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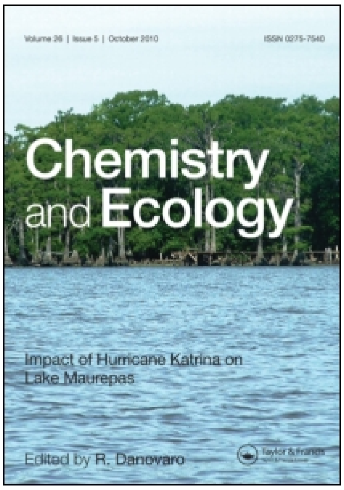

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PHOTODEGRADATION OF BENTHIOCARB

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The photodegradation of ^{14}C-benthiocarb in water, on a glass surface, on soil and silica gel TLC plates was studied. The study was designed to obtain some information of its dissipation and photodegradation under various laboratory conditions. Benthiocarb degrades readily when exposed to either sunlight or UV light (254 nm). However, it is degraded much faster by UV light than by sunlight. Also, benthiocarb decomposes faster in water or on a glass surface or silica gel surface than on a soil surface. The half-life of benthiocarb exposed to UV light was: 1 hr on glass surface; 1.5 hrs in water; 2 hrs on silica gel TLC plate; 20 hrs on soil TLC plate. Benthiocarb in water, and exposed to sunlight, had a half-life of approximately 3 days. The following major photodegradation products were identified: 4-chlorobenzyl alcohol; 4-chlorobenzaldehyde; 4-chlorobenzoic acid.

KEY WORDS: Benthiocarb, photodegradation, thiocarbamate.

INTRODUCTION

Benthiocarb [S-4-chlorobenzyl N, N-diethylthiocarbamate] is an effective and relatively low toxic herbicide chemical. It has been used in the last two decades to control weeds in rice paddies in Japan, South-east Asia and South America. Benthiocarb is particularly effective against barnyard grass (*Echinochloa crus-galli L.*). A few studies have been conducted on the metabolic and the environmental fates of this chemical. These include: animal metabolism (Casida *et al.*, 1975; Hubbell and Casida, 1977; Ishikawa *et al.*, 1973; Cheng and Hwang, 1993); plant metabolism (Hubbell and Casida, 1977; Nakamura *et al.*, 1974, 1977; Cheng and Hwang, 1994); microbial and soil metabolism (Chen *et al.*, 1976; Nakamura *et al.*, 1977) and degradation in the water environment (Cheng, 1990; Cheng and Hwang, 1990; Ishikawa *et al.*, 1977).

This study was designed to obtain information on benthiocarb dissipation and photodegradation under various conditions. Two light sources, short wavelength ultra-violet light (254 nm) and natural sunlight were employed. During irradiation, benthiocarb was exposed under four different conditions: on soil thin-layer plates, on silica gel thin-layer plates, on glass surfaces and in water. The deposit on the surfaces was about 10 $\mu g\,cm^{-2}$ and the concentration of benthiocarb in water was 16–20 ppm. At various time intervals, samples were analyzed for total ^{14}C and the nature of the ^{14}C.

MATERIALS AND METHODS

Chemical

The [ring-U-^{14}C] benthiocarb was prepared at the laboratories of Chevron chemical Company. The specific acivity was 3.82 mCi mM^{-1}, and radiochemical purity was greater than 99.5%. Compounds used for chromatography and photoproduct identification are listed in Table I.

Light Sources

A short wavelength (2537A) Hanovia UV lamp with an intensity of 2300 μ watts cm^{-2} at a distance of 10 cm and natural sunlight with intensities ranging from 3500–4500 μ watts cm^{-2} were used. Samples were exposed under the lamp at a distance of 10 cm. During irradiation, the temperature at 10 cm varied from 25 to 29°C.

Sample Treatment

Thin Film on Glass Surface The ^{14}C-benthiocarb in 10 μl acetone solution, (1 mg ml^{-1}), was applied on a microscope cover glass at approximately 10 mg cm^{-2}. Samples were exposed to light for various time intervals. Control samples were also placed in the dark. After exposure, the ^{14}C was recovered by dissolving with acetone and characterized by thin-layer chromatography and autoradiography.

