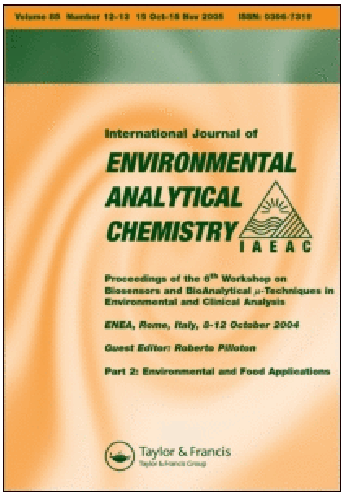

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Sensitized Photooxidation of *n*-Hexadecane in Sea Water: Identification of Non-Acidic Photoproducts

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To cite this Article Anba-lurot, F. El , Guiliano, M. , Doumenq, P. , Bertrand, J. C. and Mille, G.(1996) 'Sensitized Photooxidation of *n*-Hexadecane in Sea Water: Identification of Non-Acidic Photoproducts', International Journal of Environmental Analytical Chemistry, 63: 4, 289 — 299

To link to this Article: DOI: 10.1080/03067319608028325

URL: http://dx.doi.org/10.1080/03067319608028325

Intern. J. Environ. Anal. Chem., Vol. 63, pp. 289–299
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SENSITIZED PHOTOOXIDATION OF *n*-HEXADECANE IN SEA WATER: IDENTIFICATION OF NON-ACIDIC PHOTOPRODUCTS

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(Received, 23 June 1995; in final form, 2 November 1995)

n-Hexadecane was photooxidized in purified and sterilized natural sea water under simulated environmental conditions with anthraquinone as sensitizer. Production of all the isomers of hexadecanones and hexadecanols was proved by GC and GC-MS. Other photoproducts were detected by GC, GC-MS and GC-FTIR as methyl ketones, *n*-aldehydes, 3-substituted γ-lactones, 2,5-diketones, 1-alkenes and alkanes. Mechanisms are proposed and discussed.

KEY WORDS: Photooxidation, *n*-hexadecane, seawater, GC-MS, GC-FTIR.

INTRODUCTION

Many physical, chemical and biological processes can alter petroleum hydrocarbons in the marine environment. Among them, photooxidation reactions seem to play an important role in the evolution of petroleum hydrocarbons. A great variety of products can be formed by hydrocarbon photooxidation. During these reactions, oxygenated products are formed, these compounds being more water soluble and sometimes more toxic than the originated hydrocarbons.

In the case of straight-chain saturated hydrocarbons, several studies have demonstrated the photooxidation of these alkanes sensitized by anthraquinone[1–4] or other sensitizers[5–10].

Though production of fatty acids has been demonstrated unequivocally[3], the case of non-acidic photoproducts is not clearly established. For example, Ehrhardt and Petrick[1] and Rontani and Giral[4] have shown the production of ketones in the case of *n*-pentadecane and of a crude oil, whereas Gesser *et al.*[5] observed the formation of alcohols in the case of *n*-hexadecane.

We decided to study *n*-hexadecane photooxidation in sea water, in order to identify and to determine the possible ways of formation of these oxygenated compounds. Our work is principally focussed on the non-acidic photoproducts which have not been

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identified in the previous works. Our work has been done also with the aim of further generalizing studies related to the photooxidation of other *n*-alkanes such as dodecane, nonadecane, eicosane and docosane.

EXPERIMENTAL

Photooxidation experiments

250 µl of *n*-hexadecane (Aldrich 544–76–3, purity 99%) in 100 ml of autoclaved natural sea water, were irradiated in borosilicate round bottom flasks. Traces (few mg) of anthraquinone (Aldrich 84–65–1) were added as photosensitizer.

An artificial light source (Osram Ultra Vitalux 300W) emitting a gauss shaped spectrum which peaked at 370 nm with a cut off at 290 nm was used for irradiations. Three different samples were irradiated during 5, 10 and 17 days. Flasks with identical contents, kept in the dark for equal lenghts of time, served to check for influences other than sunlight *eg* biodegradation or direct chemical oxidation.

An adequate quantity of pristane and 2-nonadecanone as internal standards were added and irradiated solutions were ajusted 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 60 H ref. 1.07736) into three fractions: F_1 (100 ml of heptane), F_2 (150 ml of diethyl ether) and F_3 (50 ml of methanol).

For irradiations in chloroformic solutions, residues obtained after solvent evaporation were separated in the same conditions.

Reference compounds synthesis

The synthesis of 4-, 5-, 6-, 7- and 8-hexadecanols required reaction of suitable commercial aldehydes with organomagnesium halides as previously described[11].

3-Hexadecanol was obtained by reduction of 3-hexadecanone with $LiAlH_4$.[12]

The 4-, 5-, 6- and 7-hexadecanones were preparated by oxidation of homologous hexadecanols[11].

