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Photo-oxidation of *n*-alkanes in simulated marine environmental conditions

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Abstract

n-Dodecane, *n*-hexadecane, *n*-nonadecane, *n*-eicosane and *n*-docosane were photo-oxidized in purified and sterilized natural sea water under simulated environmental conditions with anthraquinone as sensitizer. GC and GCMS analyses show the production of all the isomeric ketones and alcohols with the same number of carbon atoms as the starting alkane and the formation of minor photoproducts: methylketones, 1-alkenes, 3-substituted-γ-lactones, 1,2-epoxy-alkanes, carboxylic acids, 1,2-disubstituted cyclobutanols, γ-keto-2-alcohols, *n*-aldehydes, γ-diketones and alkanes. Mechanisms are proposed and discussed. A generalization of the photo-oxidation degradation pathways of *n*-alkanes in the marine environment is proposed using these results and some previous works.

Keywords: *n*-Alkanes; Photo-oxidation; Marine environment

1. Introduction

Previous studies have investigated the photo-oxidation of *n*-alkanes in sea water under simulated environmental conditions [1–11]. The formation, in acidic photoproduct fractions, of straight-chain fatty acids with fewer than 16 carbon atoms was observed during photo-oxidation of *n*-hexadecane [4]. In the non-acidic photoproduct fractions, the principal photoproducts were ketones and alcohols with the same number of carbon atoms as in the starting alkanes [1,2,5,6]. The production of all the positional isomers of the straight-chain hexadecanones and hexadecanols during photo-oxidation of *n*-hexadecane was clearly demonstrated [1]. Minor photoproducts were also detected: 1-alkenes, methylketones with a lower number of carbon atoms [1,2], and also series of *n*-aldehydes, 3-substituted γ-lactones and 2,5-diketones [1].

In order to summarize and generalize the mechanisms of *n*-alkane photo-oxidation, we carried out in vitro photo-oxidation experiments under environmental conditions on different *n*-alkanes: dodecane, nonadecane, eicosane and docosane.

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2. Experimental details

2.1. Photo-oxidation experiments

250 μl *n*-alkane in 100 ml autoclaved natural sea water was irradiated in borosilicate round bottom flasks. Traces (few milligrams) of anthraquinone (Aldrich 84-65-1) were added as photosensitizer.

An artificial light source (Osram Ultra Vitalux 300 W) emitting a gauss shaped spectrum which peaked at 370 nm with a cut-off at 290 nm was used for irradiations. Samples were irradiated during 2 months. Flasks with identical contents, kept in the dark for equal lengths of time, served to check for influences other than photo-oxidation, for example biodegradation or auto-oxidation. Some experiments were done with sunlight irradiation.

Irradiated solutions were adjusted to alkaline pH and then extracted with CH_2Cl_2 (3 × 25 ml). The organic phases were dried on Na_2SO_4, filtered and concentrated by rotary evaporation (35 °C).

The extracted products were then separated by open column 'flash' chromatography (Merk silica gel 60H ref. 1.07736) into three fractions: F_1 (3V heptane), F_2 (5V diethyl ether) and F_3 ($2V$ methanol), V being the volume of the bed of silica gel. The well known acidic F_3 fraction was not dealt with further.

2.2. *Instrumental analyses*

GC analyses of F_1 fractions were performed on a Vega 6000 Carlo Erba gas chromatograph equipped with an on-column injector and an FID detector. The following conditions were employed: 30 m × 0.32 mm (id) × 0.25 μm fused silica capillary column coated with DB5 (JW Scientific), temperature programme from 70 to 225 °C at 3 °C $\min^{-1}$, helium carrier gas (100 kPa) and a detector temperature of 300 °C.

GC analyses of F_2 fractions were performed on a CP 9000 Chrompack gas chromatograph equipped with an on-column injector and an FID detector. The following conditions were used: 50 m × 0.25 mm (id) × 0.25 μm CP Sil 52CB fused silica capillary column (Chrompack), temperature programme from 70 to 270 °C at 1 °C $\min^{-1}$, helium carrier gas (170 kPa) and a detector temperature of 270 °C.

