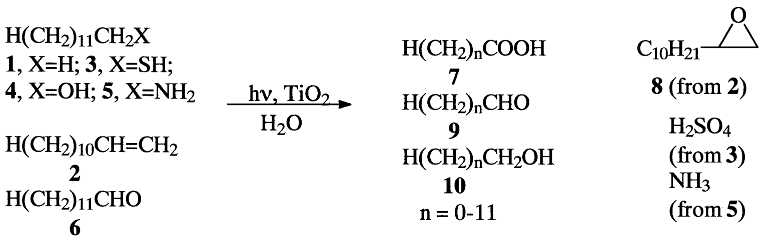


**Scheme 1.**

final stage of the overall reaction (through $CO_2$ formation). The 'organic' chemistry occurring under these conditions has been investigated to a limited extent. A detailed knowledge of the intermediates is required in order both to assess the applicability of the method, i.e. to check whether more resistant—or more toxic—compounds are formed during the course of the mineralisation, and to afford a basis for a mechanistic proposal.

**Table 2.** Product distribution upon $TiO_2$ photo-catalysed oxidation of dodecane and some of its derivatives

| Substrate | Approximate conversion | Carboxylic acids[a] | | Approximate conversion | Carboxylic acids[a] | |
|---|---|---|---|---|---|---|
| **1**, $C_{12}H_{26}$ | 50% | $C_{12}$ | 2% | 95% | $C_{12}$ | 2% |
| | | $C_9$–$C_{11}$ | 1 | | $C_9$–$C_{11}$ | 2 |
| | | $C_3$–$C_8$ | 2 | | $C_3$–$C_8$ | 5 |
| | | $C_2$ | 9 | | $C_2$ | 13 |
| | | $C_1$ | 6 | | $C_1$ | 4 |
| **2**, $C_{10}H_{23}CH{=}CH_2$ | 50% | $C_{12}$ | 4%[b] | 95% | $C_{12}$ | 3% |
| | | $C_9$–$C_{11}$ | 3 | | $C_9$–$C_{11}$ | 3 |
| | | $C_3$–$C_8$ | 7 | | $C_3$–$C_8$ | 9 |
| | | $C_2$ | 9 | | $C_2$ | 16 |
| | | $C_1$ | 6 | | $C_1$ | 4 |
| **3**, $C_{12}H_{25}SH$ | 50% | $C_{12}$ | 1% | 95% | $C_{12}$ | 3%[c] |
| | | $C_9$–$C_{11}$ | 1 | | $C_9$–$C_{11}$ | 3 |
| | | $C_3$–$C_8$ | 7 | | $C_3$–$C_8$ | 9 |
| | | $C_2$ | 14 | | $C_2$ | 26 |
| | | $C_1$ | 10 | | $C_1$ | 8 |