All these compounds were purified by open column "flash" chromatography (see above) by elution with different solvent mixtures: pentane/diethyl ether (3:1) for 3-hexadecanol and diethyl ether/hexane (from 100:2.5 to 100:8) for other hexadecanols and hexadecanones.

Instrumental analysis

GC analyses of fraction F_1 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 × 0.32mm (id) × 0.25 µm DB5 fused silica capillary column (JW Scientific), temperature program 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 fraction F_2 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 program from 70 to 270°C at 1°C min^{-1}, helium carrier gas (170 kPa) and a detector temperature of 270°C.

GC-MS analyses were carried out on a Hewlett Packard 5989A mass spectrometer (electron energy 70 eV, source temperature 240°C) coupled with a HP 5890 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 program 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 ionisation mass spectrometry, the reactant gas was methane (1 torr) ionised with an energy of 230 eV.

GC-FTIR analyses were performed on HRGC 5300 Mega Carlo Erba gas chromatograph (CP Sil 8 CB column, 30 m × 0.32 mm (id) × 0.25 μm) interfaced with a 20 SXB Nicolet FTIR spectrometer. A liquid nitrogen cooled medium range MCT detector (4000–600 cm^{-1}) was used. Sixteen data scans were collected and coadded per data file with a resolution of 8 cm^{-1} (one spectrum per 1.5 s).

RESULTS

No reaction took place in samples with photosensitizer kept in the dark for 17 days. Acidic photoproducts (which appear in fractions F_3) obtained from *n*-hexadecane irradiated under similar conditions have previously been studied after preparation of methyl derivatives by Rontani[3]. Photochemical production of straight chain fatty acids with carbon atom numbers lower or equal to 16 have been observed[3].

The GC analyses of F_1 fractions (using pristane as internal standard) showed the progressive disappearance of *n*-hexadecane (Figure 1). After 17 days, the quantity of *n*-hexadecane still present was about 10%. The total ion chromatograms of F_1 fractions also revealed the presence of alkenes (with number of carbon atoms ≤ 13) and *n*-alkanes (Figure 2).

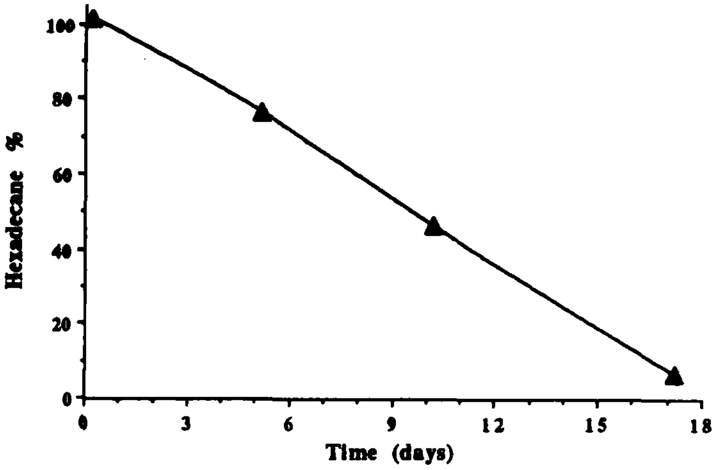


Figure 1 *n*-Hexadecane evolution versus time under artificial irradiation in natural seawater.

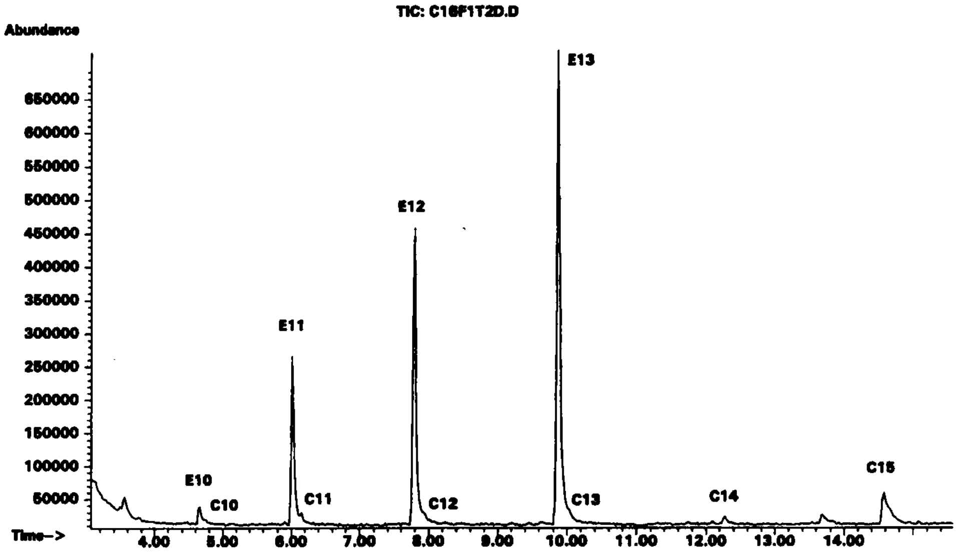


Figure 2 Total ion chromatogram of F1 fraction (t = 10 days) obtained by photooxidation of n-hexadecane in natural seawater (before elution of *n*-hexadecane)
Cn: *n*-alkanes, En: 1-alkenes,
n indicates the total carbon atom number.