GCMS analyses were carried out on a Hewlett Packard 5989A mass spectrometer (electron energy 70 eV, source temperature 240 °C) coupled with an HP 5890 gas chromatograph equipped with a splitless injector. Separations were achieved using the following conditions: HP5-MS (low bleed) capillary column (30 m × 0.25 mm (id) × 0.25 μm), temperature programme from 40 to 90 °C at 30 °C $\min^{-1}$, then 90 °C to 250 °C at 1 °C $\min^{-1}$, helium carrier gas with a constant flow rate of 1 ml $\min^{-1}$. For chemical ionization mass spectrometry, the reactant gas was methane (1 Torr) ionized with an energy of 230 eV.

3. Results

3.1. *Identification of photoproducts*

In order to identify alkane photoproducts, we studied precisely the F_1 and F_2 fractions which contain a great variety of non-acidic compounds.

Concerning the four n-alkanes, we mainly observed, as for n-hexadecane [1], the production in F_2 fractions of all the positional isomers of ketones and alcohols with the same number of carbon atoms as in the starting alkane, as shown in Fig. 1 for the n-dodecane photoproducts. The peaks were identified by GCMS, by observing (even in the case of coelutions) the characteristic molecular ions $(M)^+$, MacLafferty peaks $R\text{-}(HO)C^+ = CH_2$ and fragments resulting from α-cleavage in the ketone mass spectra. The alcohols are characterized by the usual $(M\text{-}18)^+$ and $(C_nH_{2n-1})^+$ ions and, to distinguish the isomeric secondary alcohols, by the $HO\text{–}CH^+\text{-}R$ and $(M\text{-}R)^+$ fragments.

After reduction with trimethylphosphite [12] of the F_2 fractions, the chromatograms do not show appreciable changes, indicating the absence of hydroperoxides. These compounds were probably not stable in sea water because of the presence of salts which favour cleavage of the O–O bond [13].

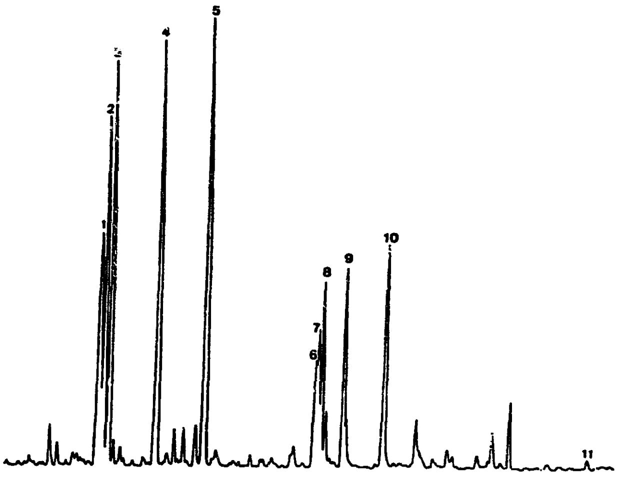


Fig. 1. Gas chromatogram of the F_2 fraction obtained by photo-oxidation of n-dodecane in natural sea water (dodecanone and dodecanol retention time range): 1, 6-dodecanone; 2, 5-dodecanone; 3, 4-dodecanone; 4, 3-dodecanone; 5, 2-dodecanone; 6, 6-dodecanol; 7, 5-dodecanol; 8, 4-dodecanol; 9, 3-dodecanol; 10, 2-dodecanol; 11, 1-dodecanol.

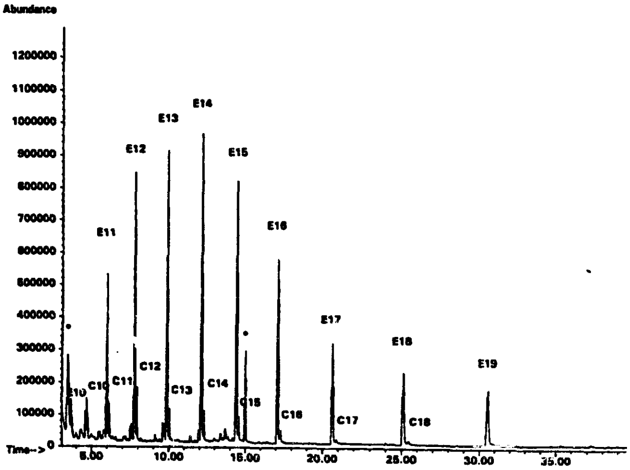


Fig. 2. Total ion chromatogram of the F_1 fraction obtained by photo-oxidation of n-docosane in natural sea water (before elution of n-docosane): E_n 1-alkenes, C_n n-alkanes, * impurities; n indicates the total number of carbon atoms.

