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Gas chromatographic–mass spectrometric study of photodegradation of carbamate pesticides

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Abstract

The photodegradation of seven carbamate pesticides (bendiocarb, isoprocarb, promecarb, ethiofencarb, furathiocarb, fenoxycarb and pirimicarb), in aqueous solution, has been examined by GC–MS. The most general result was formation of the corresponding phenols. Irradation of isoprocarb and promecarb also resulted in photo-Fries rearrangement to *ortho*- and *para*-hydroxybenzamides. In the case of ethiofencarb photocleavage of the carbon–sulfur bond gave 2-methylphenyl methylcarbamate as main product. Likewise, N–S bond cleavage occurred upon irradiation of furathiocarb, to allow the formation of the carbamate insecticide carbofuran, butyl methylcarbamate and carbofuranphenol. Under similar conditions, fenoxycarb gave *p*-phenylphenol and 2-hydroxydibenzofuran, through primary homolysis of the aryloxy–methylene bond. Finally, pirimicarb gave rise to 2-formylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate.

Keywords: Photodegradation; Environmental analysis; Carbamates; Pesticides

1. Introduction

The carbamates are a wide family of pesticides [1] whose structures ($R_1OCONR_2R_3$) are derived from carbamic acid, by the introduction of different substituents.

Many of the insecticidal carbamates of commercial significance are phenyl carbamates (the R_1 group is an aromatic ring), although some enol and oxime carbamates are also used. Concerning the other substituents, R_2 usually is a methyl group and R_3 can be either hydrogen, methyl or a more complex group.

The activity of carbamates is associated with inhibition of cholinesterase enzyme. Since many of these compounds are systemically active, they allow to control pests on the shoots and in the roots, which are otherwise difficult to reach.

Photochemical degradation is one of the factors controlling the fate of pesticides and other chemicals in the environment [2–4]. Also, photolysis is involved in the photoactivation and photocontrolled release of a number of bioactive molecules including some insecticides, fungicides and herbicides. In this context, identification of the photoproducts allows to establish the involved photolytic pathways, thus providing valuable information on possible ways of protecting the environment.

In the present work, we have examined the

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photochemical transformations of seven carbamate pesticides **1a–g** (bendiocarb, isoprocarb, promecarb, ethiofencarb, furathiocarb, fenoxycarb and pirimicarb; Fig. 1), by means of GC–MS analysis of the resulting reaction mixtures. The structures of the photoproducts have been confirmed by ^{1}H NMR spectroscopy and, in many cases, by comparison with authentic samples. Only two of the above carbamates (**1d** and **1g**) have been previously studied with similar purposes, although using different photolysis conditions [5–7]. Isopropanol, cyclohexane and cyclohexene have been employed as solvents for the irradiation of ethiofencarb [5] and pirimicarb [7]. The latter carbamate has also been photolyzed in aqueous solutions, either for kinetic purposes at very low concentrations (5 mg/l) or for preparative studies (1.7 g/l), in which very long irradiation times (53 h) are used [6]. In these cases, the individual photoproducts have been separated by HPLC and subsequently identified by spectroscopic methods. The use of GC–MS is advantageous in that it is highly sensitive (even the very minor peaks are identified through their MS spectra) and less time-consuming, since it allows a rapid analysis of the photomixtures.

The carbamates and their major photoproducts are listed in Table 1.

2. Experimental

2.1. Chemicals

Bendiocarb (2,2-dimethyl-1,3-benzodioxol-4-yl methylcarbamate, **1a**) and ethiofencarb (2-ethylthiomethylphenyl methylcarbamate, **1d**) were kindly supplied by Schering España (Valencia, Spain) and Bayer Hispania Industrial (Valencia, Spain), respectively. Isoprocarb (2-isopropylphenyl methylcarbamate, **1b**), promecarb (3-methyl-5-(1-methylethyl)phenyl methylcarbamate, **1c**), furathiocarb (2,2-dimethyl-2,3-dihydrobenzofuran-7-yl N,N′-dimethyl-N,N′-thiodicarbamate, **1e**) fenoxycarb (2-(3-phenoxyphenoxy)ethyl ethylcarbamate, **1f**) and pirimicarb (2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate, **1g**) were purchased from Riedel-de Haen (Barcelona, Spain). Water obtained with a Milli-Q water purification system (Millipore) was used throughout the experiments. The solvents used were of analytical grade (Probus).