The analyses of F_2 fractions, which contain non-acidic photoproducts, revealed a surprising variety of compounds. Preliminary chromatograms, obtained with a basic apolar DB5 (JW Scientific) column showed numerous peaks and a very prominent group of unresolved peaks. Separation of these different peaks was done using more specific chromatographic conditions: polar CP52CB capillary column, 50 m × 0.25 mm (id) × 25 μm, temperature programmed at 1°C min^{-1} (Figure 3).

The identification of these photoproducts was carried out by comparison of their retention times with those of the synthesized reference substances and confirmed by co-injection. Consequently, 2-, 3-, 4-, 5-, and 6-hexadecanones and 1-, 2-, 3-, 4- and 5-hexadecanols were identified unequivocally.

In GC-MS analyses the stationary phase used (HP-5 MS) did not provide such good seperation of hexadecanones and hexadecanols. The mass spectra of hexadecanones and hexadecanols (present in the NBS library or obtained by injection of synthesized compounds) permited the determination of their characteristic fragmentations. For aliphatic ketones, molecular ions $(M)^+$, Mac Lafferty peaks $R\text{-}(HO)C^+ = CH_2$ and fragments resulting from α-cleavage adjacent to the carbonyl group, are the most useful for structural characterization[1]. More precisely, the α-cleavages give mass fragments at m/z 225, 221, 197, 183, 169, 155 and 141 respectively for 2-, 3-, 4-, 5-, 6-, 7-, and 8-hexadecanones.

In the total ion chromatogram of the F_2 fractions, the first peak in the main group of peaks gives a mass spectrum that exhibits significant fragments at m/z 155 and 141. This indicates that 7- and 8-hexadecanones are produced and are coeluted in the gas chromatogram (Figure 3).

The mass spectra of the straight-chain saturated hexadecanols, present in the NBS library or obtained by injection of synthesized compounds, show the usual $(M\text{-}18)^+$ and

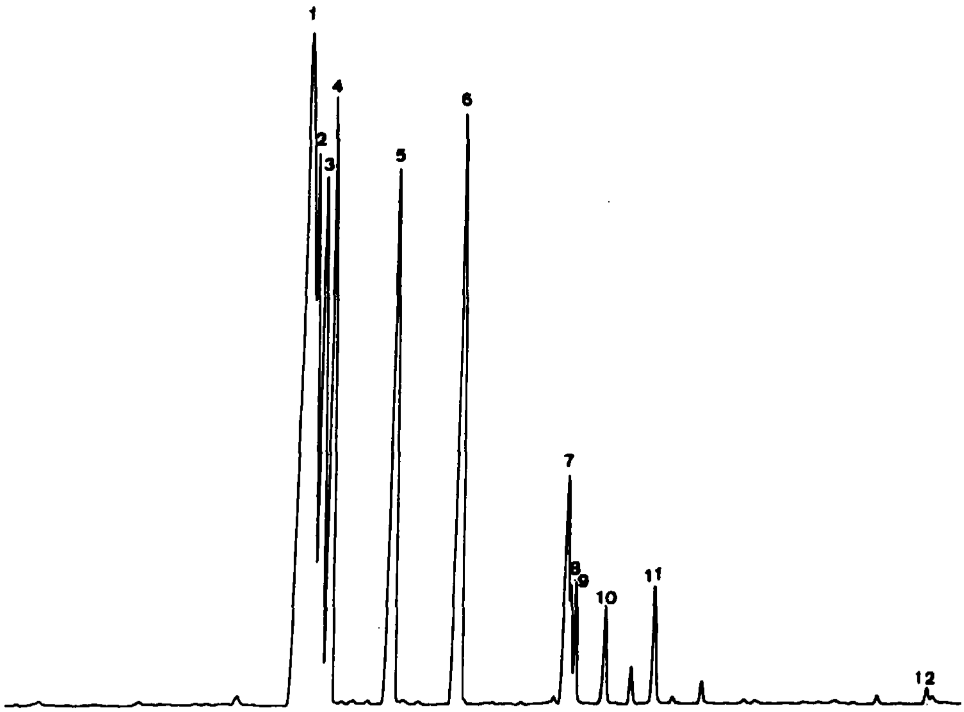


Figure 3 Gas chromatogram of F2 fraction (t = 5 days) obtained by photooxidation of n-hexadecane in natural seawater (hexadecanones and hexadecanols retention time range).
1:7- and 8-hexadecanone, 2:6-hexadecanone, 3:5-hexadecanone, 4:4-hexadecanone, 5:3-hexadecanone, 6:2-hexadecanone, 7:6-, 7- and 8-hexadecanol, 8:5-hexadecanol, 9:4-hexadecanol, 10:3-hexadecanol, 11:2-hexadecanol, 12:1-hexadecanol.