Table I Compounds used in this study.

Code No.	*Name*
C1	S-[(4-chlorophenyl) methyl]diethylcarbamothioate (benthiocarb)
C2	S-[(4-chlorophenyl) methyl] ethylcarbamothioate (desethylbenthiocarb)
C3	S-[(4-chlorophenyl) methyl] carbamothioate
C4	S-[(4-chloro-2-hydroxyphenyl)methyl] diethylcarbamothioate
C5	S-[(4-chloro-2-hydroxyphenyl)methyl] ethylcarbamothioate
C7	S-[(4-chloro-3-hydroxyphenyl)methyl] diethylcarbamothioate
C8	S-[(4-chloro-3-hydroxyphenyl)methyl] ethylcarbamothioate
C15	S-oxy-S-[(4-chlorophenyl)methyl] diethylcarbamothioate (benthiocarb sulphoxide)
C16	S-dioxy-S-[(4-chlorophenyl)methyl] diethylcarbamothioate (benthiocarb sulphone)
A1	4-chlorobenzoic acid
A2	4-chloro-2-hydroxybenzoic acid
A3	4-chloro-3-hydroxybenzoic acid
A10	α-(4-chlorotoluene) sulphonic acid (4-chlorobenzyl sulphonic acid)
L1	4-chlorobenzyl alcohol
L2	4-chloro-2-hydroxybenzyl alcohol
L3	4-chloro-3-hydrozybenzyl alcohol
L4	4-chlorobenzyl mercaptan (4-chlorobenzylthiol)
N1	bis-(4-chlorobenzyl) disulphide
N4	4-chlorobenzaldehyde

Silica Gel Chromatoplates The ^{14}C benthiocarb in 20 μl acetone solution (0.5mg ml^{-2}) was spotted on a silica gel F-254 precoated chromatoplate with 0.25 mm thickness at about 10 μg cm^{-2}. After irradiation, the chromatoplates were developed with solvent and then exposed to X-ray film. The radioactive products were detected by autoradiography and quantitated by scraping the appropriate gel region free from the glass support into scintillation vials, and counted.

Soil Thin-Layer Chromatoplates Soil taken from a rice growing area was used. The physico-chemical properties and mechanical analysis of this soil is shown in Table II. Soil thin-layer plates were prepared according to the procedure of Stahl (1969). The ^{14}C-benthiocarb in an acetone solution was spotted on the soil plates as for the silica gel thin-layer plates. After exposure to light the treated soil area was scraped from the plates and extracted with acetone, then with methanol. The ^{14}C in the extracts was determined by scintillation counting and characterized by thin-layer chromatography.

Water Solution Two ml of water solution containing 20 ppm ^{14}C-benthiocarb was placed in a 10 ml pyrex beaker and exposed to light. The light was positioned 10 cm above the solution. The pH of the water was 7.0. After exposure, the solution was directly analyzed by thin-layer chromatography and autoradiography. In a separate experiment, the light irradiated solution was acidified to pH 1 and extracted with ether. The ether extractable ^{14}C was further separated into acidic and phenolic and/or neutral fractions by extracting with 5% potassium bicarbonate solution.

In order to prevent loss of parent compounds and/or photoproducts by volatilization, one experiment was done in a sealed flask with sunlight exposure only. The ^{14}C benthiocarb in water (50 ml, 16 ppm) was placed in a 125 ml Pyrex Erlenmeyer flask with a ground glass stopper. The flask was exposed to natural sunlight from August 20 (2:00 P.M.) to August 26 (10:00 A.M.). The total sunlight exposure was about 40 hrs. During exposure, the light intensities ranged from 3000–4500 μwattcm^{-2}, and the temperature from 15°C to 24°C. To determine the rate of degradation, 1 ml samples were taken at various intervals for ^{14}C analysis.