2.2. Instrumental

The photoproducts were analyzed by ^{1}H NMR spectroscopy (Varian VXR-400 S, 400 MHz) and

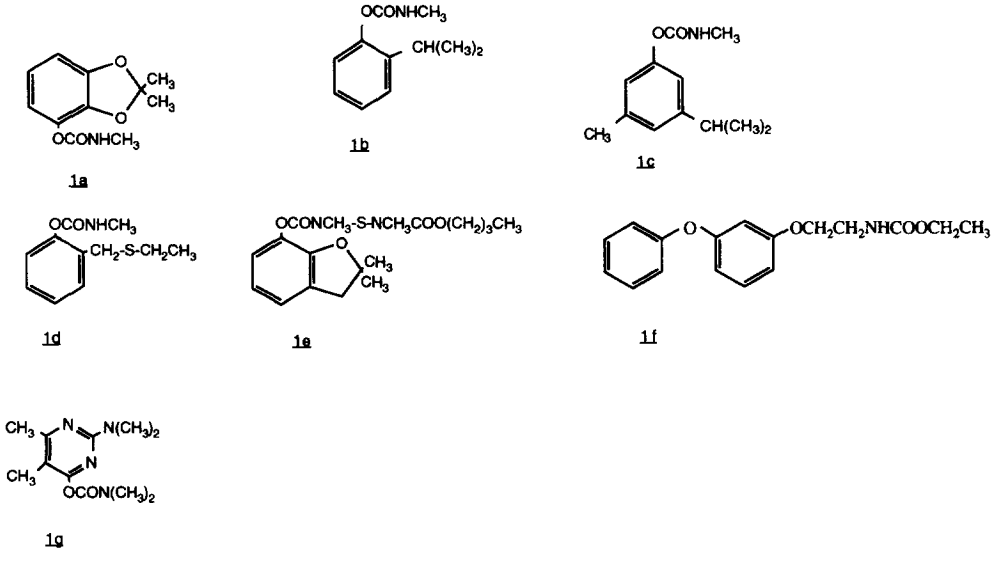

Fig. 1. Structures of the seven carbamate insecticides.

Table 1
Parent carbamates and their major photoproducts

Carbamate	Photoproducts
Bendiocarb (**1a**)	2,2-Dimethyl-1,3-benzodioxol-4-ol (**2a**)
Isoprocarb (**1b**)	2-Isopropylphenol (**2b**)
	2-Hydroxy-3-isopropyl-N-methylbenzamide (**3b**)
	4-Hydroxy-3-isopropyl-N-methylbenzamide (**4b**)
Promecarb (**1c**)	3-Methyl-5-(1-methylethyl)phenol (**2c**)
	2-Hydroxy-4-isopropyl-5-methyl-N-methylbenzamide (**3c**)
	4-Hydroxy-2-isopropyl-6-methyl-N-methylbenzamide (**4c**)
Ethiofencarb (**1d**)	2-Ethylthiomethylphenol (**2d**)
	2-Methylphenyl methylcarbamate (**5d**)
	o-Cresol (**6d**)
Furathiocarb (**1e**)	Carbofuranphenol (**2e**)
	Carbofuran (**7e**)
	Butyl N-methylcarbamate (**8e**)
Fenoxycarb (**1f**)	*p*-Phenylphenol (**9f**)
	2-Hydroxydibenzofuran (**10f**)
Pirimicarb (**1g**)	2-Dimethylamino-5,6-dimethyl-4-hydroxypyrimidine (**2g**)
	2-Formylamino-5,6-dimethylpyrimidin-4-yl-dimethylcarbamate (**11g**)
	2-Methylamino-5,6-dimethylpyrimidin-4-yl-dimethylcarbamate (**12g**)

GC–MS, using a Varian Saturn II (Star 3400 spectrometer) provided with a 25 m capillary column of cross-linked 5% phenylmethyl silicone.

