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The photodecomposition of flurecol-butyl (*n*-butyl-9-flurenol-9-carboxylate)

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Abstract

The photolysis of flurecol-butyl in sunlight and by UV irradiation in laboratory in benzene has been examined. Flurecol-butyl is found to be a rapidly degradable pesticide. The photoproducts formed in sunlight and by UV irradiation in the laboratory are the same. The two major photoproducts are dibutyl-9,9′-bifluorene-9,9′ dicarboxylate and 1-hydroxy-9-fluorenone. Stabilization of fast degradable flurecol-butyl was studied via formation of inclusion complex with β-cyclodextrin.

Keywords: Photolysis; Flurecol-butyl; Molecular encapsulation; β-Cyclodextrin

1. Introduction

In tropical countries, degradation of pesticides by sunlight cannot be ignored. Some pesticides degrade very rapidly in light while the rate of degradation of other pesticides is slow [1]. The degradation product of some pesticides may not be inactive biologically while, in others, activity is actually increased [2]. In some cases, more potent pesticides after degradation may lead to less potent but safer compounds [3,4] whereas, in other cases, photoproducts may be more toxic than their precursors [5]. In view of this, the photodegradation of flurecol-butyl was studied by irradiation with UV light and sunlight.

Pesticides can be complexed with cyclodextrin just as are drug molecules or food flavours [6]. This "molecular encapsulation" frequently results in advantageous modifications of the properties of complexed substances [7]. Flurecol-butyl was subjected to inclusion studies as inclusion is expected to lend stability to such degradable and sensitive (to light, heat, oxygen etc.) pesticides [8–12].

2. Experimental details

2.1. Equipment and materials

IR spectra were determined using a Perkin–Elmar Spectrophotometer model 682. The nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-360 L (60 MHz) spectrometer using tetramethylsilane as an internal standard. Mass spectroscopy (MS) was carried out on a Finagan Mat 1020B GC-MS.

Flurecol-butyl (melting point (m.p.), 68 °C (68–69 °C [13])) was synthesized from 9,10-phenanthrenequinone. Its spectral properties as determined by us are listed below.

MS: M^+ 282. NMR (CCl_4): δ 0.9–1.8 (m, 7H, $-CH_2-CH_2-CH_3$), 4.19–4.5 (m, 3H, –OH and $-OCH_2$), 7.35–8.0 (m, 8H, ArH) ppm. IR: ν 3480 (tertiary –OH), 2960–2880 (–CH stretching), 1710 (ester carbonyl), 1610 and 1590 (aromatic ring) cm^{-1}. UV (methanol): λ_{max} 212, 227, 234 and 271 nm ($\log_{10} \epsilon$ 4.36, 4.31, 4.23 and 4.0 respectively).

USHIO-UM-452 high pressure mercury vapour lamps were used for photoirradiation (lamp electric current, 3.8 A ± 0.2 A; lamp voltage, 130 V ± 10 V).

β-Cyclodextrin (β-CD) was obtained from Fluka. X-ray powder diffractograms were recorded on a Rigaku Geigerflex D/max-B series X-ray diffractometer with Cu Kα radiation.

2.2. Photochemical procedures

2.2.1. In sunlight

Flurecol-butyl (50 mg) was dissolved in 50 ml of spectral grade benzene and kept in sunlight. Similarly, the inclusion compound of flurecol-butyl was treated with a drop of dimethyl formamide (DMF) to declathrate the complex and kept in sunlight.

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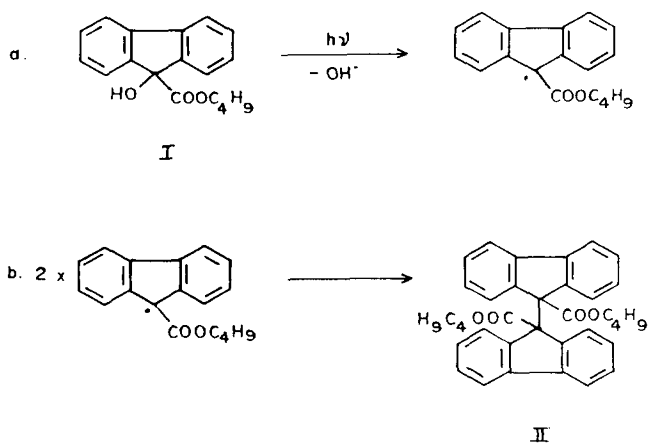
2.2.2. In laboratory