Minor photoproducts were also detected. In the total ion chromatograms resulting from the photo-oxidation of the C_nH_{2n+2} alkanes, we observed in the F_1 fractions, in addition to the residual starting alkane, the presence of $C_{n'}H_{2n'}$ 1-alkenes with $n' \leq n-3$ and alkanes and, in the F_2 fractions, the production of $C_{n''}H_{2n''}O$ methylketones with $n'' \leq n-2$. Fig. 2 presents the total ion chromatogram of the F_1 fraction obtained by photo-oxidation of n-docosane and shows the production of 1-alkenes (noted E_{10} to E_{19}) and alkanes (noted C_{10} to C_{18}). The formation of methylketones is shown in the total ion chromatogram of the F_2 fraction resulting from the photo-oxidation of n-eicosane (Fig. 3, noted O_{11} to O_{17}). In Fig. 3, 2-octadecanone is coeluted with the residual n-eicosane.

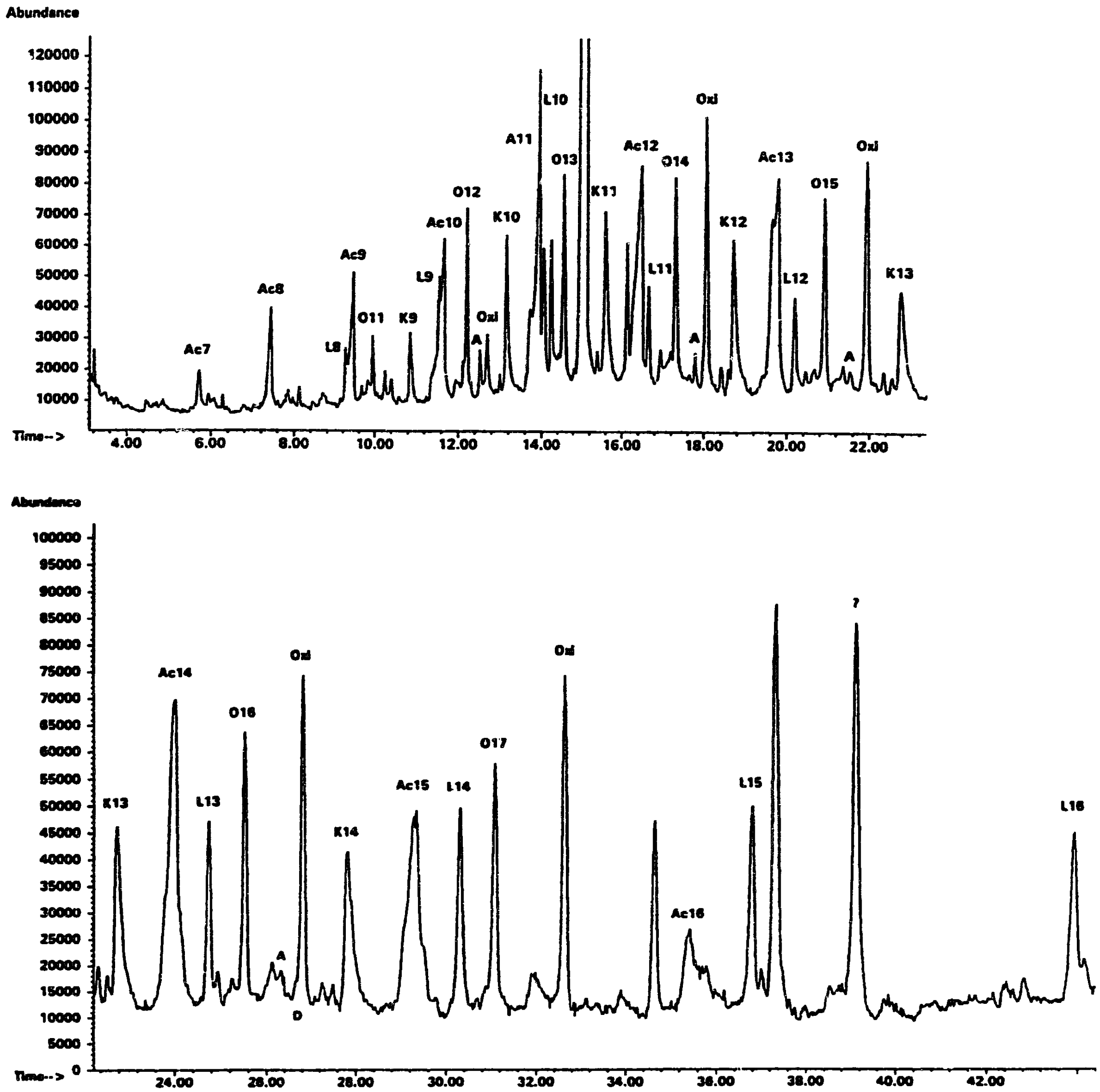


Fig. 3. Total ion chromatogram of the F_2 fraction obtained by photo-oxidation of *n*-eicosane in natural sea water (before elution of eicosanones and eicosanols): O_n methylketones, A_{cn} carboxylic acids, L_n γ-lactones, Oxi epoxide, A *n*-aldehydes, D 2,5-diketones, K_n 1-methyl-2-alkyl cyclobutanols, * impurities, # residual *n*-eicosane.

As for the photo-oxidation of *n*-hexadecane [1], we observed in the total ion chromatograms of the F_2 fractions of the other alkanes, the production of the following:

- 3-substituted γ-lactones (noted L_8 to L_{16} in Fig. 3);
- *n*-aldehydes (noted A in Fig. 3) in small quantities because of the longer irradiation time (transformation in carboxylic acids) [1];