2.3. Chromatographic conditions

GC–MS conditions were: initial oven temperature 80°C for 3 min, rate 20 °C/min up to 300°C for 10 min. Injection port temperature was 250°C. Helium was the carrier gas (1.5 ml/min).

2.4. Photolysis procedure

The irradiation of seven carbamate insecticides (ca. $3.3 \cdot 10^{-3}$ *M*) was carried out for a period of 4 h in aqueous solution, at room temperature, using a 125 W medium-pressure mercury lamp, installed within an immersion-well photoreactor provided with cooling jacket for refrigeration with water. The sample–lamp distance was ca. 2 cm. Each solution was extracted three times with 25 ml dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and rota-evaporated at room temperature. The residue was analyzed by GC–MS. Subsequently it was purified by preparative layer chromatography (silica gel) using dichloromethane as eluent. The isolated products were analyzed by ^1H NMR and GC–MS. Parallel irradiation experiments were carried out using cyclohexane as solvent. After evaporation under reduced pressure the residues were submitted to the same treatment.

2.5. Identification of the photoproducts

The structures of photoproducts were established by comparison of their spectral properties with those of authentic samples. Table 2 lists their GC retention times and MS fragmentation patterns.

3. Results and discussion

Irradiation of bendiocarb (**1a**), isoprocarb (**1b**) and promecarb (**1c**) was conducted in aqueous solution, using a Pyrex filter. As the degrees of conversion were extremely low, the same experiments were repeated with quartz-filtered light in order to identify the photoproducts.

Upon irradiation of **1a** (30% conversion) the only product detected was the corresponding phenol **2a**. Irradation of **1b** (29% conversion) resulted in photo-Fries rearrangement, to afford the *ortho*- and *para*-hydroxybenzamides **3b** (12%) and **4b** (1%) together with the phenol **2b** (2%).

Likewise, photolysis of **1c** (24% conversion) led to the phenol derivative **2c** (22%) as major product.

Table 2
GC–MS data of the photoproducts

Photoproduct	Retention time (min)	MS spectrum *m/z* (%)
2a	6.39	166(M^+, 18), 15 1(2), 126(24), 108(100), 107(21), 80(15), 79(14), 52(16), 51(17), 43(15)
2b	5.52	136(M^+, 17), 121(100), 103(31), 91(4), 77(3)
3b	9.58	193(M^+, 100), 178(26), 165(12), 164(12), 163(11) 162(4), 161(8), 147(52), 134(22), 133(16), 119(5), 106(7), 91(16)
4b	11.07	193(M^+, 57), 178(11), 163(100), 147(8), 134(6), 121(6), 107(9), 91(16)
2c	4.05	150(M^+, 92), 136(36), 135(100), 121(22), 115(37), 107(58), 105(25), 91(79), 79(30), 77(40)
3c	10.03	207(M^+, 50), 192(16), 177(28), 176(100), 175(19), 161(42), 133(69), 105(16), 91(15), 89(8), 79(12), 77 (20)
4c	10.40	207(M^+, 91), 189(10), 177(55), 176(100), 161(23), 148(26), 133(68), 105(22), 91(19), 89(10), 77(18)
2d	7.51	168(M^+, 52), 107(100), 77(2)
5d	9.04	165(M^+, 100), 147(13), 135(22), 134(26), 108(3), 107(15), 106(43)
6d	4.07	108(M^+, 100), 107(80)
2e	6.52	164(M^+, 100), 149(61), 131(20), 123(16), 122(15), 121(24), 107(12), 103(20)
7e	10.10	222(M^+, 30), 164(16), 149(15), 131(63), 123(71), 122(100), 121(90), 107(70), 103(91)
8e	4.24	131(M^+, 25), 101(100), 76(95), 58(66), 41(42)
9f	10.07	170(M^+, 100), 141(6), 141(85), 115(66), 102(27), 89(17), 77(14), 63(23)
10f	11.06	184(M^+, 100), 156(12), 155(12), 128(42), 127(22), 102(13), 63(11)
2g	9.17	167(M^+, 50), 152(50), 138(100), 124(39), 123(67), 110(46)
11g	10.10	252(M^-, 4), 224(4), 124(8), 123(9), 72(100), 44(14), 42(26)
12g	10.44	224(M^+, 24), 153(6), 152(28), 138(19), 124(50), 123(26), 110(22), 109(30), 83(8), 72(100)