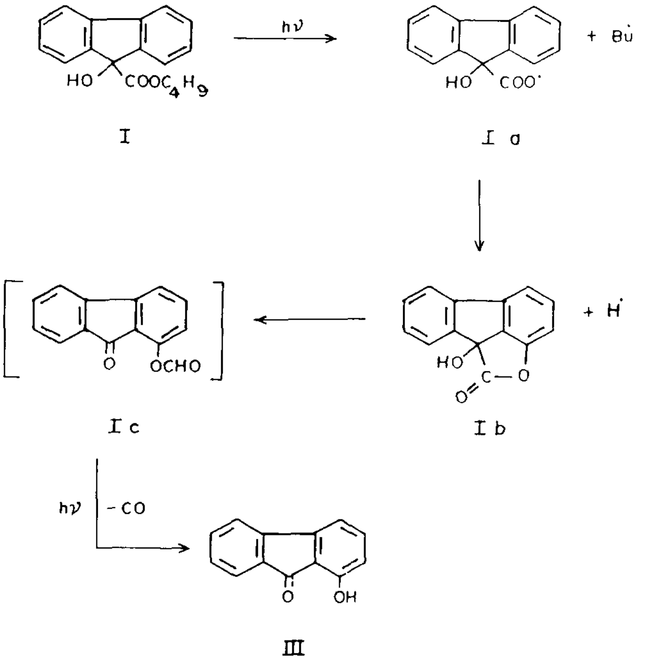
Flurecol-butyl (300 mg, 0.001 mol) was dissolved in 300 ml of benzene and irradiated with a high pressure mercury lamp. Detection of photoproducts was carried out by the thin layer chromatography (TLC) technique, whereas isolation was done on a silica gel column.

2.3. Preparation of inclusion complex

Flurecol-butyl dissolved in a minimum quantity of ethanol was added to an aqueous solution of β-Cd at 80 °C. After homogenizing at 80 °C, further mixing was carried out at 15 °C for 2 h. The residue settled overnight and was filtered. The untrapped feed was removed by washing with acetone and the complex was dried at 100 °C in an oven.



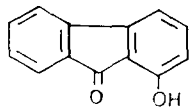
Scheme 1.



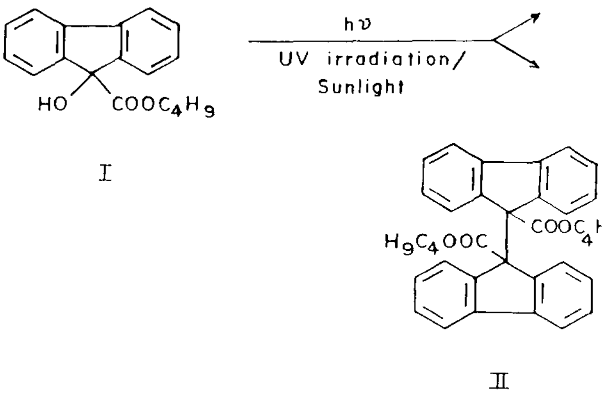
Scheme 2.

3. Results and discussion

Flurecol-butyl (**I**) was found to be a rapidly degradable pesticide. In sunlight, irradiation for 15 min showed the formation of five to six photoproducts (75% degradation), whereas a similar pattern of photoproducts on TLC was observed after irradiation of **I** with UV light within 5 min. The major photoproducts 25% were isolated:



III



(1)

Their spectral characteristics as determined by us are given below.

Dibutyl-9,9′-bifluorene-9,9′ dicarboxylate (II): m.p., 128 °C. MS: M^+ 530. NMR (CCl_4): δ 6.8–7.4 (m, 16H, aromatic protons), 3.9–4.3 (m, 4H, $-OCH_3\times2$), 0.7–1.8 multiplet (4H, $-\mathrm{C}H_2-\mathrm{CH}_3\times2$) (6H, $-\mathrm{CH}_3\times2$) (4H, $-\mathrm{C}H_2-\mathrm{CH}_2-\mathrm{CH}_3\times2$) ppm. IR: ν 3080–2840 (CH stretching), 1610 and 1590 (aromatic ring), 1740 and 1720 (ester carbonyls) cm^{-1}.

1-Hydroxy-9-fluorenone (III): m.p., 115 °C (115 °C [14]). MS: M^+ 196. NMR ($CDCl_3$): δ 6.6–7.7 (m, 7H, ArH), 8.3 (s, H–OH) ppm. IR: ν 3370 (–OH), 1690 (carbonyl), 1600 (aromatic ring) cm^{-1}.

Dibutyl-9,9′-bifluorene-9,9′ dicarboxylate (**II**) is a dimer formed by loss of –OH from flurecol-butyl (**I**). Its formation can be rationalized as in Scheme 1.

The formation of 1-hydroxy-9-fluorenone (**III**) can occur by the loss of butyl radical from **I** to form **Ia**. Abstraction of a hydrogen from the ring to give **Ib** and a rearrangement involving a 1,3 shift can lead to the formation of *o*-formyl derative **Ic**. The loss of carbonyl from **Ic** would result in the formation of **III** (Scheme 2). This proposal is entirely tentative and further experimental verification is in progress.