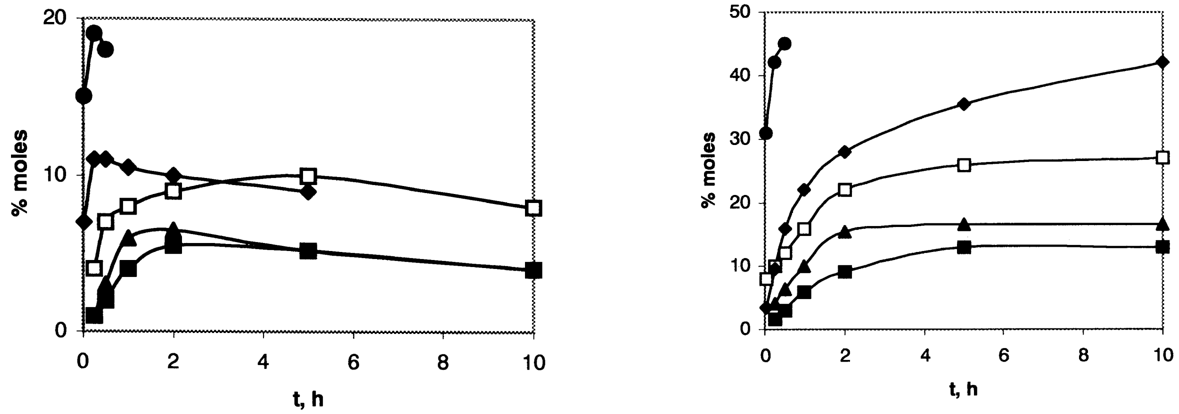
| Substrate | Approximate conversion | Carboxylic acids | | Aldehydes or ketones | | Alcohols | |
|---|---|---|---|---|---|---|---|
| **4**, $C_{12}H_{25}OH$ | 50% | $C_{12}$ | 7.5% | $C_{12}$ | 7% | | |
| | | $C_9$–$C_{11}$ | 1.5 | $C_9$–$C_{11}$ | 8.5 | $C_9$–$C_{11}$ | 5.5 |
| | | $C_3$–$C_8$ | 8 | | | | |
| | | $C_2$ | 16 | | | | |
| | | $C_1$ | 12 | | | | |
| | 95 | $C_{12}$ | 4.5 | $C_{12}$ | 6% | | |
| | | $C_9$–$C_{11}$ | 1 | $C_9$–$C_{11}$ | 7 | $C_9$–$C_{11}$ | 2 |
| | | $C_3$–$C_8$ | 12 | | | | |
| | | $C_2$ | 26 | | | | |
| | | $C_1$ | 9 | | | | |
| **5**, $C_{12}H_{25}NH_2$ | 50% | $C_{12}$ | 11 | $C_{12}$ | 2 | $C_{12}$ | 1 |
| | | $C_9$–$C_{11}$ | 1 | $C_9$–$C_{11}$ | <1 | $C_9$–$C_{11}$ | <1 |
| | | $C_3$–$C_8$ | 1 | | | | |
| | | $C_2$ | 36 | | | | |
| | | $C_1$ | 14 | | | | |
| | 95 | $C_{12}$ | 7 | $C_{12}$ | 3 | $C_{12}$ | 1[d] |
| | | $C_9$–$C_{11}$ | 19 | $C_9$–$C_{11}$ | 9 | $C_9$–$C_{11}$ | 4 |
| | | $C_3$–$C_8$ | 1 | | | | |
| | | $C_2$ | 27 | | | | |
| | | $C_1$ | 33 | | | | |
| **6**, $C_{11}H_{23}CHO$ | 50% | $C_{12}$ | 14 | | | | |
| | | $C_9$–$C_{11}$ | 2.5 | $C_9$–$C_{11}$ | 2.5 | $C_9$–$C_{11}$ | 3 |
| | | $C_3$–$C_8$ | 1 | | | | |
| | | $C_2$ | 36 | | | | |
| | | $C_1$ | 19 | | | | |
| | 95 | $C_{12}$ | 14 | | | | |
| | | $C_9$–$C_{11}$ | 2 | $C_9$–$C_{11}$ | 5 | $C_9$–$C_{11}$ | 5 |
| | | $C_3$–$C_8$ | 1 | | | | |
| | | $C_2$ | 46 | | | | |
| | | $C_1$ | 15 | | | | |

[a] Aldehydes, ketones, alcohols, each <1% except when noted.

[b] 1% Undecanal and 2% 1,2-dodecane epoxide also detected.

[c] 53% $H_2SO_4$.

[d] 70% $NH_3$.



(a) (b)

**Figure 2.** Formation of (a) formic acid and (b) acetic acid during the photocatalytic degradation of $C_{12}H_{26}$, **1** (■); $C_{10}H_{21}CH{=}CH_2$, **2** (▲); $C_{12}H_{25}SH$, **3** (□); $C_{12}H_{25}OH$, **4** (◆); $C_{11}H_{23}CHO$, **6** (●).

In particular, photocatalysis is known to be effective also with inactivated substrates, such as linear alkanes or their simple derivatives.[3] The success with these otherwise unreactive pollutants opens useful perspectives since this allows the application of the method in various fields, ranging from oil spill cleaning[4a] to self-cleaning glasses,[4b] or to the elimination of surfactants for recovering industrial water.[5] However, the chemical paths followed in the degradation and the effect of substituents have not been investigated with such aliphatic derivatives, while a detailed knowledge would be particularly useful in this case, where photocatalysis may have greater application than thermal alternatives.