Besides, minor amounts of the isomers arising from photo-Fries rearrangement to the *ortho* and *para* position (**3c**, **4c**) were also obtained (Fig. 2).

The formation of these photoproducts can be explained by primary photochemical cleavage of the carbonyl–oxygen bond, to give an acyl-aryloxy radical pair enclosed in the solvent cage. Diffusion out of the cage would give rise to the corresponding phenols (**2a–c**), while recombination to the *ortho* or *para* position justifies the obtention of rearranged *o*-hydroxycarbonyl compounds (**3b**, **4b**, **3c**, **4c**). Such type of processes (photo-Fries rearrangement) are well documented in the literature [8–10].

The involvement of aryloxy radicals as intermediates was further supported by the results obtained upon photolysis of isoprocarb in cyclohexane solution. Most of the starting material remained unreacted, but GC–MS analysis allowed to detect the corresponding cyclohexyl ether [*m/z* (%): 218(10), 136(5), 121(100), 107(20), 103(19), 91(12)] together with solvent-derived photoproducts such as cyclohexylcyclohexane and cyclohexyloxycyclohexane. This indicates formation of the cyclohexyl radical, which can undergo cross-coupling with the aryloxy radical or dimerize with or without the participation of oxygen.

In the case of ethiofencarb (**1d**) irradiation in aqueous solution (66% conversion) gave 2-

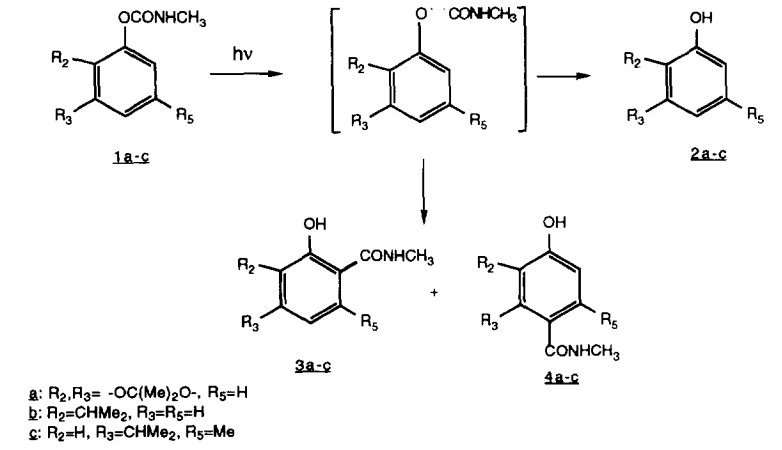

Fig. 2. Photochemistry of bendiocarb (**1a**), isoprocarb (**1b**) and promecarb (**1c**).

methylphenyl methylcarbamate (**5d**) as main product (58%) through photocleavage of the carbon–sulfur bond. Again, the corresponding phenols **2d** and **6d** were also obtained, albeit in markedly lower yields (1 and 6%, respectively; Fig. 3).

