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Journal of Photochemistry and Photobiology A: Chemistry 136 (2000) 169–174

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Direct photolyses of thiobencarb and ethiofencarb in aqueous phase

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Received 19 June 2000; received in revised form 25 July 2000; accepted 28 July 2000

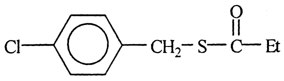
Abstract

The direct photolyses of thiobencarb and ethiofencarb in water were investigated by product studies and laser flash photolysis. At 253.7 nm and in air-saturated solution, thiobencarb is photoconverted into 4-chlorobenzaldehyde and 4-chlorobenzylalcohol with a good efficiency ($\phi = 0.14 \pm 0.02$). Ethiofencarb is phototransformed with a close efficiency ($\phi = 0.12 \pm 0.02$) into sulfoxide, 2-methylphenyl-methylcarbamate and two unidentified oxidation products. The homolytic cleavage of the C–S bonds takes place as proved by the detection of benzylic-type radicals by transient absorption spectroscopy. With thiobencarb, this reaction yields finally 4-chlorobenzaldehyde. On the other hand, 4-chlorobenzylalcohol and 2-methylphenyl-methylcarbamate are likely to arise from the heterolytic cleavage of the C–S bonds. The sulfoxide formation observed in the case of ethiofencarb may result from an electron transfer from the triplet excited state to oxygen and involve a peroxysulfoxide as intermediate. © 2000 Elsevier Science S.A. All rights reserved.

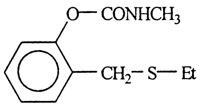
Keywords: Thiobencarb; Ethiofencarb; Photolysis; Water; Mechanism

1. Introduction

Thiobencarb (*S*-[(4-chlorophenyl)methyl]diethylcarbamothioate) and ethiofencarb (2-[(ethylthio)methyl]phenyl methylcarbamate) are plant products used in agriculture and as a consequence potential pollutants of the aquatic environment in which they are susceptible to be photochemically degraded.



thiobencarb (TB)



ethiofencarb (EF)

Literature data concerning the photochemical behaviour of these two compounds are very scarce. According to the Pesticide Manual [1], the photodegradation of ethiofencarb in solar-light is very rapid. Sulfoxide and sulfone are the main degradation products in water and soil. By contrast, thiobencarb is considered as photostable. Such a difference in the photochemical behaviour is somewhat surprising because ethiofencarb and thiobencarb exhibit similarities from the structural point of view having in common a benzyl sulfide moiety.

Photocleavage of S–C bonds is well-know [2]; it is in line with the low C–S bond strength (272 kJ mol^{-1}) [3]. Many examples of C–S bond photoscission have been reported in the literature. Evidences supporting the radical nature of this process have been described, see for example [4,5]. Photolysis of benzyl sulfides in organic solvents was studied in details by Fleming et al. [6–8]. These authors irradiated substituted benzyl phenyl sulfides in deoxygenated *t*-butyl alcohol and found photoproducts arising from the benzyl-sulfur bond scission. They proved by trapping reactive intermediates with a hexenyl side chain that this reaction is homolytic. On the basis of the product studies they ruled out the occurrence of an heterolytic cleavage. The reaction of benzyl phenyl sulfide with singlet oxygen in benzene [9] and $CDCl_3$ [10] was reported too. Benzaldehyde was found as main photoproduct and sulfoxide as minor.

We found useful to undertake a detailed study of the photochemical reactivities of ethiofencarb and thiobencarb in water to get a better insight in the mechanisms of reaction. We gathered experimental data on both compounds in the hope to draw some parallels in the behaviours. These compounds absorb poorly at $\lambda > 270$ nm (see Fig. 1). Phototransformations were investigated by steady state irradiations at 253.7 nm and by laser flash photolysis mainly at 266 nm.