$(C_nH_{2n-1})^+$ ions at m/z 41, 55, 69, 83, 97, 111... To distinguish the isomeric secondary hexadecanols, the HO-HC$^+$-R and $(M-R)^+$ fragments are most useful. They give peaks at m/z 101 and 171, 115 and 157, 129 and 143 respectively for 6-, 7- and 8-hexadecanols. The observation of these fragments in the total ion chromatogram indicates that 6-, 7- and 8-hexadecanols are produced by photooxidation and that these three isomers are coeluted in the gas chromatogram (Figure 3).

We may thus conclude that all the positional isomers of the straight-chain hexadecanones and hexadecanols are formed during photooxidation of *n*-hexadecane in simulated environmental conditions.

We also observed by GC (using 2-nonadecanone as internal standard) that the quantities of these principal photoproducts decreased with irradiation time.

In the total ion chromatogram of the F_2 fractions, in addition to the peaks due to hexadecanones and hexadecanols, we observed principally four series of other photoproducts (Figure 4):

- a series of linear methyl ketones characterized by an intense peak at m/z 43, the MacLafferty peak at m/z 58, $(M)^+$ and $(M-15)^+$ ions. The methyl ketone with the longest carbon chain observed in the total ion chromatogram was 2-tetradecanone. They are noted O_8 to O_{14} in Figure 4.

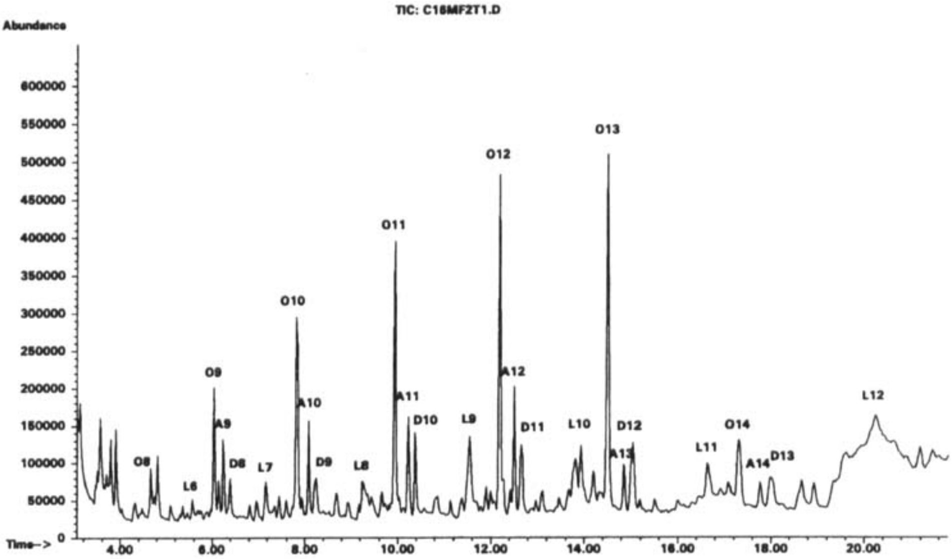
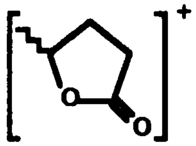


Figure 4 Total ion chromatogram of F2 fraction (t = 5 days) obtained by photooxidation of n-hexadecane in natural seawater (before elution of hexadecanones and hexadecanols)
On: methyl ketones, An: n-aldehydes, Ln: γ-lactones and Dn: 2,5-diketones.
n indicates the total carbon atom number.

- a series of *n*-aldehydes (noted A_9 to A_{14} in Figure 4) characterized by "ion clusters" with predominating individual ions at m/z 57, 70, 82... in cunjunction with an $(M-44)^+$ ion. We noticed that, as for the main photoproducts, the quantity of these aldehydes decreased with irradiation time.

The compounds of these two series were identified unequivocally by spectral search

- a series of 3-substituted γ-lactones (noted L_6 to L_{12} in Figure 4) and characterized by a very intense peak at m/z 85 (base peak) resulting from the cleavage of the side chain at the ring:



GC-FTIR analyses confirmed these structures. Because of the low quantities of these compounds (giving poor signal to noise ratio spectra) we correctly obtained only the GC-FTIR spectrum of γ-nonalactone (Figure 5) with specific vapour IR frequencies[13] at: 2937, 2878 cm^{-1} (CH_2, CH_3), 1154 cm^{-1} (C-O-C) and the very characteristic 1810 cm^{-1} band (C = O).