Table II Physico-chemical properties and mechanical analysis of soil.

pH	4.6
Conductivity (millimhos/cm)	0.584
Saturation percentage	48.8
Saturation extract	
Ca - meq l^{-1}	1.62
Mg - meq l^{-1}	1.13
Na - meq l^{-1}	3.09
Cation exchange capacity (meq 100 g^{-1})	32.5
Organic matter (%)	1.95
Estimated field capacity (%)	21.8
Mechanical analysis	
Type	Clay
Sand (%)	18
Silt (%)	26
Clay (%)	56

Scintillation Counting

Aliquots (10–100 µl) of the organic extracts and silica gel regions scraped from thin-layer chromatoplates were added to 16 ml of scintillation mixture containing 8 ml 2-methoxyethanol and 8 ml PPO in toluene (8.25 $\mathrm{g\,l^{-1}}$) and counted in a Nuclear Chicago Isocap/300 liquid scintillation spectrometer. For counting, aqueous solution samples (0.1 to 0.5 ml) were dissolved in 10 ml of Scintisol (Isolabs, Inc.) and counted. The counting efficiencies ranged from 79 to 90%. The background counts ranged from 24 to 36 cpm. The counting times were 1, 2, 4, or 10 minutes depending on the radioactivity in samples. In most cases, samples were counted for 1 to 2 minutes when radioactivity in the sample was more than 2000 cpm and for 4 to 10 minutes when radioactivity in the sample was less than 2000 cpm.

Thin-layer Chromatography and Autoradiography

The ^{14}C (benthiocarb and its photodegradation products) was characterized by thin-layer chromatographic and autoradiographic techniques. Silica gel F-254 pre-coated chromatoplates (20 × 20 cm, E. M. Laboratories, Inc., Elmsford, New York) with 0.25 mm thickness were used. The solvent systems used for separation of the ^{14}C photoproducts and for co-chromatography with authentic compounds were: (A) hexane-benzene (1:1); (B) chloroform-ether (4:1); (C) benzene saturated with formic acid-ether (3:1); (D) chloroform-acetic acid (4:1). Various combinations and sequential developing solvents were also used for adequate resolution of the degradation products.

Autoradiography was employed to detect the radioactive spots. The chromatoplates were exposed to a single coated blue sensitive X-ray film (Eastman Kodak., Co., Rochester, New York) for one to three weeks. The radioactivity spotted on the plate ranged from 5×10^3 dpm to 1×10^5 dpm per spot.

For qualitative identification ^{14}C spots were scraped from TLC plates and co-chromatographed with standards for confirmation. Plates were developed 2-dimensionally. Authentic compounds used for co-chromatography were detected a) by their quenching of gel fluorescence when the plate was viewed under short wavelength ultraviolet light with Chromato Vue (Ultra-Violet Products, Inc., San Gabriel, California), b) by exposing the plate to iodine vapour to form yellow spots, c) by spraying the plate with 0.5% 2,6-dibromo-N-chloro-p-benzoquinonimide in cyclohexane (for low oxidized state sulphur derivative). To detect 4-chlorobenzyl sulphonic acid, a spray reagent composed of 10 ml of 10% aqueous silver nitrate and 50 ml of 0.2 g sodium-fluorescein in 100 ml absolute ethanol was used to give yellow spots on a pink background.

RESULTS

Photodegradation of Benthiocarb by UV light (254 *nm*)

Benthiocarb Deposited on Silica Gel F254 TLC Plates After exposure at intervals of 10 minutes, 2 and 6 hrs, the total ^{14}C recoveries were approximately 99% at 10 minutes, 71% at 2 hrs, and 45% at 6hrs. The photoproducts were characterized as shown in

Table III. The major photodegradation products identified were 4-chlorobenzyl alcohol, 4-chlorobenzyl aldehyde, 4-chlorobenzoic acid, 4-chlorobenzyl sulphonic acid and benthiocarb sulphoxide.

Benthiocarb Deposited on Soil TLC Plates After exposure at various intervals, the treated soil areas were scraped from the plates and extracted with acetone, then with methanol. The ^{14}C recovered from the soil plates was approximately 99% at 10 minutes, 97% at 2 hrs and 95% at 6 hrs. Characterization of the ^{14}C in the acetone and methanol extracts showed that approximately 98% at 10 minutes, 91% at 2 hrs and 86% at 6 hrs was benthiocarb. The major degradation products isolated from acetone and methanol extracts (6 hr sample) were 4-chlorobenzaldehyde, 4-chlorobenzyl alcohol, 4-chlorobenzoic acid, and 4-chlorobenzyl sulphonic acid (tentative).