Very recently, the photodegradation of ethiofencarb in organic solvents has been reported [5]. The operating pathways under these conditions appear to be those involving oxidation at the sulfur atom, to give ethiofencarbsulfoxide, ethiofencarbsulfone and oxidation at the benzylic position, to afford a benzoxazine-2,4-dione as minor product. In water solution, these photoproducts were not detected (neither by GC–MS nor by ^{1}H NMR of the reaction mixture). By contrast, attempts to reproduce the photolysis of **1d** in cyclohexane through pyrex confirmed in fact oxidation at the sulfur atom, as well as formation of minor amounts of the benzoxazine-2,4-dione. In addition, the corresponding cyclohexyl ether [*m/z* (%): 250(0), 221(12), 168(4), 166(13), 111(18), 108(38), 107(34), 83(100), 82(36)] and cyclohexyloxycyclohexane were detected, as in the irradiation of isoprocarb. Analogous results were obtained using quartz filter, although the amounts of sulfoxide and sulfone experimented a substantial decrease.

After irradiation of furathiocarb (**1e**) in aqueous solution (41% conversion) two photoproducts arising from N–S bond cleavage were detected: the carbamate insecticide carbofuran (**7e**, 15%) and butyl N-methylcarbamate (**8e**, 16%; Fig. 4). Besides,

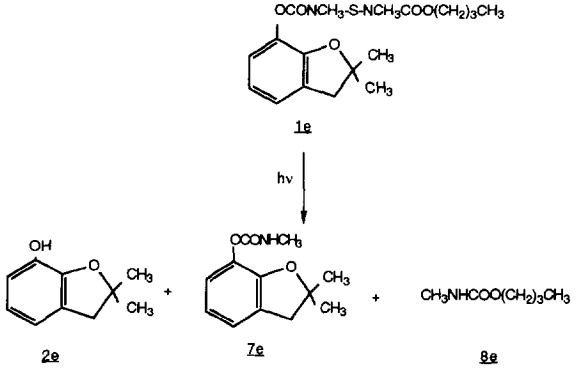

Fig. 4. Photochemistry of furathiocarb (**1e**).

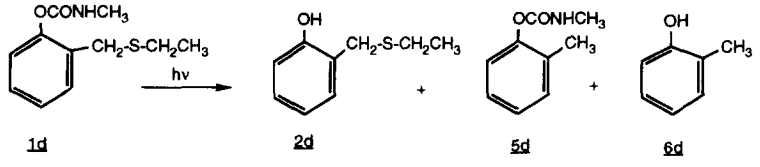

Fig. 3. Photochemistry of ethiofencarb (**1d**).

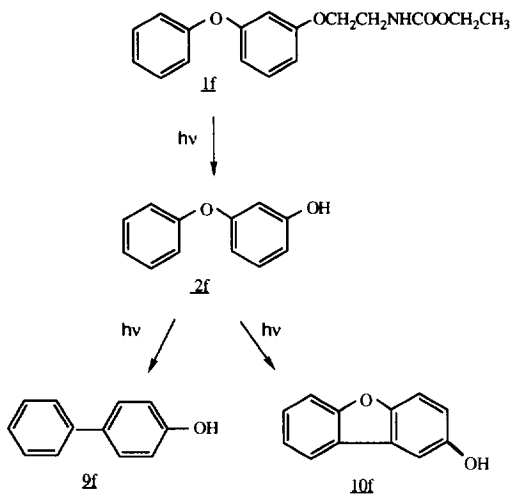

Fig. 5. Photochemistry of fenoxycarb (**1f**).

carbofuranphenol (**2e**, 10%) was also found in the reaction mixture. The latter product can be a secondary photoproduct arising from photolysis of carbofuran, a process which has been reported in the literature [11]. Analogous results were obtained in cyclohexane, although in this case. The cyclohexyl trapping product of the primary radical formed after N–S bond cleavage was also obtained.