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PII: S1010-6030(00)00344-0

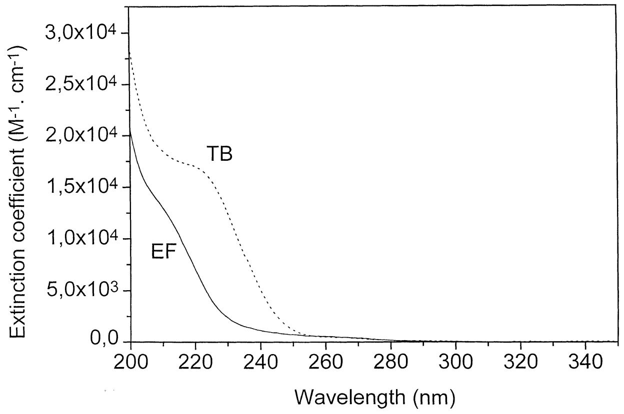


Fig. 1. UV absorption spectra of TB and EF in water.

2. Experimental

2.1. Materials

TB and EF were purchased from Riedel De Haën (purity 96–97%) and used as received. Ethiofencarb sulfoxide and ethiofencarb sulfone (Riedel De Haën), 4-chlorobenzaldehyde and 4-chlorobenzylalcohol (Fluka) used as reference compounds were of the highest grade available. Water was purified with a MilliQ-Millipore device.

2.2. Methods

For analytical purpose, samples were irradiated in a quartz cylindrical reactor in devices equipped with either six germicidal lamps ($\lambda = 253.7$ nm) or six sunlamps emitting within the wavelength range 275–350 nm. Polychromatic irradiations at $\lambda > 300$ nm were performed using a 900 W xenon lamp and a glass filter to cut off wavelengths shorter than 300 nm. An IR filter was placed to avoid overheating and the solutions were constantly stirred by means of magnetic stirrers. Solutions containing the substrates and Rose Bengal were irradiated at 546 nm using a high pressure mercury lamp equipped with a monochromator Bausch and Lomb. For quantum yield measurements purpose, we irradiated samples in parallel beams using the 900 W xenon lamp equipped with a Schoeffel monochromator ($\lambda = 270$ nm, bandwidth at mid-height $= 10$ nm) or using a germicidal lamp. The chemical actinometer was potassium ferrioxalate.

The irradiated samples were analysed by analytical HPLC using a Waters apparatus equipped with a photodiode array detector (model 996) and a reverse phase column Spherisorb S_5 ODS_2 (Waters). For TB, the eluent was a mixture water–*ortho*-phosphoric acid (0.1%)/acetonitrile. The proportions were the following: 60–40% from 0 to 5 min, then regular increase of acetonitrile up to 90% reached at 10 min. For EF, the proportions were 80–20% from 0 to 5 min, then 10–90% reached after 10 min. ^{1}H-RMN spectra were recorded on a Bruker AC400 MHz. Gas chromatography–mass spectrometry (GC–MS) analyses were performed in Centre Régional de Mesures Physiques (Université Blaise Pascal). Chemical ionisation with methane was used.

Laser flash photolysis experiments were performed using a frequency quadrupled Nd-YAG laser ($\lambda_{exc} = 266$ nm, pulse duration $= 9$ ns). The experimental device was described elsewhere [11].

3. Results

3.1. Direct photolyses

3.1.1. Steady state irradiations

3.1.1.1. Phototransformation of thiobencarb. The irradiation at 253.7 nm of an air-saturated aqueous solution of TB (4.5×10^{-5} M) yields 4-chlorobenzylic alcohol and 4-chlorobenzaldehyde (Fig. 2). Chemical yields of formation are equal to 32 and 49%, respectively, after a conversion extent of 16%. The quantum yield of TB disappearance is equal to 0.14 ± 0.02. In nitrogen-saturated solution, only 4-chlorobenzylic alcohol is detected. Due to the high volatility of TB, we cannot give any accurate value for the chemical yield of formation of this product. The irradiation of TB at $\lambda > 300$ nm yields only 4-chlorobenzaldehyde.

For comparison, TB was also irradiated in acetonitrile. The reaction is the same as in water from the kinetic point of view, but it is different from the analytical point of view: in acetonitrile, the chemical yield of 4-chlorobenzylic alcohol is significantly reduced (8% instead of 20% in water).