Benthiocarb Deposited on Glass Surface Irradiation of ^{14}C benthiocarb on a glass surface caused rapid loss of radioactivity. The recoveries of the ^{14}C from glass surface were approximately 99% at 5 minutes, 97% at 10 minutes, 64% at 2 hrs, and 35% at 6 hrs. After 2 hr exposure, at least 16 photodegradation products were detected. Isolation of the ^{14}C in the acetone extract showed that about 86% at 10 minutes, 41% at 2 hrs and 10% at 6 hrs was parent compound. In the 2 hr exposure sample, the following photoproducts were found (values given as % of initial ^{14}C): bis-(4-chlorobenzyl) disulphide (0.2%), 4-chlorobenzaldehyde (0.6%), desethylbenthiocarb (3%), benthiocarb sulphone (1%), benthiocarb sulphoxide (1%), 4-chlorobenzyl alcohol (1%) and 4-chlorobenzoic acid (6%).

Benthiocarb in Deionized Water When ^{14}C benthiocarb in water was irradiated, the ^{14}C in the water rapidly disappeared. The total ^{14}C recovered from the water solution was approximately 97% at 10 minutes, 82% at 30 minutes, 67% at 2 hrs and 42% at 6 hrs. The recoveries of benthiocarb were approximately 92% at 10 minutes, 66% at 30 minutes, 39% at 2 hrs and 2% at 6 hrs. The 30 minute exposure sample contained the following photoproducts (values given as % of initial ^{14}C): 4-chlorobenzoic acid (4%),

Table III ^{14}C-benthiocarb photodegradation by UV light (254 nm) exposure on thin-layer chromatoplate.

^{14}C Compound	*Rf**	*% of initial of ^{14}C*		
		10 minutes	*2 hrs*	*6 hrs*
bis(4-chlorobenzyl) disulphide	0.75	0.0	0.0	0.0
4-chlorobenzaldehyde	0.58	3.7	6.4	1.8
benthiocarb	0.50	85.6	52.0	25.7
desethylbenthiocarb	0.42	1.7	1.8	0.9
X1	0.34	1.7	1.0	0.5
4-chlorobenzyl alcohol	0.22	2.0	2.6	3.9
benthiocarb sulphoxide	0.15	1.0	1.1	0.9
X2	0.10	0.8	0.7	1.4
Original material**	< 0.05	2.6	5.4	7.7

*Developed sequentially with chloroform-ether (4:1) v/v) to 8 cm then with hexane-benzene (1:1 v/v) to 16 cm.

**Contains 4-chlorobenzoic acid, 4-chlorobenzyl sulphonic acid and others.

bis-(4-chlorobenzyl) disulphide (2.4%), 4-chlorobenzyl alcohol (1.2%), desethylbenthiocarb (0.8%) and 4-chlorobenzaldehyde (0.2%).

Photodegradation of Benthiocarb by Natural Sunlight

Benthiocarb Deposited on Silica Gel F254 TLC Plates The total ^{14}C recovery was approximately 96% at 2 hrs, 95% at 6 hrs and 94% at 12 hrs. Table IV gives quantitative data for the radioactive spots on the plate following the application of ^{14}C-benthiocarb, exposure to light for various times, and solvent development of the plate. At 6 hrs, at least 6 degradation products were found on the autoradiogram; the three major photoproducts (values calculated as % of initial ^{14}C) were benthiocarb sulphoxide (1.4%), 4-chlorobenzaldehyde (0.4%) and 4-chlorobenzyl alcohol (0.3%).