Fenoxycarb (**1f**) was photolyzed under similar conditions, giving *p*-phenylphenol (**9f**, 19%) and 2-hydroxydibenzofuran (**10f**, 12%; Fig. 5). Since the carbamate side-chain is lacking in the photoproducts, a common precursor of the latter could be *p*-phenoxyphenol (**2f**). As a matter of fact, independent irradation of **2f** under the same conditions led to a mixture of **9f** and **10f**, together with 2-phenylhydroquinone (PHQ) and the corresponding quinone (PQ). Prior to our work, the photolysis of *p*-phenoxyphenol was reported [12] to give PHQ as the result of photo-Claisen rearrangement, but none of the other photoproducts (**9f**, **10f** or PQ) was found in the photomixture as analyzed by TLC. Later, the same reaction was found to produce **9f** and PQ, the latter as auto-oxidation product of PHQ [13]. In our case, control experiments have shown that photolysis of PQ leads to **10f** in good yield, while under similar conditions PHQ is transformed into a mixture of **10f** and PQ. Thus, the photoproducts found during the photolysis of fenoxycarb can be accounted for in terms of primary homolysis of the aryloxy-methylene bond to give *p*-phenoxyphenol as the only primary photoproduct.

On irradation of pirimicarb (**1g**, 57% conversion) the major product was the corresponding hydroxypyrimidine (**2g**, 41%). A small amount of 2-formylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (**11g**, 2%) was also detected.

When **1g** was irradiated in alkaline medium, degradation occurred more rapidly and led to **2g** (80%), the photooxidation product **11g** (1%), 2-methylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (**12g**, 8%) and some starting material (7%) remained unreacted. The origin of **12g** can be attributed to N-dealkylation of the 2-dimethylamino group.

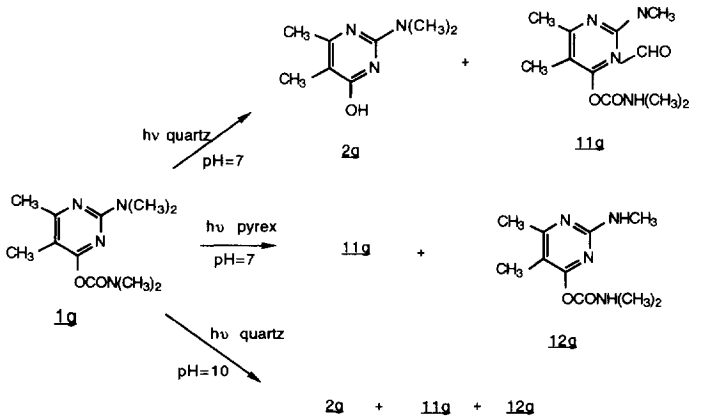

Fig. 6. Photochemistry of pirimicarb (**1g**).

Photolysis of **1g** was also performed with $\lambda > 280$ nm in aqueous solution (through pyrex) giving the photodegradation products **12g** (58%) and **11g** (24%) and starting material **1g** (7%) (Fig. 6). These results agree with those recently reported by Romero et al. [6].

An additional experiment was carried out in cyclohexane, through quartz filter. Under these conditions, a complex photomixture consisting of more than 12 products was obtained. This mixture was not resolved into its components, but CG–MS analysis allowed to identify N,N,N′,N′-oxaldiamide. This product is obviously the dimer arising from C–C coupling of dimethylaminocarbonyl radicals and its detection provides an unambiguous evidence of oxygen-carbonyl bond cleavage.

4. Conclusions

Analysis by GC–MS appears to be a convenient method to monitor the photodegradation of carbamate pesticides. The most general photoprocess undergone by these compounds in aqueous solution is formation of the phenols. Depending on the particular structures, other photoreacctions also occur, such as photo-Fries rearrangement, cleavage of the C–S, N–S or aryloxymethylene bonds or oxidative N-demetylation.

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