## 2. Results and discussion

We deemed it worthwhile to carry out a comparative study of the $TiO_2$ photocatalysed degradation of dodecane and some of its derivatives bearing a chemical functionality and to determine the products distribution during the course of the degradation. Mechanistic hypotheses could be formulated on this basis. The substrates considered were dodecane (**1**) and some of its derivatives having a substituent in position 1 (C=C double bond, OH, SH, $NH_2$, CHO, compounds **2**–**6**). Stirred suspensions of $TiO_2$ (0.5 g/L) in water containing aliphatic derivatives **1**–**6** (initial concentrations in the range 30–220 ppm were used) were irradiated at 360 nm by phosphor coated lamps. The course of the reaction was monitored under standardised conditions both by gas chromatography and by ionic chromatography in order to determine both non-ionic and ionic products. The kinetics of degradation as well as the intermediates formed at various stages of the reaction was determined. The substrates and the products were transparent in the wavelength range used and blank experiments omitting $TiO_2$ showed no significant decomposition on the time scale observed for photocatalysis, ascertaining that no direct photochemistry was involved.

Dodecane (**1**) was slowly oxidised (several hours) under this condition. The substrate consumption followed first-order kinetics ($k_{\mathrm{ap}}$ $4\times10^{-5}$ $\mathrm{s}^{-1}$ for $c_0<50$ ppm, see Fig. 1, Table 1; the kinetics tended to zero order for larger values of $c_0$). The only products detected in a significant amount during the degradation process were the homologous aliphatic carboxylic acids from formic to dodecanoic (**7**, see Scheme 1). When a high conversion was reached (e.g. 8 h for the 95% conversion of 100 ppm), the main product was acetic acid (13 mol%, see Table 2, Fig. 2). Both formic acid (4%) and longer chain ($C_3$–$C_{12}$) carboxylic acids (9%) were present in lower amounts. In separate experiments it was shown that formic acid ($c_0$ 10 ppm) was consumed 20 times faster than acetic acid under the same conditions of the experiments above. Neither in this nor in the following cases were significant amounts of dicarboxylic acids formed (tested: malonic and succinic, but other derivatives would be likewise detected by ionic chromatography). At very long irradiation times (e.g. 15–20 h for the case above), the carboxylic acids were in turn consumed and the mineralisation of the organic compounds was completed. In this and in the following cases the product composition (mol%) at ca. 50 and 95% consumption of the starting material has been reported in Table 2.

The photo-oxidation of 1-dodecene (**2**) took place at a somewhat faster rate (Fig. 1); the product distribution was similar to the case of **1** and again gave homologous aliphatic acids as the products (Fig. 2, Table 2). These were accompanied in this case by small amounts of 1,2-epoxydodecane (**8**) and of undecanal (**9**, $n=10$). Likewise, *n*-dodecylsulfide (**3**) was photo-oxidised to give carboxylic acids, accompanied by sulfuric acid as the only sulfur derived product.

In the case of *n*-dodecanol (**4**) the reaction differed both in being considerably faster and in giving a detectable amount of primary alcohols (**10**), aldehydes (**9**) and (to a minor extent, <20% of the corresponding aldehydes) ketones along with carboxylic acids (**7**, see Scheme 1). Although these products were in turn degraded at a rate equal or larger than that of the starting substrate, their concentration reached a measurable value at an intermediate conversion. This is shown for some long-chain derivatives in Fig. 3.