3.1.1.2. Phototransformation of ethiofencarb. At 253.7 and 270 nm, the quantum yield of EF photolysis is equal to 0.12 ± 0.02. A typical HPLC chromatogram obtained upon irradiation of an aerated aqueous solution of EF within the wavelength range 275–350 nm is given in Fig. 3. Four photoproducts appear on the chromatogram. The injection of ethiofencarb sulfone and ethiofencarb sulfoxide as

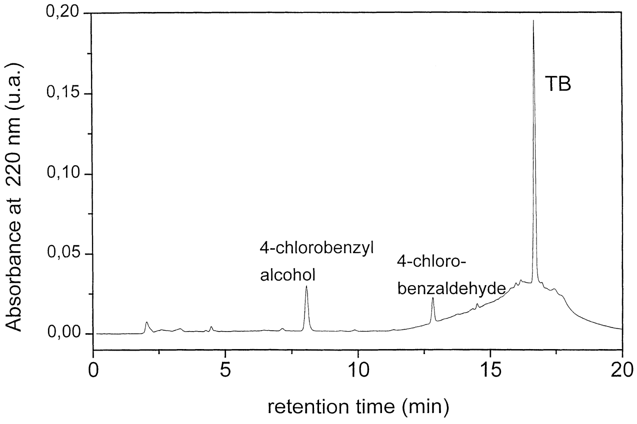


Fig. 2. HPLC chromatogram of an air-saturated solution of TB (4.5×10^{-5} M) irradiated at 254 nm. Conversion extent equal to 70%.

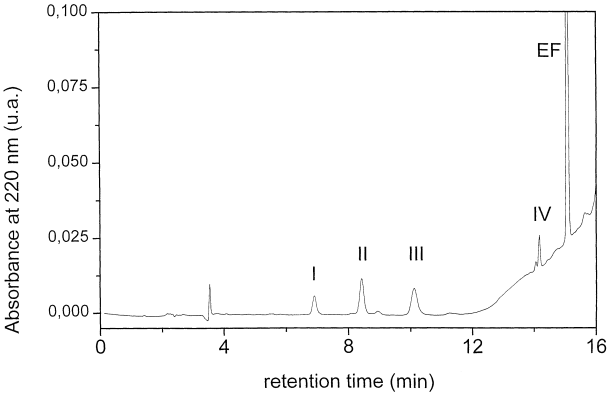
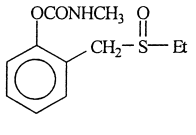


Fig. 3. HPLC chromatogram of an air-saturated solution of EF (5.5×10^{-4} M) irradiated with sunlamps. Conversion extent equal to 70%.

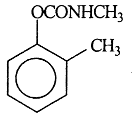
reference compounds allowed the assignment of III as the sulfoxide and showed that ethiofencarb sulfone was not a photoproduct. The chemical yield of III is equal to 10% after a conversion extent of 50%.

The products I, II and IV were separated by HPLC. The fraction enriched in IV was analysed by ^{1}H-RMN and GC–MS CH_4-CI. We found: δ (ppm, $CDCl_3$) 2.25 (3H, s), 2.90 (3H, d, $J = 4.8$ Hz), 5.00 (1H, s), 7.07 (1H, dd, $J = 8$ and 1.3 Hz), 7.12 (1H, td, $J = 7.3$ and 1 Hz), 7.19 (2H, td and dd, $J = 7.5$ and 1 Hz). The CH_4-CI mass spectrum showed signals at $m/z = 166$, 194 and 206. Since methane gives adducts at $m/z = M+1$, $M+29$ and $M+41$, it comes that the mass of product IV is 165. Based on these data, it is concluded that IV is 2-methylphenylmethylcarbamate.

The fractions containing I and II were analysed too. Unfortunately, they were not pure enough to allow the identification of the products. Data collected in GC–MS and NMR showed small molecules having lost the methyl group bound to the nitrogen atom and the ethyl group bound to the sulfur atom. These compounds are, therefore, secondary products. In N_2-saturated solutions, I and II are not detected. This result confirms that they are oxidation products. Actually, only 2-methylphenylmethylcarbamate is produced upon photolysis of EF in the absence of oxygen. Photolyses of ethiofencarb sulfone and ethiofencarb sulfoxide were studied too. They do not yield either I nor II.



ethiofencarb
sulfoxide (III)



2-methylphenyl
methyl carbamate (IV)

At $\lambda > 300$ nm, the phototransformation of EF is more specific: ethiofencarb sulfoxide and II are the only products detected. The chemical yield of the sulfoxide is equal to 46% after a conversion extent of 10%.