- 2,5-diketones with a shorter chain than the starting alkane but only as very small peaks or shoulders (noted D in Fig. 3).

New photoproducts were detected in the case of photo-oxidation of long-chain hydrocarbons (*n*-nonadecane, *n*-eicosane and *n*-docosane).

- A series of terminal epoxides (noted Oxi in Fig. 3), identified by spectral search (Fig. 4, groups of peaks with predominant fragments at m/z 71, 82, 96, 109...).
- A series of compounds noted K_9 to K_{14} in Fig. 3. Their mass spectra show, as for the series of methylketones, the m/z 43, 58 and 71 ions. These compounds can be attributed to 1-methyl-2-alkyl cyclobutanols. These structures were confirmed by the presence in the mass spectra of the (M-28) ion and by their fragmentation pathways described previously [14]. Similar cyclobutanols have been previously observed [4]. The mass spectrum of one of these compounds is shown in Fig. 5.
- A series of carboxylic acids (noted A_{cn} in Fig. 3). These photoproducts are generally observed in the acidic F_3 fraction and are identified after methylation by their characteristic mass spectra.

Two series of photoproducts, previously observed but not attributed in the case of *n*-hexadecane photo-oxidation [1], are also present: a series of γ-diketones (noted C in Fig. 6) already mentioned by Ehrhardt and Petrick [2,15], and a series of 1,2-dialkyl cyclobutanols (noted A in Fig. 6) both with the same number of carbon atoms as the original alkane.

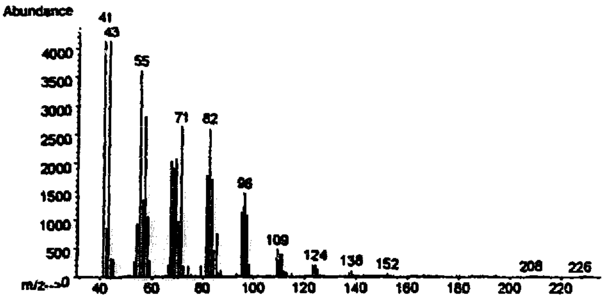


Fig. 4. Electron impact mass spectrum of one terminal epoxide produced during the photo-oxidation of *n*-eicosane (1,2-epoxypentadecane).