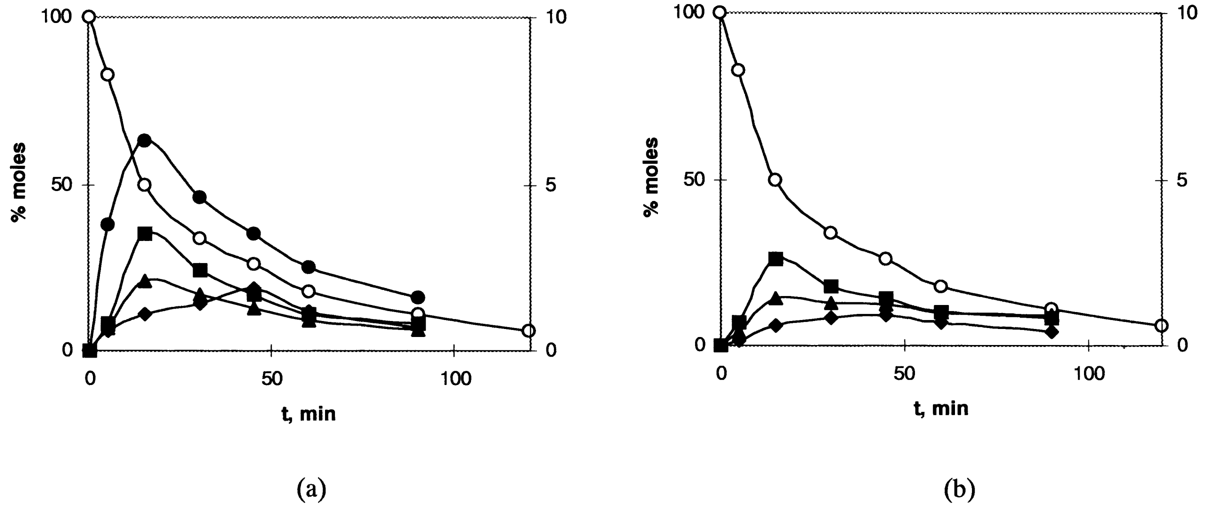


**Figure 3.** Photocatalytic degradation of dodecanol, **4** (○, left-hand ordinate scale) and formation of intermediates (filled symbols, right-hand scale): (a) aldehydes, (b) alcohols: $C_{12}$ (●), $C_{11}$ (■), $C_{10}$ (▲), $C_9$ (◆).

The behaviour of *n*-dodecylamine (**5**) was similar to that of **4** as far as the product distribution was concerned, with ammonia as the only nitrogen containing product. With this substrate, however, the reaction was more than 20 times faster than with dodecanol (Fig. 1, Table 1).

Finally, dodecanal (**6**) was also rapidly oxidised, giving carboxylic acids, including a significant amount of the long-chain acids, as well as aldehydes and alcohols (Fig. 4).