Benthiocarb Deposited on Soil TLC Plates As for silica gel plates, there were only small losses of radioactivity when ^{14}C-benthiocarb was exposed to sunlight on soil thin-layer plates. The ^{14}C recoveries were approximately 97% at 2 hrs and 95% at 6 and 12 hrs. The recovery of benthiocarb at 2, 6 and 12 hr exposure was about 94%, 87% and 84% respectively. In an acetone extract (about 92% of the ^{14}C applied) of the 12 hr exposure sample, the following degradation products were identified (values calculated as % of initial ^{14}C): benthiocarb sulphoxide (3.1%), 4-chlorobenzaldehyde (2.0%), desethylbenthiocarb (1.7%), 4-chlorobenzyl alcohol (0.7%), 4-chlorobenzoic acid (0.4%) and bis-(4-chlorobenzyl) disulphide (0.4%). The 12 hr methanol extract contained less than 3% of the total ^{14}C.

Benthiocarb Deposited on Glass Surface When ^{14}C-benthiocarb was deposited on a glass surface as a thin film and exposed to sunlight, the ^{14}C on the glass surface quickly disappeared. The total ^{14}C recoveries varied from 85 to 98% at 2 hrs, from 71 to 82% at 6 hrs and from 58 to 69% at 12 hrs. Identification of the ^{14}C in an acetone extractfrom

Table IV ^{14}C-Benthiocarb photodegradation by natural sunlight on TLC plates.

^{14}C Compound	*Rf**	*% of initial ^{14}C*		
		2 hrs	*6 hrs*	*12 hrs****
bis(4-chlorobenzyl) disulphide	0.75	0.0	0.0	0.0
4-chlorobenzaldehyde	0.58	0.3	0.4	0.2
benthiocarb	0.50	94.7	92.7	90.3
desethylbenthiocarb (and benthiocarb sulphone)	0.42	0.1	0.4	0.4
4-chlorobenzyl alcohol	0.22	0.1	0.3	0.5
benthiocarb sulphoxide	0.15	0.5	1.4	1.4
Original material	< 0.05	0.2	0.8	1.0

*Developed sequentially with chloroform-ether (4:1) v/v) to 8 cm then with hexane-benzene (1:1) to 16 cm.

**Contains 4-chlorobenzoic acid, 4-chlorobenzylsulphonic acid.

*** Plus 15 hrs stored in dark room.

the 12 hr sample showed that about 81% of the ^{14}C in the extract was benthiocarb, about 6% of the ^{14}C was benthiocarb sulphoxide, about 5% of the (^{14}C was 4-chlorobenzoic) acid, about 3% of the ^{14}C was desethyl benthiocarb, and a trace amount of the ^{14}C was 4-chlorobenzaldehyde and bis-(4-chlorobenzyl) disulphide.

Benthiocarb in Water When ^{14}C-benthiocarb in water was exposed to sunlight in an open beaker, the ^{14}C in the water disappeared rapidly. The ^{14}C loss was variable probably due to "weather" factors (such as wind, humidity, temperature, light intensity). The total ^{14}C recoveries varied from 73 to 95% at 2 hrs, 42 to 85% at 6 hrs and 20 to 70% at 12 hrs. Benthiocarb photodecomposed in water to form several photodegradation products. Two products, benthiocarb sulphoxide and desethyl benthiocarb, were identified in the 12 hr exposure sample.

Benthiocarb in water in a stoppered Erlenmeyer flask is photodecomposed by sunlight relatively fast. Analysis at Day 6 showed that over 99% of the ^{14}C benthiocarb had degraded. The recoveries of ^{14}C-benthiocarb were 70% at Day 2, (1:00 P.M.), and about 1% at Day 6 (10:00 A.M.). The degradation products (values calculated as % of initial ^{14}C) found at Day 2 were 4-chlorobenzaldehyde (5%), 4-chlorobenzyl alcohol (8%), benthiocarb sulphoxide (4%), 4-chlorobenzoic acid (5%), and 4-chlorobenzyl sulphonic acid plus highly polar materials (8%). Degradation products isolated at Day 6 were 4-chlorobenzaldehyde (18%), 4-chlorobenzyl alcohol (6%), benthiocarb sulphoxide (1%), 4-chloroben-zoic acid (35%) and 4-chlorobenzylsulfphonic acid plus highly polar materials (38%).