- a series which was not identified by spectral search. We propose for these compounds the following structure:

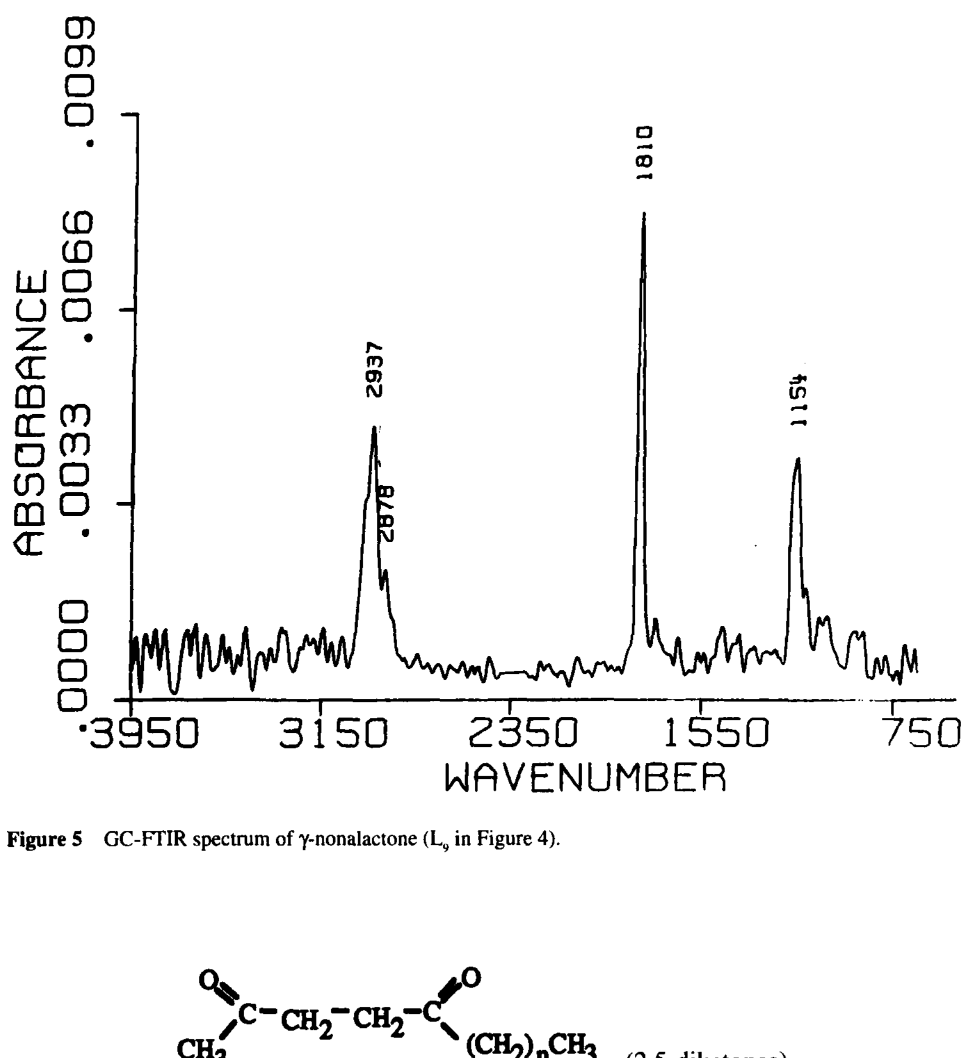
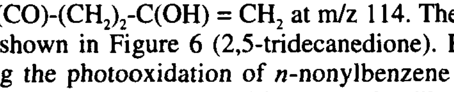


Figure 5 GC-FTIR spectrum of γ-nonalactone (L_9 in Figure 4).



(2,5-diketones).

They are noted D_8 to D_{13} in Figure 4. The characteristic mass fragments of these compounds are $(M)^+$, $(M\text{-}43)^+$, $H_3C\text{-}(CO)\text{-}(CH_2)_2\text{-}C^+ = O)$ at m/z 99 and the MacLafferty fragment $H_3C\text{-}(CO)\text{-}(CH_2)_2\text{-}C(OH) = CH_2$ at m/z 114. The mass spectrum of one of these compounds is shown in Figure 6 (2,5-tridecanedione). Rontani *et al.*[14] also found a γ-diketone during the photooxidation of *n*-nonylbenzene in seawater and Ehrhardt and Petrick[1,15] found all possible positional isomers of γ-diketones with the same number of carbon atoms as the original *n*-alkane, but not the homologous series of 2,5-diketones.