In the case of *n*-dodecane, a new series of γ-keto-alcohols is observed, with $(M)^+$ and $(M-18)^+$ mass ions and characteristic fragments at *m/z* 55, 73, 83, 101 and 116. Peaks at *m/z* 101 and *m/z* 73 are due to respectively $[^+O{=}C{-}(CH_2)_2{-}CH(OH){-}CH_3]$ and $[{-}CH_2{-}CH_2{-}CH(OH){-}CH_3]^+$ ions which lead by the loss of a water molecule to the *m/z* 55 and 83 ions. The peak at *m/z* 116 results from a MacLafferty rearrangement $CH_3{-}CH(OH){-}(CH_2)_2{-}C(^{+\cdot}OH){=}CH_2$. This attribution is also confirmed by the presence of the molecular ions $(M-101)^+$ and $(M-73)^+$.

3.2. *Influence of different parameters*

n-Nonadecane was photo-oxidized in sea water by sunlight during 12 days in the presence of different aromatic photosensitizers. The percentages of degradation are as follows: 9-fluorenone 2.4%, 1-naphthol 10.0%, xanthone 13.5% and anthraquinone 36.6%. Anthraquinone is the best photosensitizer because its absorption band at 475 nm corresponds to the maximal solar spectrum energy and to the optimal transmission level in sea water. Anthraquinone is an excellent photosensitizer for photo-oxidation in natural or simulated environmental conditions, because of its efficiency and its presence in the marine environment resulting from the photo-oxidation of anthracene [3,4,16].

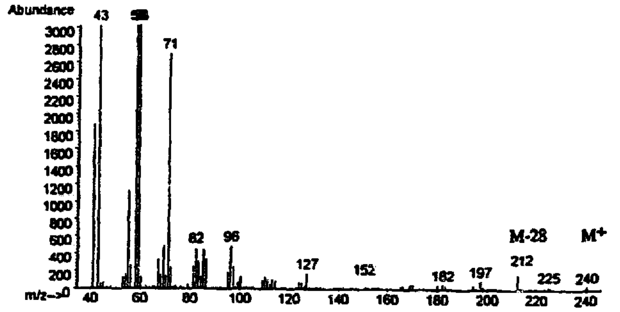


Fig. 5. Electron impact mass spectrum of one 1-methyl-2-alkyl cyclobutanol produced during the photo-oxidation of *n*-eicosane (1-methyl-2-undecyl cyclobutanol).

Irradiations of *n*-alkanes in natural or artificial conditions leads to the formation of the same photoproducts.

Irradiations of *n*-alkanes under identical conditions show a degradation rate which decreases with the length of the chain.

For photo-oxidations in organic solvents such as $CHCl_3$ and concerning the principal photoproducts, a greater quantity of alcohols compared with ketones is observed. This may be explained by the formation of hydroperoxides, stabilized in $CHCl_3$ and not in sea water, which are degraded during GC injection giving more alcohols than ketones.

3.3. *Mechanisms*

The extent of photodegradation of *n*-alkanes under simulated environmental conditions to new compounds (dodecane, nonadecane, eicosane and docosane) asserts the formation of all the isomers of ketones and alcohols with the same number of carbon atoms as the starting alkanes.