Another product formed was hydrogen peroxide, but alkyl

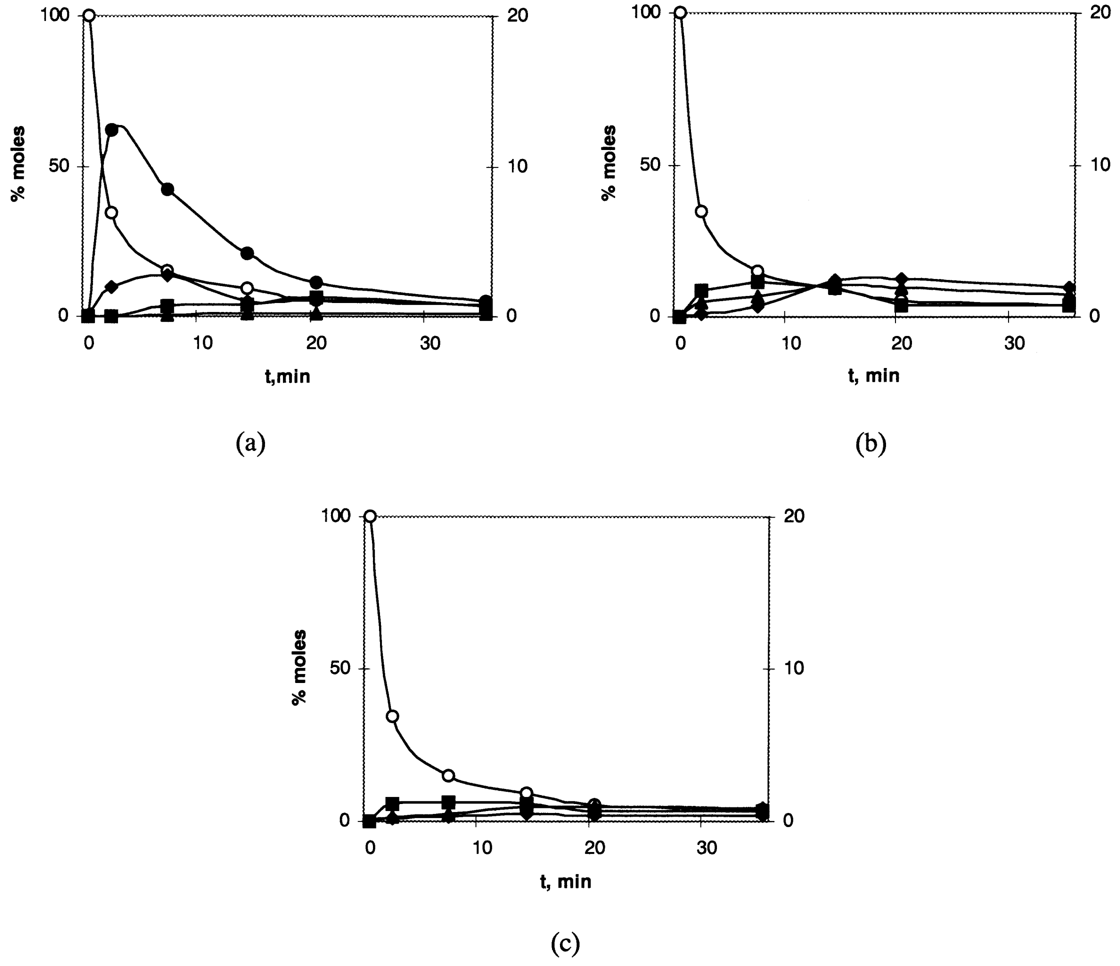


**Figure 4.** Photocatalytic degradation of dodecanal, **6** (○, left-hand ordinate scale) and formation of intermediates (filled symbols, right-hand scale): (a) carboxylic acids, (b) aldehydes, (c) alcohols: $C_{12}$(●), $C_{11}$ (■), $C_{10}$ (▲), $C_9$ (◆).

hydroperoxides did not accumulate in a significant amount, as shown by the fact that treatment with reducing agents such as sodium sulfite or triphenylphosphine did not yield new volatile products.

The incident flux in these experiments was of ca. $8\times10^{-9}$ Einstein $s^{-1}$ $cm^{-2}$, with a 320–390 nm wavelength range, peak emission at 360 nm. There is some controversy about measuring the quantum yield in a photocatalytic process, since this requires that the amount of light absorbed—rather than reflected—by the semiconductor powder is determined. An acceptable alternative is measuring the 'apparent' quantum yield on the basis of the impinging light flux, provided that this is compared with that of a well known model taken as standard.[6] We thus measured the photo-oxidation of phenol under the same conditions in order that the results could be compared with what is reported in literature for other substrates. Phenol has been found to be oxidised in air saturated solution by Degussa P-25 titania with an apparent quantum yield of 0.11 under conditions comparable to our own.[6c] We found a similar value, $\Phi_{ap}=0.12$, in our set up and thus the values of $\Phi_{ap}$ for substrates **1**–**6** (reported in Table 1) are directly comparable. These are proportional to quantum yields and set a lower limit for the actual value.

One of the typical examples of the potential of $TiO_2$ heterogeneous photocatalysis for the recovery of polluted water is its effectiveness for degrading such resistant substrates as alkanes. Indeed, previous studies had shown that dodecane (**1**) is mineralised under such conditions giving ca. 100% $CO_2$, and the same holds for dodecanol (**4**).[3b] The present work extends the investigation to several aliphatic derivatives and monitors the intermediates formed in the oxidation process. In the following, the chemical paths occurring are discussed and compared with the known reactivity of possible intermediate radicals in order to check the viability of degradation mechanisms.

Significant indications are the following. The efficiency of the photo-oxidation process changes by a factor of 300 from alkane **1** to alkylamine **5**. The apparent quantum yield, which is a lower limit, is somewhat above 1 for the latter compound and also the oxidation of aldehyde **6** (0.4) is remarkably more efficient than that of phenol (0.11) and of substituted phenols (which arrives at a value of 0.3 for some derivatives).[6]

Importantly, several oxidation intermediates are formed in easily detectable amounts. Indeed, with the most easily degraded substrates, i.e. **5** and **6**, the sum of identified intermediates is a significant fraction of the consumed starting material (at limited conversion, often 50% or more), although with less reactive substrates this percentage is low and most intermediates are barely detectable. The structure of the intermediates formed provides evidence that a stepwise degradation of the carbon skeleton takes place and involves carboxylic acids, primary alcohols, and aldehydes (Figs. 3 and 4). The latter two classes of compounds are detected only with rapidly reacting substrates (**4**–**6**) and their formation in preference to ketones is evidence for a selective reaction at the functional group at position 1 rather than at the aliphatic backbone. Aldehydes (or ketones) and alcohols are presumably also formed with the more slowly reacting derivatives **1**–**3**, but then are degraded at a faster rate than the starting material, and therefore are not accumulated to a degree allowing identification, though carboxylic acids are.