3.1.2. *Laser flash photolysis experiments*

The photolysis of TB in mixture water–acetonitrile (80/20, v/v) at 266 nm produces at pulse end a transient species exhibiting two absorption maxima at 270 and 318 nm and disappearing in deoxygenated solution within the first 60 μs following the pulse end (Fig. 4 and inset). Oxygen significantly enhances its rate of decay. On the basis of literature data,

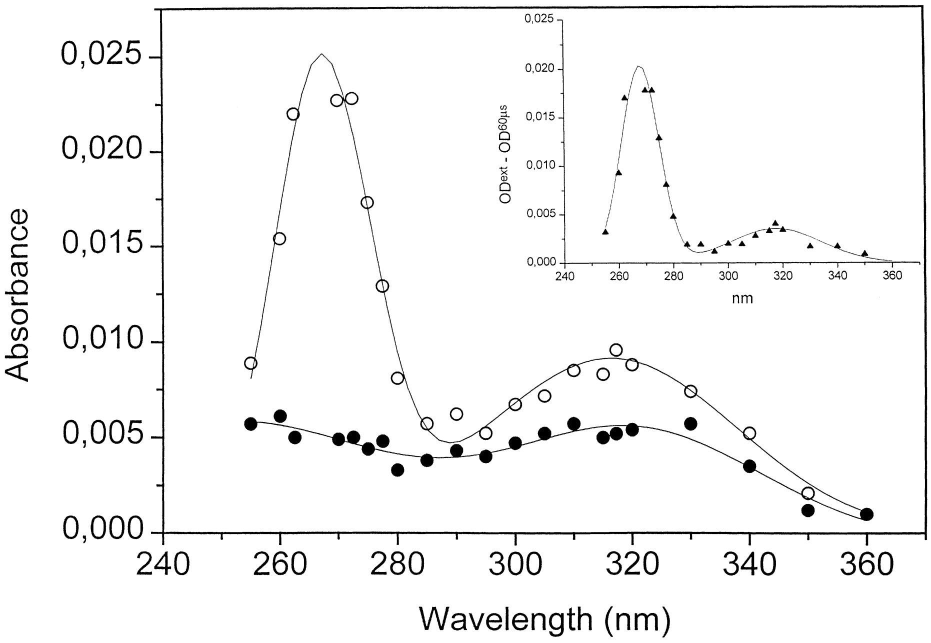


Fig. 4. Transient absorption spectra measured from a deoxygenated solution of TB in a mixture water–acetonitrile (80/20, v/v). Absorbance at 266 nm equal to 0.16. (●): End pulse; (○): 60 μs after the pulse end; inset A: difference between absorbances measured at the pulse end and 60 μs after the pulse end.

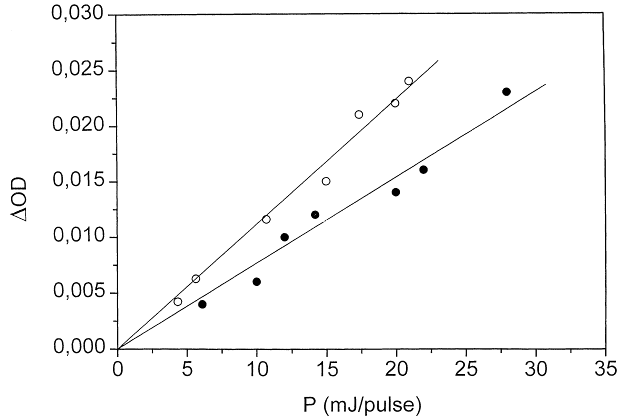


Fig. 5. Plots of ΔOD vs. *P*. (○): $\mathrm{OD}^{\mathrm{ext}} - \mathrm{OD}^{60\,\mu\mathrm{s}}$ from a solution of TB in water–acetonitrile (80/20, v/v), absorbance at 266 nm equal to 0.16; (●): $\mathrm{OD}^{\mathrm{ext}} - \mathrm{OD}^{30\,\mu\mathrm{s}}$ from a solution of EF in water–acetonitrile (95/5, v/v), absorbance at 266 nm equal to 0.50.