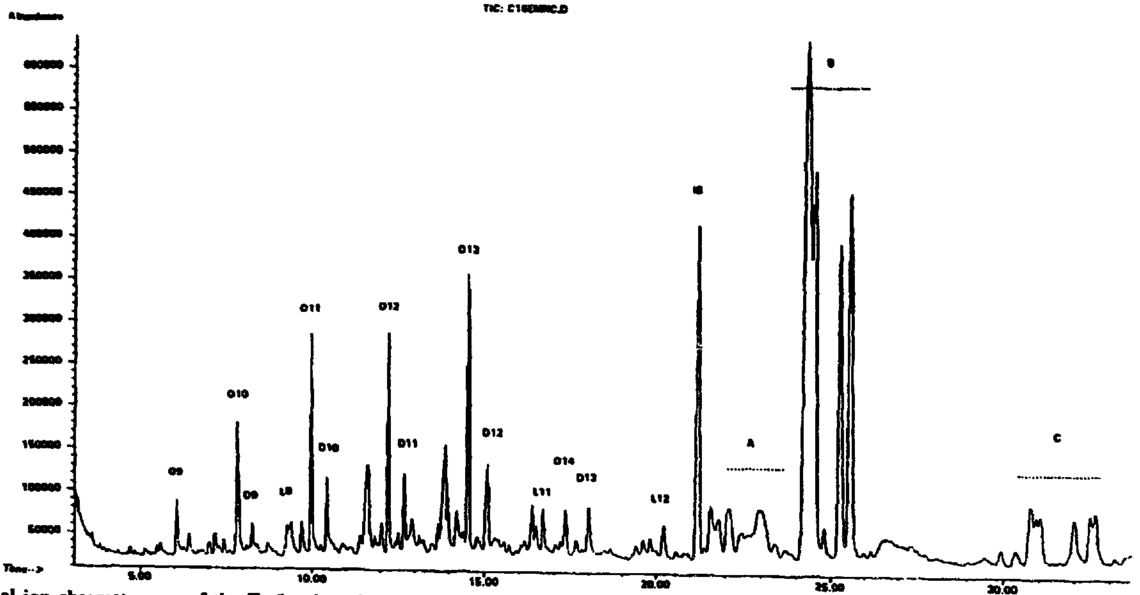
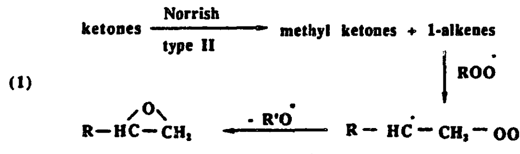
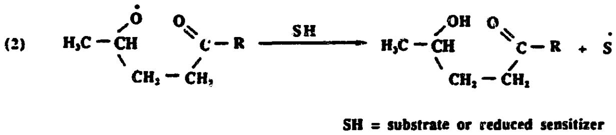


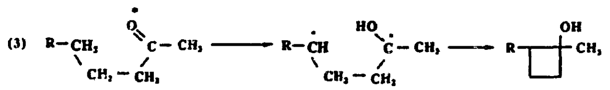
Fig. 6. Total ion chromatogram of the F_2 fraction obtained by photo-oxidation of *n*-hexadecane in natural sea water: IS internal standard, A 1,2-dialkyl cyclobutanols with 16 carbon atoms, B hexadecanones and hexadecanols, C γ-diketones with 16 carbon atoms.



Scheme 1.



Scheme 2.



Scheme 3.

When an alkane C_nH_{2n+2} is irradiated, the formation of 1-alkene $C_{n'}H_{2n'}$ with $n' \leq n-3$ and methyl ketones $C_{n''}H_{2n''}O$ with $n'' \leq n-2$ can be generalized to all the studied alkanes, as well as the mechanisms initially proposed by Ehrhardt and Petrick [2].

The formations of carboxylic acids, aldehydes, 3-substituted γ-lactones and 2,5-diketones have been already described [1,4].

Terminal epoxides may be produced by reaction of peroxy radicals and 1-alkenes coming from ketones (Scheme 1)