In order to reduce the rate of degradation of flurecol-butyl, attempts were made to include **I** in β-CD. Encapsulation of **I** in β-CD was confirmed by the m.p. (262–266 °C), TLC analysis, UV spectra in DMF (λ_{max} = 275 nm) and X-ray diffraction technique.

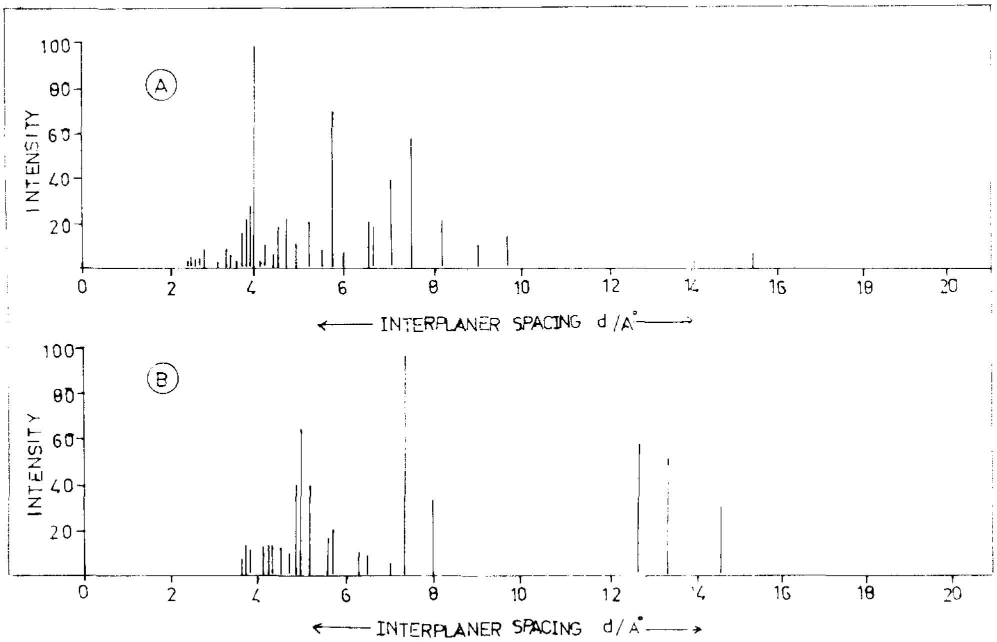


Fig. 1. X-ray line diagrams: A, flurecol-butyl–β-CD physical mixture; B, flurecol-butyl–β-CD inclusion complex.

A typical diffraction pattern line diagram of flurecol-butyl–β-CD physical mixture and flurecol-butyl–β-CD inclusion complex (Fig. 1) illustrates the entry of the guest in β-CD moiety.

Irradiation of the standard **I** and inclusion complex of **I** in sunlight was carried out for $\frac{1}{2}$ h. TLC analysis showed that the number and concentration of photoproducts in the case of inclusion compound after irradiation was low, compared with the degradation of standard **I**.

From this it can be deduced that the photodegradation rate was slowed down on inclusion, which may be due to the slow release of **I** from inclusion complex after the addition of DMF. It is possible therefore to stabilize these types of rapidly degradable pesticide by encapsulating them in β-CD.

Acknowledgements

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References

[1] M.J. Zabik and Z.M. Chen, *Ind. Eng. Prod. Res. Dev., 23* (1984) 5.
[2] D.G. Crosby and G.L. Henderson, *J. Agric. Food Chem., 15* (1967) 888.
[3] D.D. Phillips and G.E. Pollard, *J. Agric. Food Chem., 10* (1962) 217.
[4] J.D. Rosen and D.G. Lipton, *Bull. Environ. Contam. Toxicol., 1* (1966) 133.
[5] W.F. Spencer and Y. Iwata, *Bull. Environ. Contam. Toxicol., 18* (1977) 656.
[6] Mikasa Chemical Industrial Co. Ltd., *Jpn. Kokai 80, 81, 806,* 1980; *Chem. Abstr., 93* (1980) 182725.
[7] J. Szejtli, *Starch/Starke, 37* (1985) 382.
[8] Agency of Industrial Sciences and Technology, *Jpn. Kokai 58, 99, 437,* 1983.
[9] K. Tsuji, T. Maeda, H. Guyama, M. Kawashima, N. Kasamatsu, J. Ohnishi and Y. Fujita, *5th Int. Congr. on Pesticide Chemistry (IUPAC), Kyoto, 1982.*
[10] K.K. Nikata Shokai, *Jpn. Kokai 80, 149, 204,* 1980.
[11] Takeda Chemical Industries Ltd., *Jpn. Kokai 81, 75, 496,* 1981.
[12] Hokko Chemical Industry Co. Ltd., *Jpn. Kokai 58, 21, 602,* 1983.
[13] R.L. Jones and W.A. Sexton, *J. Sci. Food Agr., 5* (1954) 32.
[14] L. Horner, *Justus Liebigs Ann. Chem.,* (1973) 910.