By comparison of *n*-hexadecane photooxidation experiments made in natural sea water and in chloroformic solution, we observed that (i) the same principal photoproducts were formed in $CHCl_3$ but in greater quantities (ii) formation of *n*-hexadecanols was enhanced compared to *n*-hexadecanones in the case of $CHCl_3$ (iii) fatty acid methyl esters were produced by photooxidation in $CHCl_3$ resulting from esterification of fatty acids by ethanol present in $CHCl_3$ as stabilizer (0.4%).

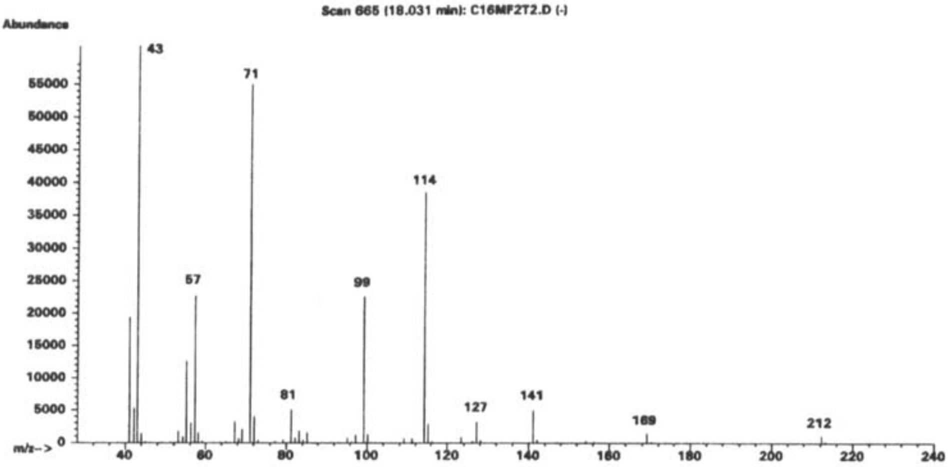


Figure 6 Mass spectrum of 2,5-tridecanedione (D_{13} in Figure 4).

DISCUSSION

It is now generally admitted that photooxidation sensitized by anthraquinone involves the initial abstraction of H• from an alkane to form a radical R• which then reacts with molecular oxygen forming a peroxy radical ROO•[5,6]. This latter stabilizes itself as hydroperoxide ROOH by incorporation of a hydrogen atom. Homolytic cleavage of the O-O bond[16], generates an alkoxy radical RO•.

The formation of hexadecanols can be explained by the reaction of alkoxy radicals with the starting alkane (eq. 1).

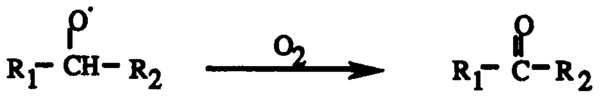
(1)

$$R_1-\overset{O^\bullet}{CH}-R_2 \xrightarrow{RH} R_1-\overset{OH}{CH}-R_2$$

Hexadecanol-1 is a minor photoproduct among the hexadecanols obtained because the primary alkoxy radical ($R_2 = H$) is less stable than the different secondary radicals; it can be oxidized to *n*-hexadecanoic acid in the presence of oxygen.

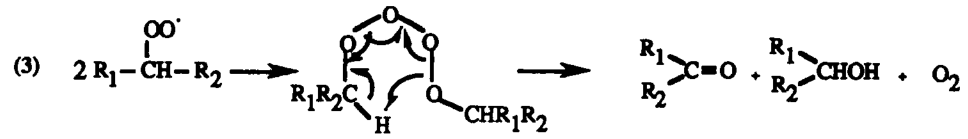
All the secondary alkoxy radicals produced from *n*-hexadecane possess a hydrogen atom in α position and may react with O_2 to give the different hexadecanones[17] (eq. 2).

(2)



$$R_1-\overset{O^\bullet}{CH}-R_2 \xrightarrow{O_2} R_1-\overset{O}{\overset{\|}{C}}-R_2$$

The formation of ketones and alcohols with 16 carbon atoms can also be explained by involving the combination of two peroxy radicals (eq. 3)[18-20].

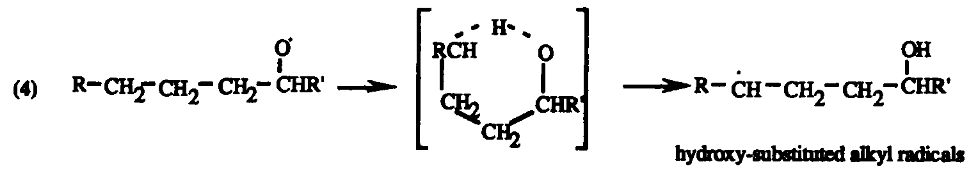
(3) 

Formation of several pentadecanones have been observed already by Ehrhardt and Petrick[1] who have studied the photooxidation of *n*-pentadecane in purified natural seawater under simulated environmental conditions with anthraquinone as sensitizer. They did not note the formation of pentadecanols. Production of ketones was also observed by Rontani and Giral[4] by photooxidation of a crude oil hydrocarbon fraction as a surface film on sea water under simulated environmental conditions. Gesser *et al.*[5] have observed production of hexadecanols by photooxidation of *n*-hexadecane in presence of xanthone as sensitizer.