this transient can be assigned to the 4-chlorobenzylic radical ($\varepsilon_{269} = 40700\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ and $\varepsilon_{317} = 8100\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ in cyclohexane [12]). The absorbance at 270 nm was monitored for several pulse energy values, *P*. The differences between the end pulse absorbance and the absorbance measured 60 μs after the pulse end ($\mathrm{OD}^{t=0} - \mathrm{OD}^{t=30\,\mu\mathrm{s}}$) are plotted versus *P* (Fig. 5). The plot is linear, indicating that the transient is produced by a monophotonic process. The slope of the straight line is connected to the $\varepsilon \times \phi$ value: by chemical actinometry with $K_2S_2O_8$, we found $\varepsilon_{270} \times \phi = 2200\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ giving finally a quantum yield of radical formation equal to 0.054. A long-lived transient with maximum around 320 nm can be observed after the complete disappearance of the 4-chlorobenzylic radical (see Fig. 4).

The photolysis of EF in a mixture water–acetonitrile (95/5, v/v) produces two species (Fig. 6). The first one shows two absorption maxima at 257 and 320 nm (inset of Fig. 6), disappears by an apparent first order kinetics in deoxygenated medium ($k = 1.0 \times 10^5\,\mathrm{s}^{-1}$) and reacts with oxygen ($k_{O_2} = 1.5 \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$). Based on the analogies with the 4-chlorobenzylic radical, it is reasonable to assigned this first intermediate to the 2-methylcarbamate benzylic radical. The differences $\mathrm{o.d.}^{t=0} - \mathrm{o.d.}^{t=30\,\mu\mathrm{s}}$ measured at 257 nm increase linearly with *P* (Fig. 5) yielding $\varepsilon_{257} \times \phi = 240\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$.The second transient is long-lived, exhibits a broad absorption band with maximum around 320 nm and is insensitive to oxygen.

3.2. Photosensitised oxidations

The oxidations by singlet oxygen were studied using Rose Bengal as sensitiser. Solutions containing EF or TB (4.5×10^{-5} M) and Rose Bengal (1×10^{-5} M) were buffered at pH 7 with phosphates and irradiated at 546 nm under oxygen bubbling. In these conditions, no consumption of TB is observed. By contrast, EF is oxidised into ethiofencarb sulfoxide (chemical yield = 66%) and II. The rate of EF transformation is 3.4-fold reduced upon the addition of N_3^- (1.8×10^{-3} M) in agreement with the involvement of singlet oxygen in the reaction. H_2O_2 was detected in irradiated solutions and titrated by a colorimetric method [13] (chemical yield = 20%).

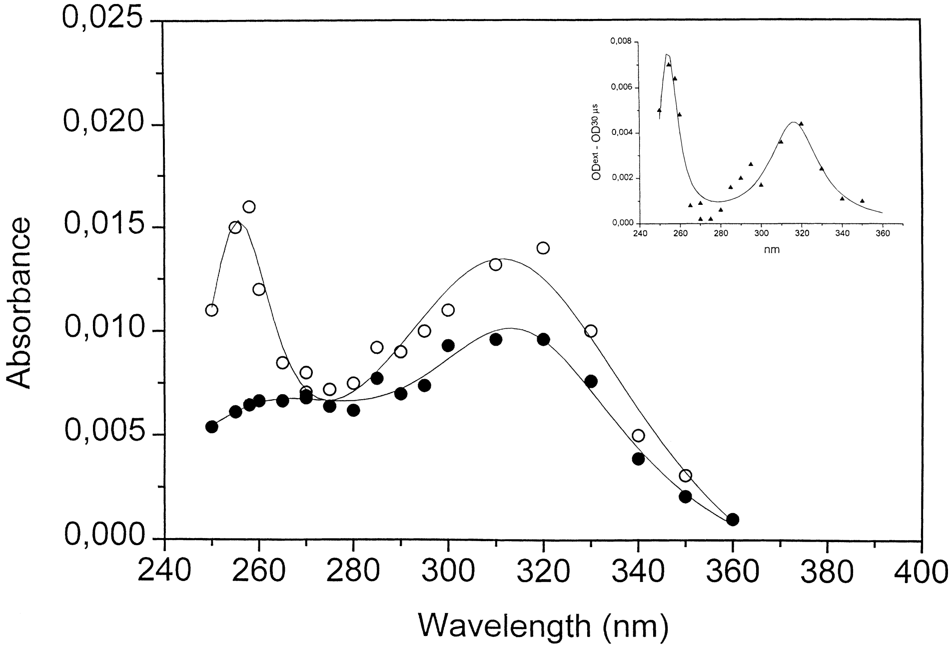
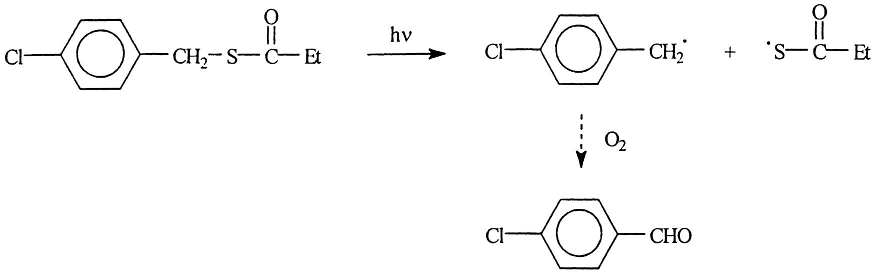