DISCUSSION

Benthiocarb is readily degraded by natural sunlight and artificial UV light (254 nm). The rate of degradation is determined not only by the light sources, but also by environmental factors. Figures 1 and 2 show the rate of benthiocarb photodegradation in water and on soil, glass and silica gel surfaces. The loss of ^{14}C is more rapid in water or on a glass or silica gel surface than on a soil surface. It was also found that the ^{14}C benthiocarb degraded less rapidly on a soil surface than on a silica gel or glass surface or in water solution, indicating that binding materials in soil can prevent the loss of benthiocarb and/or degradation product from volatilization and photodecomposition.

The adsorption and volatilization of benthiocarb have been studied. The results showed that benthiocarb was rapidly and rather strongly adsorbed on soil. Also, adsorption on soil essentially eliminated volatilization losses of benthiocarb.

The proposed photodegradation pathways are shown in Figure 3. Several photochemical reactions occurred when benthiocarb was exposed to natural sunlight and UV light (254 nm). These reactions include:

1. Cleavage at the S—C bond to form a 4-chlorobenzyl radical which is further oxidized to form 4-chlorobenzyl alcohol, then 4-chlorobenzaldehyde and finally 4-chlorobenzoic acid.
2. Oxidation at the sulphur atom gives benthiocarb sulphoxide and sulphone. These oxidation products are unstable and are decomposed to their corresponding sulphinic and sulphonic acids. These further undergo photo-oxidation to form 4-chlorobenzoic acid.

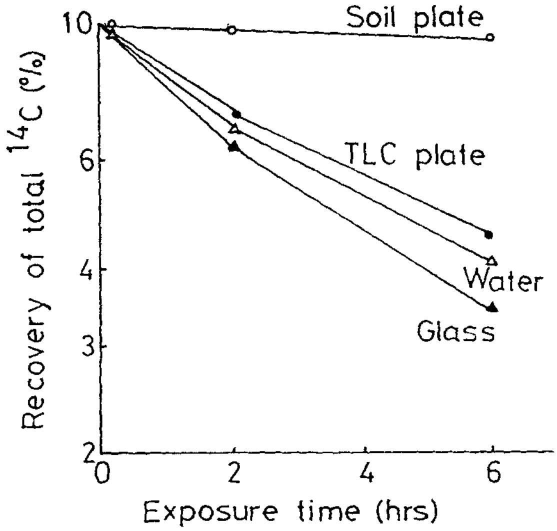

Figure 1 Total ^{14}C recovery after exposure of ^{14}C-benthiocarb to UV light (254 nm).

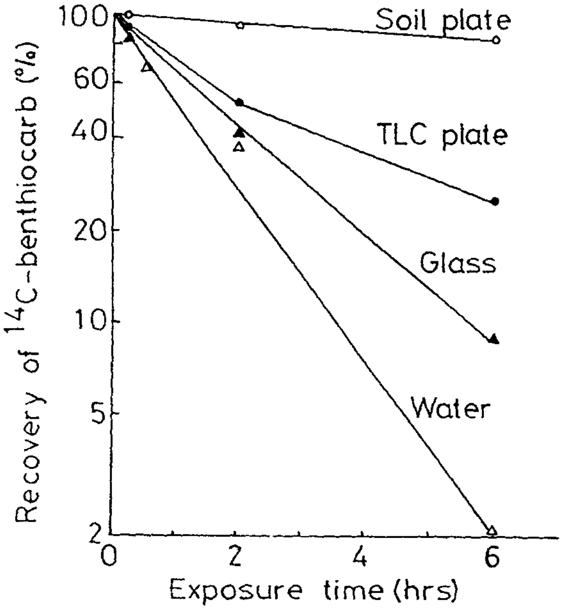

Figure 2 ^{14}C-Benthiocarb recovery after exposure to UV light (254 nm).