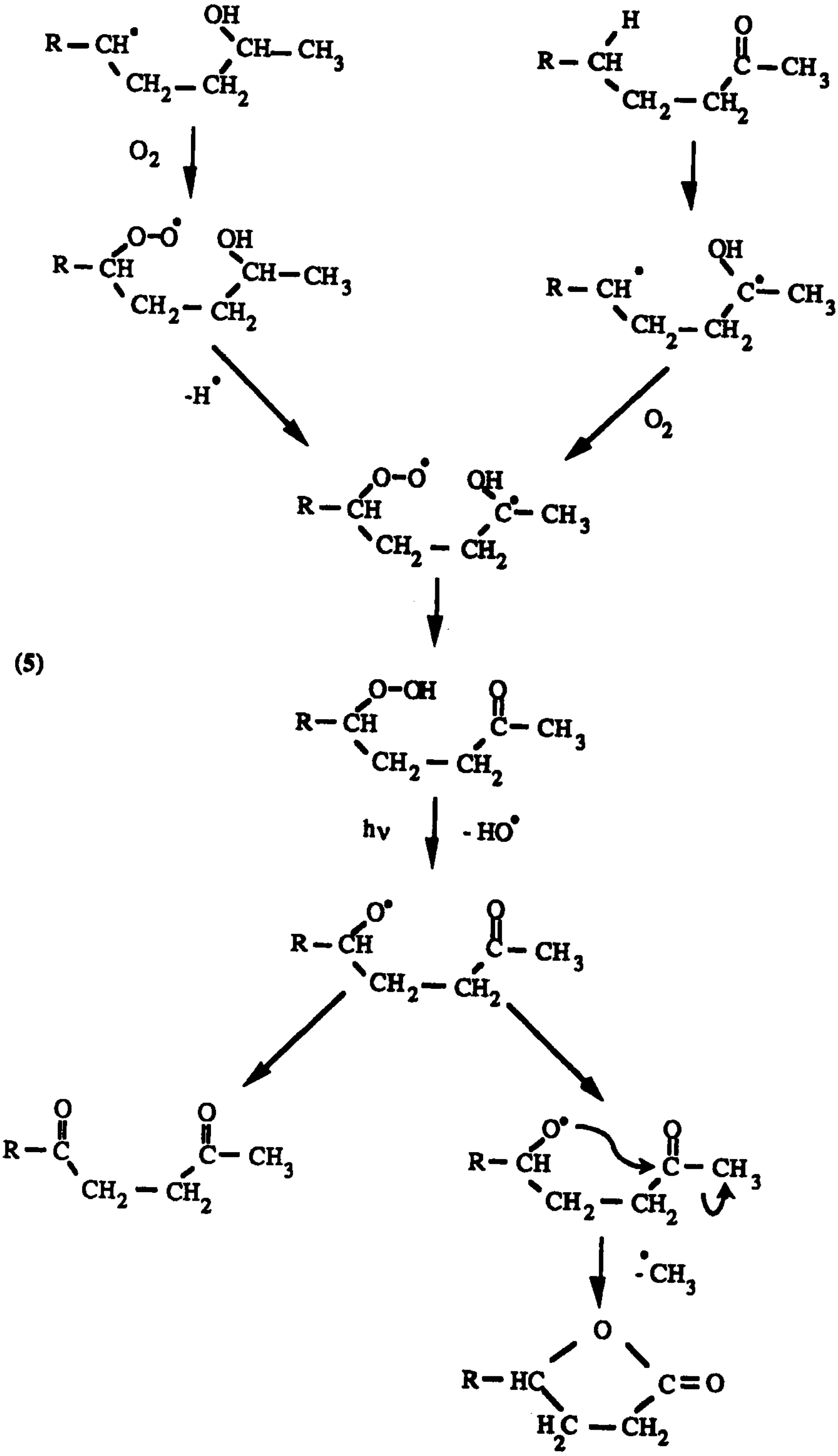
The observation (Figure 2) in F_1 fractions of 1-alkenes (C_nH_{2n} with $n \leq 13$) and in F_2 fractions of methyl ketones ($C_nH_{2n}O$ with $n \leq 14$) confirms the mechanisms of cyclic rearrangement involving the alkoxy radical previously proposed by Ehrhardt and Petrick[1]. This mechanism implies, if γ hydrogen atoms are available, an intramolecular electron rearrangement similar to a Norrish type II photodecomposition that was already clearly described[1]. These authors note that ketones, using *n*-undecanone-2 as a model compound, exposed to sunlight with and without added photosensitizer, remained unchanged. We have irradiated without anthraquinone hexadecanone-3 and observed by GC-MS the formation of *n*-dodecene-1, *n*-tridecane and *n*-tridecanal. The production of *n*-dodecene-1 can be explained by a Norrish type II rearrangement and the formation of tridecane and tridecanal by a Norrish type I rearrangement via an alkyl radical $H_{27}C_{13}\bullet$[21]. These photoreactions of hexadecanones explain the decrease of the quantities of the principal photoproducts with irradiation time.