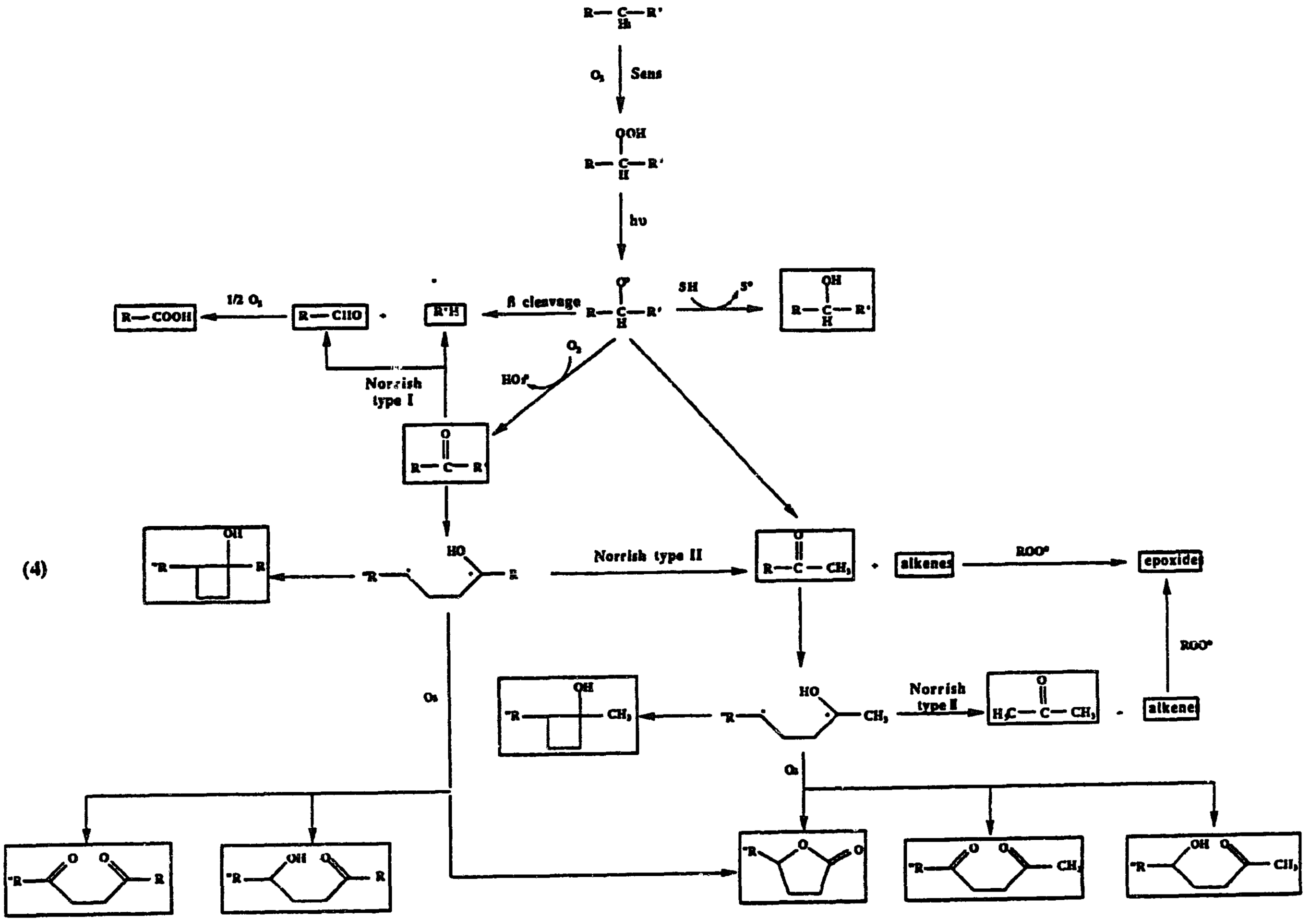
The absence of epoxides in the case of photo-oxidation of dodecane may be explained by the volatility of the 1-alkenes involved (number of carbon atoms less than nine).

γ-Keto-alcohols may be formed by the same mechanism proposed to explain the formation of γ-lactones and 2,5-diketones (Eqs. (4) and (5) in Ref. [1]) from alkanes or methylketones via a γ-ketoalkoxy radical (Scheme 2).

Cyclobutanols may be produced via a 1,4-biradical from methylketones or ketones (Scheme 3) with the same number of carbon atoms as the starting alkane [17].

4. Conclusion

The photo-oxidation under simulated environmental conditions with anthraquinone as sensitizer of *n*-pentadecane [2], *n*-hexadecane [1,4], *n*-dodecane, *n*-nonadecane, *n*-eicosane and *n*-docosane (present work) leads principally to the production of ketones and alcohols with the same number of carbon atoms as the starting alkane. The formation of all the isomers of these ketones and alcohols is clearly established (see [1] and the present work). The quantities of these principal photoproducts depend on several parameters: the time of irradiation, the radiation energy, the solubility and



Scheme 4.

quantities of *n*-alkanes, and the experimental conditions. However, the quantities are always greater than 70%.

Several series of minor photoproducts are also detected. The formation of the different photoproducts identified is summarized in Scheme 4.

Nevertheless our experimental conditions favoured the formation and the accumulation of photo-oxidation products because of high sensitizer concentrations and the lack of micro-organisms. If untreated sea water were used, photo-oxidation and bacterial degradation reactions could take place simultaneously [18]. The interactions between these two types of degradation might accelerate the elimination of the *n*-alkanes owing to the use of photo-oxidation products by the bacteria and photochemical enhancement of the assimilation of some metabolites of the substrates [18].

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