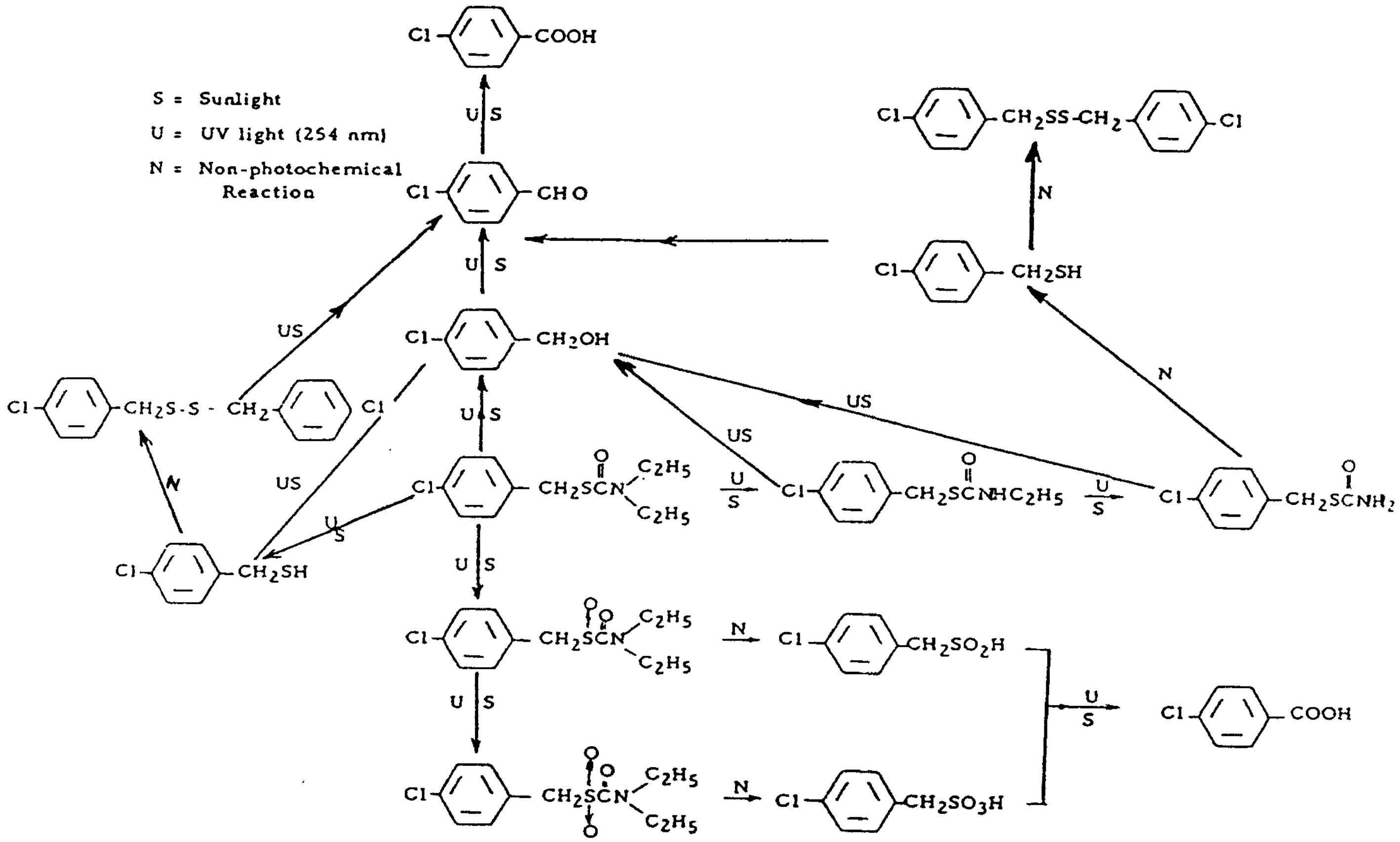

Figure 3 Proposed photodegradation pathways of ^{14}C-ring labelled benthiocarb.

3. Photolysis of the thiolcarbamate moiety forms 4-chlorobenzylthiol which is readily oxidized to form bis-(4-chlorobenzyl) disulphide. This is further cleaved and oxidized to form benzyl alcohol, benzaldehyde and benzoic acid derivatives.
4. N-dealkylation gives desethylbenthiocarb (probably by way of oxidative cleavage). When the two ethyl groups are removed the thiocarbamate is unstable and will degrade to form 4-chlorobenzylthiol.
5. Hydroxylation of the aromatic ring to form ring hydrolyated benthiocarb (a minor reaction when exposed to UV light (254 nm) in water).