Rontani[3] has explained the formation of fatty acids with fewer than 16 carbon atoms by mechanisms involving the corresponding aldehydes. The observation in fractions F_2 of these aldehydes and their decrease with irradiation time confirms the proposed mechanisms[3] Alkanes (observed in F_1 fractions) can be produced by decarboxylation of fatty acids: we have irradiated *n*-hexadecanoic acid and observed formation of alkanes C_nH_{2n+2} with n = 15 to 12. Formation of aldehydes and alkanes can also be explained by Norrish type I rearrangement of hexadecanones as seen above.

The different alkanes produced lead to alkoxy radicals. The longer chain alkoxy radicals can undergo isomerization via cyclic transition states to form hydroxy-substituted alkyl radicals[17]. Thermochemically the most favourable process involves the relatively unstrained six-member ring transition state (eq. 4).

(4) 

When this process is possible, it generally dominates over competing reactions of the alkoxy radical[17] and may explain the formation of bifunctional products (eq. 5). The bifunctional products can also be obtained from the produced methyl ketones (eq. 5).



(5)

Acknowledgement

This work has been done in the framework of the GDR Elf Aquitaine/CNRS: "HYCAR" 1123.

References

1. M. Ehrhardt and G. Petrick, *Marine Chem.*, **16**, 227–238 (1985).
2. M. Ehrhardt and R. R. Weber, *Fresenius J. Anal. Chem.*, **339**, 772–776 (1991).
3. J. F. Rontani, *Intern. J. Environ. Anal. Chem.*, **45**, 1–9 (1991).
4. J. F. Rontani and P. J. P. Giral, *Intern J. Environ. Anal. Chem.*, **42**, 61–68 (1990).
5. H. D. Gesser, T. A. Wildman and Y. B. Tewari, *Environ. Sci. Technol.*, **11**, 605–608 (1977).
6. A. E. Klein and N. Pilpel, *J. Chem. Soc.*, **69**, 1729–1736 (1973).
7. G. B. Shul'pin and M. M. Kats, *React. Kinet. Catal. Lett.*, **41**, 239–243 (1990).
8. C. Giannnotti, S. Legreneur and O. Watts, *Tetrahedron Lett.*, **24**, 5071–5072 (1983).
9. T. Sakakkura, T. Sodeyama, K. Sasaki and M. Tanaka, *J. Am. Chem. Soc.*, **112**, 7221–7229 (1990).
10. S. N. Sharma, H. R. Sonawane and Sukh Dev, *Tetrahedron*, **41**, 2483–2491 (1985).
11. A. I. Vogel, *Practical Organic Chemistry*, (Longmans, Green and Co, 3rd edition, London 1956) pages 252 and 337.
12. J. L. Pierre, H. Handel and R. Perraud, *Tetrahedron*, **31**, 2795–2798 (1975).
13. R. A. Nyquist, *The Interpretation of Vapor-phase Infrared Spectra*, (Sadtler Heyden, London 1984) pages 346–350.
14. J. F. Rontani, P. Bonin and G. Giusti, *Mar. Chem.*, **22**, 1–12 (1987).
15. M. Ehrhardt and G. Petrick, *ACS National Meeting, Miami,'Fl.*, Conference Proceeding, 338–341 (1986).
16. R. G. Zika, *Marine Organic Chemistry*, (E. K. Duursma and R. Dawson Eds, Elsevier, Amsterdam 1981) pages 299–325.
17. W. P. L. Carter and R. Atkinson, *J. Atmosph, Chem.*, **3**, 377–405 (1985).
18. G. A. Russel, *J. Am. Chem Soc.*, **19**, 3871–3877 (1957).
19. J. E. Bennett, D. M. Brown and B. Mile, *Trans. Faraday Soc.*, **66**, 386–395 (1970).
20. D. Swern, *Organic peroxides Vol. (II)*, (Ed. Wiley-interscience 1971) pages 90–91.
21. K. Lang D. M. Wagnerova, P. Stopka and W. Domeran, *J. Photochem. Photobiol.*, **67**, 187–195 (1992).
22. J. Grotewold, C. M. Previtali, D. Soria and J. C. Scaiano, *J. Chem. Soc. Chem. Commun.*, **207**, (1973).