It is generally agreed that irradiation leads to the formation of hydroxyl radicals (or $Ti^{IV}$–$OH^\cdot$ groups) and the superoxide anion (or, upon protonation, the hydroperoxyl radical $OOH^\cdot$) on the catalyst surface (Eq. (1)).

$$TiO_2(H_2O, O_2) \xrightarrow{h\nu} TiO_2(H^+, OH^\cdot, O_2^{\cdot -}) \qquad (1)$$

Although the active species are destroyed through fast charge recombination ($OH^\cdot + e^-$),[7] adsorbed substrates may undergo hydrogen abstraction by such intermediates and finally lead to irreversible oxidation.[1,8] (Eq. (2))

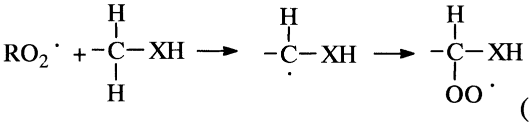
$$TiO_2(H^+, OH^\cdot, O_2^{\cdot -}) + R\text{–}H \rightarrow R^\cdot \overset{O_2}{\Rightarrow} RO_2^\cdot \qquad (2)$$

However, hydrogen abstraction from C–H bonds by $OH^\cdot$ radicals—or equivalent Ti-bonded $OH^\cdot$ groups—is non-specific, since it is strongly exothermic, and is not per se the cause of the observed large difference in the rate of degradation of the investigated alkyl derivatives. This is rather to be referred to the following reaction of the alkylperoxyl radicals formed by oxygen addition to the alkyl radicals (Eq. (2)), which are known as less efficient, and thus more selective, hydrogen abstracting species (Eq. (3))[9,10]

$$RO_2^\cdot + R'\text{–}H \rightarrow RO_2H + R'^\cdot \qquad (3)$$

Among the substrates investigated, amine **5** and aldehyde **6** are distinguished by the much larger rate of degradation and by the higher proportion of characterised intermediates (acids, aldehydes and alcohols). These pertain to classes known for their relatively high reactivity with peroxyl radicals, e.g. a rate of 21 $M^{-1}$ $s^{-1}$ has been measured for the reaction of *tert*-$BuO_2^\cdot$ with piperidine (and 380 $M^{-1}$ $s^{-1}$ for pyrrolidine)[11] and the rate of reaction with aliphatic aldehydes is similar.[12] This is five orders of magnitude larger than that with alkanes, where reaction rates (per equivalent hydrogen) in the range $k$ $1\times10^{-5}$–$3\times10^{-4}$ $M^{-1}$ $s^{-1}$ have been measured for linear derivatives in autooxidation processes.[13] Therefore, once a peroxyl radical has been formed in any part of the chain, efficient hydrogen transfer from the activated position will take place, whether inter- or intramolecularly.

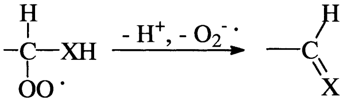
In the case of substrate **5**, hydrogen abstraction from position 1 and oxygen addition leads to α-aminoperoxyl radicals **11** (X=NH, Eq. (4))



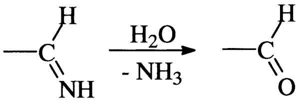
$$RO_2^\cdot + -\underset{H}{\overset{H}{C}}-XH \longrightarrow -\underset{\cdot}{\overset{H}{C}}-XH \longrightarrow -\underset{OO^\cdot}{\overset{H}{C}}-XH \qquad (4)$$

**(11)**

Elimination is known to be efficient with this type of radical (Eq. (5))[14] and yields an imine, which would hydrolyse to the corresponding aldehyde and ammonia (Eq. (6))