Photodechlorination of herbicides such as halogenated-phenoxyacetic acids, -phenylacetic acid, -benzoic acid, and -phenols has been reported (Crosby, 1969). It was found that photodechlorination, followed by ring hydroxylation, formed hydroxybenzoic acids as intermediates which further undergo polymerization to form materials like humic acid. No major effort was made in this study to isolate and identify these types of compounds. However, if present, they were present in very trace amounts only.

This investigation shows that oxygen plays an important role in photodecomposition of benthiocarb. Essentially all photoreaction products are oxidized derivatives. They are not toxicologically significant.

An independent study in Japan showed that benthiocarb in water photodecomposed rapidly in sunlight and confirmed that desethylbenthiocarb, 4-chlorobenzyl alcohol and 4-chlorobenzoic acids are the major photoproducts.

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References

Casida, J. E., Kimmel, E. C., Ohkawa, H. and Ohkawa, R. (1975) Sulfoxidation of thiocarbamate herbicides and metabolism of thiocarbamate sulfoxides in living mice and liver enzyme systems. *Pesticide Biochemistry and Physiology*, **5**: 1–11.

Chen, Y. L., Fang, H., Chen, L. J. and Wang, Y. S. (1976) Photodecomposition and some behavior of herbicides benthiocarb and DCPA in soils. *J. Chinese Agric. Chem. Soc.*, **14**: 59–67.

Cheng, H. M. (1990) Identification of benthiocarb degradation products in chlorinated water. *J. Chinese Agric. Chem. Soc.*, **28**: 77–85.

Cheng, H. M. and Hwang, D. F. (1990) Dissipation of benthiocarb herbicide in deionized water containing chlorine. *J. Chinese Agric. Chem. Soc.*, **28**: 296–300.

Cheng, H. M. and Hwang, D. F. (1993) Metabolism of ^{14}C-ring labeled benthiocarb in mice and rats. *J. Chinese Biochem. Soc.*, **22**: 27–35.

Cheng, H. M. and Hwang, D. F. (1994) Characterization of ^{14}C terminal residues in rice plants treated with ^{14}C ring-labeled benthiocarb. *Journal of Food and Drug Analysis*, **2**: 103–112.

Crosby, D. G. (1969) Pesticide photodecomposition. In Gunther, F. A. (Ed.), *Residue Reviews*, Vol. **25**. Springer-Verlag, New York, 1–12.

Hubbell, J. P. and Casida, J. E. (1977) Metabolic rate of the N, N-dialkylcarbamoyl moiety of thiocarbamate herbicides in rats and corn. *J. Agric. Food Chem.*, **25**: 404–413.

Ishikawa, K., Okuda, I. and Kuwatsuka, S. (1973) Metabolism of benthiocarb (4-chlorobenzyl N,N-diethylthiolcarbamate) in mice. *Agric. Biol. Chem.*, **37**: 165–173.

Ishikawa, K., Nakamura, Y., Niki, Y. and Kuwatsuka, S. (1977) Photodegradation of benthiocarb herbicide. *J. Pesticide Sci.*, **2**: 17–25.

Nakamura, Y., Ishikawa, K. and Kuwatsuka, S. (1974) Uptake and translocation of benthiocarb herbicide by plants. *Agric. Biol. Chem.*, **38**: 1129–1135.

Nakamura, Y., Ishikawa, K. and Kuwatsuka, S. (1977) Metabolic fate of benthiocarb herbicide in plants. *Agric. Biol. Chem.*, **41**: 1613–1620.

Nakamura, Y., Ishikawa, K. and Kuwatsuka, S. (1977) Degradation of benthiocarb in soil as affected by soil conditions. *J. Pesticide Sci.*, **2**: 7–16.

Stahl, E. (1969). *Thin-Layer Chromatography–A Laboratory Handbook.* Springer-Verlag, New York. pp. 52–64.