Fig. 6. Transient absorption spectra measured from a deoxygenated solution of EF in a mixture water–acetonitrile (95/5, v/v). Absorbance at 266 nm equal to 0.50. (●): End pulse; (○): 30 μs after the pulse end; inset A: difference between absorbances measured at the pulse end and 30 μs after the pulse end.

These results contrast with those reported in the case of benzyl phenyl sulfide [9,10]. It shows that substituents on the aromatic ring, presence of the carbonyl in α-position with respect to the S atom and polarity of the solvent drastically influence the oxidation reaction.

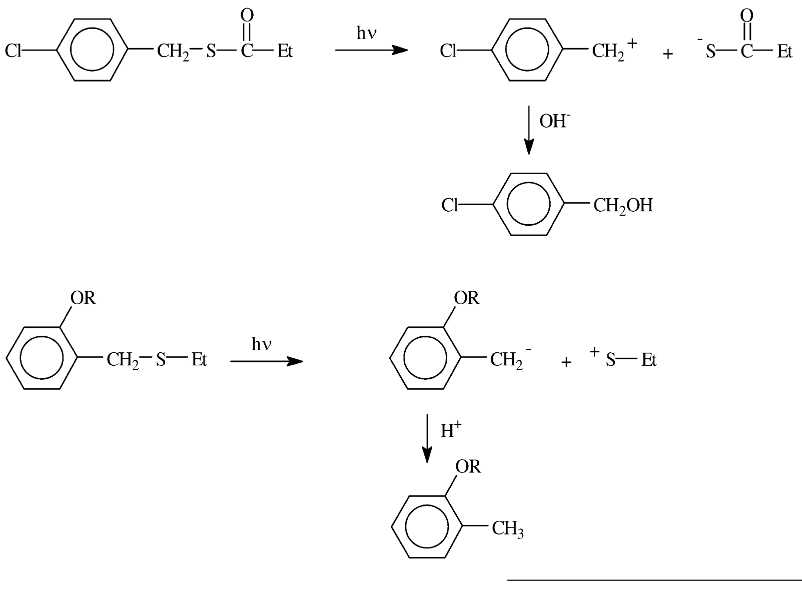
4. Discussion

The detection of the 4-chlorobenzylic radical by laser flash photolysis of TB shows that homolytic scission of the C–S bond occurs. Quantum yields measurements indicate that this route accounts for about 50% of the phototransformation. Formation of 4-chlorobenzaldehyde in oxygenated medium can be rationalised by the further oxidation of the benzylic-type radical.



In the case of EF, homolytic scission of the C–S bond also occurs as shown by laser-flash photolysis experiments but it is a minor pathway (about 5%). By product studies we did not detect any aldehyde formation.