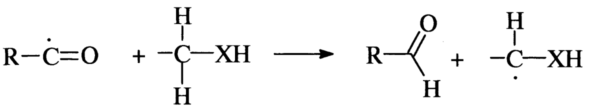
(5)



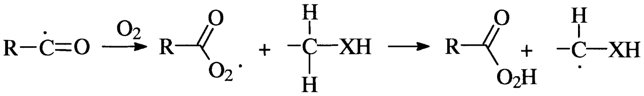
(6)

A mechanism which proceeds via the imine reasonably explains the formation of ammonia previously reported as the main product from the $TiO_2$ photocatalytic decomposition of various nitrogen-containing compounds (nitrate only being formed at long irradiation times).[15]

Hydrogen abstraction from dodecanal **6** (whether this is the initial substrate or is formed during the process, as it is the case with **5**, see Table 2; the corresponding imine would react in the same way)[16] leads to an acyl radical and from this to an acylperoxyl radical, both known to abstract hydrogen much more efficiently (Eqs. (7) and (8)). Such steps may lead to a chain reaction



(7)



(8)

Initially a high proportion of dodecanoic acid is formed (Table 2, Fig. 4), then degradation pursues. Intermediate peracids would be at least in part decaboxylated by alkyl radicals according to the process in Eq. (9), which has been previously been demonstrated to occur[17]

$$RCO_3H + R'^{\cdot} \rightarrow R^{\cdot} + CO_2 + R'\text{–}OH \quad (9)$$

The contribution of a chain process (via chain-carrying acyl and acylperoxyl radicals) accounts for the fact that amine **5** and aldehyde **6** react at a faster rate than phenol, which efficiently traps $OH^{\cdot}$ but forms stabilised radicals,[18] that with **5** the apparent quantum yield (which is a lower limit) is slightly greater than 1, and for the above mentioned selective attack at position 1.

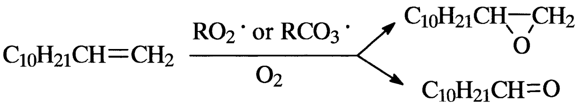
The reaction with alcohol **4** follows a similar course, with the formation of a detectable amount of intermediate aldehydes and alcohols (Fig. 3), though the process is much slower. This fits with the fact that the rate for hydrogen abstraction from alcohols by alkylperoxyl radicals (Eq. (4), X=O) is three orders of magnitude lower than for amines.[19] Similarly to the related amino derivatives, α-hydroxyperoxyl radicals cleave to aldehydes (Eq. (5), X=O)[20] and from these acyl and acylperoxyl radicals are formed as above.

With dodecane or dodecene, radical abstraction by peroxyl radicals is still slower, and it is expected that bimolecular coupling becomes a significant termination path (see Eq. (10), as an example the rates $k=4\times10^7\ M^{-1}\ s^{-1}$ for $n$-$BuO_2^{\cdot}$ and $1.5\times10^6\ M^{-1}\ s^{-1}$ for $sec$-$BuO_2^{\cdot}$ have been reported).[21] The envisageable formation of singlet oxygen is not relevant in the present case, where an unreactive substrate such as an alkane or a poorly reacting one such as a primary alkene are involved

$$2R_2CHOO^{\cdot} \rightarrow R_2CO + R_2CHOH + O_2 (\text{or } 2R_2CO + H_2O_2) \quad (10)$$

This leads again to aldehydes and ketones as well as alcohols (via a concerted or non-concerted mechanism),[22] but since under these conditions the reactivity of such intermediates far exceeds that of the starting hydrocarbons, their concentration remains below the detection limit.[23] Therefore, with hydrocarbons **1** and **2**, only aliphatic carboxylic acids, the penultimate products of oxidation before final mineralisation to $CO_2$, accumulate to a sizeable extent.

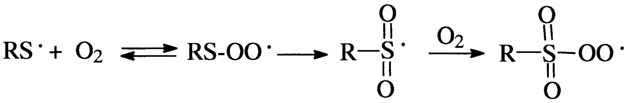
In the case of dodecene **2** the oxidation is somewhat faster than with **1**. Alkenes are known to undergo both allylic hydrogen abstraction and addition (to form epoxides) with peroxyl radicals.[13,25] A small amount of dodecene oxide (as well as of undecanal, Eqs. (12) and (13)) is indeed formed during the present $TiO_2$ photooxidation of **2** (Table 2)



(12)

(13)

In the case of dodecanethiol **3**, thiyl radicals are obviously formed. It is known that in aqueous oxygenated solutions these easily add oxygen (though the reaction is an equilibrium, Eq. (14)) to yield thioperoxyl radicals.[26] Exothermic rearrangement and further oxidation lead to sulfonyl and sulfonylperoxyl radicals (Eq. (14)), which are efficient hydrogen abstracting species[27]



$$RS^{\cdot} + O_2 \rightleftarrows RS\text{-}OO^{\cdot} \longrightarrow R-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}{}^{\cdot} \xrightarrow{O_2} R-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-OO^{\cdot} \quad (14)$$

This explains both the somewhat enhanced rate for the photo-oxidation in the long-chain thiol and the formation of sulfate as a major product.[28] On the other hand, disulfides which may be expected from the dimerizations of thiyl radicals[30] were not detected, possibly as a consequence of their low steady state concentration which makes reaction (14) predominating in oxygen equilibrated solution.

In conclusion, the analysis of the intermediates formed during the course of the $TiO_2$ photocatalytic degradation of long-chain hydrocarbons and of some simple functional derivatives is in accord with a process with alkylperoxyl radicals as the key intermediates. The low reactivity of such radicals at ambient temperature makes the progress of the reaction slow, except when a reactive group is present. This is the case with amines and aldehydes, with which radical chain processes are established and lead to a fast degradation of the substrates. This product study contributes to the knowledge of the mechanism, which would further require a positive spectroscopic identification of the intermediate radicals via spin traps, as has been done for the $OH^{\cdot}$ reaction,[31] as well as the evaluation of the fraction of the reaction occurring on the catalyst surface or in solution through the calculation of the kinetics of the adsorption process.[32]

From the point of view of the degradation of organics, it is remarkable that even alkanes are removed in a not inconveniently slow process and the only intermediates result from the progressive oxidative cleavage of the hydrocarbon chain up to complete mineralisation, with carboxylic acids as the only intermediates accumulated to an important extent. $TiO_2$ photocatalysis is an efficient method for the recovery of polluted water, which in the overall mechanism is reminiscent of the degradation of organic molecules by ionising radiation,[34] but occurs under extremely mild conditions.[1]

## 3. Experimental

The aliphatic derivatives **1–6** and the reference compounds **7**, **9** and **10** were commercial products. 1,2-Epoxydodecane (**8**) was prepared from **2** by peracetic acid oxidation.[35] 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. After that the appropriate amount of substrate was added, the suspension was stirred for 30 min and then irradiated using two 15 W phosphor-coated lamps (320–390 nm, centre of emission, 360 nm). With compounds **1–4** the aqueous solution was extracted with 2×3 ml ethyl acetate, filtered with a 0.2 μm porosity filter under vacuum and concentrated at the rotary evaporator in the cold. The residue was taken up in ethyl acetate (1 ml total volume, containing an appropriate internal standard) and examined by GC/MS. In the case of amine **5**, the suspension was analogously extracted with chloroform after the addition of hydrochloric acid and sodium chloride. With aldehyde **6** dichloromethane (3×3 ml) was used for the extraction. In every case, the aqueous solution was filtered with a water-compatible 0.2 μm porosity filter under vacuum and either as such or after concentration at the rotary evaporator examined by ionic exchange chromatography.

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 determinations were performed using an HP 5970B instrument operating at an ionising voltage of 70 eV, connected to an HP 5890 instrument equipped with the same column as above. The mass spectra were compared to those of authentic samples. Calibration curves for the determination of the residual starting material and of the photo-degradation 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. Ionic products were determined by means of a Dionex QIC ionic chromatograph fitted with a conductimetric detector by using an anionic exchange column and eluting with $Na_2CO_3$/NaOH solutions with a 1 ml/min flux.

The reaction of phenol was measured in the same experimental set-up. The light flux was measured by means of ferrioxalate actinometry according to the procedure by Hatchard and Parker.

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$$RO_2^{\cdot} + HO_2^{\cdot} \rightarrow RO^{\cdot} + O_2 + HO^{\cdot} \tag{11}$$

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