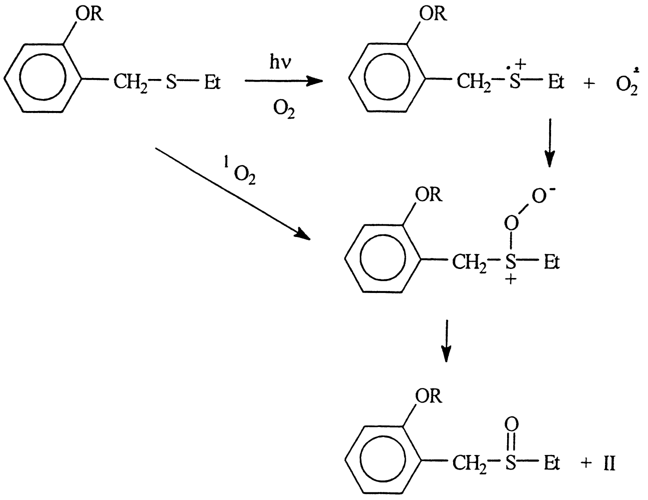
Formations of 4-chlorobenzylalcohol from TB and 2-methylphenylmethylcarbamate from EF can be tentatively explained by the heterolytic scission of C–S bonds followed by hydrolysis:



To rationalise the experimental results, we have to postulate the formation of a carbanion in the case of EF and of a carbocation in the case of TB. The carbanion formation is in line with the alkyl phenyl sulfide structure since, in this case, the C–S bond is polarised with the negative charge on the benzylic carbon atom. The presence of a carbonyl in α-position with respect to the S atom, on the other hand, favours the formation of the carbocation by stabilising the negative charge on the S atom.

Two additional results confirm this heterolytic reaction. First, the formation of 2-methylphenylmethylcarbamate is not influenced by oxygen. A reaction pathway involving an homolytic cleavage is, therefore, ruled out. Second, in acetonitrile, the chemical yield of 4-chlorobenzylalcohol is drastically reduced. It shows that the presence of water is required in the alcohol formation.

Photo-oxidation of EF into sulfoxide is observed, II being produced along with the sulfoxide. The sulfoxide and II are also yielded in the photosensitised oxidation of EF. It suggests that the two reactions have a common intermediate. The oxidation of sulfides by singlet oxygen has been extensively studied. In polar medium, the formation of peroxysulfoxides giving rise to sulfoxide and sulfone is strongly suggested [10,14,15]. Such an intermediate may be also produced in direct photolysis by electron transfer reaction from the triplet excited state of EF to oxygen and further recombination of the radical cation with the superoxide anion.



Formation of a sulfoxide is not observed with TB. This result indicates that one of the two reactions (electron transfer or radical recombination) does not occur. The fact that TB is not oxidised by singlet oxygen, whereas EF is, suggests that the presence of the carbonyl hinders the oxygen addition onto the S atom. As a consequence, the recombination between the radical cation and the superoxide ion, if formed, should be difficult too. On the other hand, the radical cation from TB was produced using 9,10-dicyanoanthracene as electron acceptor [16] and 4-chlorobenzaldehyde was shown to be one of the main photoproducts. Oxidation of TB into the radical cation upon irradiation in the presence of oxygen cannot be, therefore, ruled out.

This study shows analogies in the primary steps of TB and EF photolysis but also differences in the rearrangements of the primary intermediates.

- The homolytic cleavage of the C–S bond occurs in both cases. This reaction produces finally a benzaldehyde with TB but not with EF. The presence of the carbamate substituent in *ortho*-position with respect to the CH_2 radical may favour intramolecular reactions preventing the aldehyde to be produced in the case of EF.
- The heterolytic cleavage of the C–S bonds explains both the formation of 4-chlorobenzylalcohol from TB and that of 2-methylphenylmethylcarbamate from EF.
- An electron transfer from triplet excited states to oxygen yielding radical cations is likely to take place. However, the radical cations show distinct reactivities. In the case of EF, it recombines with the superoxide ion yielding finally the sulfoxide. In the case of TB, it cleaves yielding the benzaldehyde derivative.

In conclusion, thiobencarb and ethiofencarb are phototransformed in water with good efficiencies. Homolytic cleavage of the C–S bonds is proved to occur. The formations of 4-chlorobenzylalcohol and 2-methylphenylmethylcarbamate, on the other hand, are explained by an heterolytic cleavage of the C–S bonds. Oxidation of the S atom also takes place and a sulfoxide is produced in the case of EF. The differences of photoreactivity between EF and TB are mainly due to the presence of the carbonyl in α-position with respect to the S atom; it reverses the polarisation of the C–S bond and hinders the addition of oxygenated species onto the S atom.

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