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PHOTODEGRADATION OF THE ORGANOPHOSPHORUS INSECTICIDE 'PHORATE'

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The photolysis of Phorate(I) (0,0-diethyl *S*-ethyl thiomethyl phosphordithioate) has been studied as a thin film on a glass surface and in a solution of methanol-water (60:40) by ultraviolet light ($\lambda > 290$ nm). The rate of disappearance of Phorate in the solution show first order Kinetics with a rate constant of 4.9×10^{-5} S^{-1}. The half-life of (I) exposed on a glass surface is found to be 5 hours. The structure of the major photoproducts were characterised by ^{1}H NMR and mass spectroscopy.

KEY WORDS: Phorate, photodegradation, organophosphate, insecticide.

INTRODUCTION

Photogradation plays a very important role in the environmental decomposition of insecticides and have broad significance in regard to formulating environmental usage and persistence parameters[1–2]. In this context, it is required to determine the photo-transformation rate constants or half-lives for the pesticides at the environmentally significant concentration levels and identification of the photoproducts.

Phorate(I) (0,0-diethyl *S*-ethyl thiomethyl phosphorodithioate) has both systemic and contact insecticidal action and controls sucking and biting insects and mites in brassicas, beet-root and sugar beet[3]. It has been reported[4] the in vitro 'Toxic' effect of (I) on the yarn (Dioscorea alata) nematode "Scutellonema bradys". In plants, animals and in insects phorate is oxidised to the corresponding sulphoxide and sulphone as the major metabolites and provides an example of the metabolism of a sulphide group[5]. Some workers[6] have found that the Pseudomonas sp. was able to degrade phorate in the soil. The present paper describes the investigations on photolysis of Phorate(I).

MATERIALS AND METHODS

Phorate(I) was obtained from Khaton Jhunkar India (95%). It is a colourless liquid, b.p. −118–120° at 1 m bar, vapour pressure 1.1×10^{-3} m bar at 20°C, miscible in organic solvents. Distilled solvents were used in irradiation experiments. Solvents used for extraction and analysis were of analytical grade.

Chromatography

Gas liquid chromatography (GLC) analysis was carried out on Hawlett-Packard model 5890 A equipped with a flame-ionisation detector and glass column (2 M × i.d. 2 mm) packed with 3% OV-17 on 80–100 mesh chromosorb. The oven, injector and detector temperatures were 220, 240 and 270°C respectively. Nitrogen was used as carrier gas at flow rate of 30 ml min^{-1}. Thin layer chromatography (TLC) was carried out on glass plates coated with 0.5 mm layer Silica Gel G. The spots on TLC were visualised by iodine vapours. The purity of the various products was checked by GC.

Spectrometric analysis

Proton magnetic resonance (^{1}H NMR) spectra of various photoproducts were recorded on a 60 MHz – FT.NMR [R-600 Hitachi (Japan) Model] spectrometer. The solvent used was deuterochloroform ($CDCl_3$) or CCl_4 containing 1% tetramethyl silane as the internal standard. Mass spectra (MS) was recorded on a Jeol-JMS-DX-300 combined with a JMA-2000 data analysis system, mass spectrometer at 70 eV using electron impact ionisation. Infra-red spectra was recorded on IR-435 model (Shimadzo, Japan) as KBr pellet.

Photolysis

In Solution: The exposure of the phorate in solution was carried out with UV-light from a medium pressure Hg lamp (Phillips, 125 W) emitting a radiation energy of approximately 2000 J m^{-2} S^{-1} and using quartz tubes as carried out in our earlier work[7].

The kinetic studies were performed on a 5 ppm solution of phorate in methanol —H_2O (60:40). Two tubes were kept in the dark as control and as the t = 0 sample and the remaining amount is taken 20 ml each in seven photolysis tubes. These sample tubes were withdrawn from the photolysis reactor at intervals of 1, 3, 5, 7, 9, 11 or 13 hours of exposure and analysed by GLC along with the control samples. Since photolysis at the 5 ppm level did not provide sufficient material for convenient mass spectral, nmr and tlc procedures for identification of photoproducts, a solution of 4 g in 500 ml of CH_3OH was photolysed for 15 hours and no attempt was made to remove naturally dissolved gases from the solution before photolysis. The alcohol was removed by a rotary evaporation at a bath temperature of 40°C. The oily residue was subjected to chromatography for analysis.

As thin Film: The photolysis studies of Phorate(I) were conducted as thin films on glass surface. A solution of phorate in CH_2Cl_2 was pipetted into a 50 mm i.d. pyrex petridish and the solvent allowed to evaporate in the dark to give a layer 6 μ thick. These dishes were placed under the germicidal lamp (λ – 254 nm) in such a manner so that the film was parallel to the axis of the lamps. The samples were withdrawn at intervals of 1, 3, 5, 7, 9, 11 and 13 hours. The glass plates after irradiation were

extracted thoroughly with acetone (10 ml). Acetone was evaporated and a final volume was made to 2 ml and analysed by GLC.

In all cases a dark control experiment was conducted to ensure that the degradation of the phorate was initiated from photochemical processes. All dark control samples in this study gave only phorate. No evidence of any other products was detectable at the 0.5% level.

PREPARATION OF DEGRADATION PRODUCTS

Phorate sulphoxide

It was prepared by mixing Phorate (500 mg) and *m*-chloroperbenzoic acid (500 mg) with continuous stirring for half an hour. The reaction mixture was kept for 12 hours in a freezer. It was then filtered. After evaporating the solvent from the filterate, the mixture was subjected to preparatory thin layer chromatography over Silica gel to get pure product. ^{1}H NMR ($CDCl_3$) δ1.4(6H, t, J = 7 Hz), δ4.1(4H, m) δ4.24(2H, S) and δ2.84(q, 2H). MS: $-$m/e at 276, the singlet at δ4.28 for 2 protons corresponding to $CH_2\begin{smallmatrix}S\\S\end{smallmatrix}$ gp, and the peaks at δ2.84(q, 2H), appear at low field due to the presence of sulphoxide group.

Phorate sulphone

Phorate sulphone was prepared by mixing Phorate (200 mg) with a solution of glacial acetic acid (5 ml) and a solution of cold hydrogen peroxide (5 ml, 30%). This mixture was heated gently on a water bath for 30 minutes and kept for overnight at R.T. The viscous off white mass was neutralised with $NaHCO_3$ solution (10%) and extracted with chloroform (2 × 50 ml). The chloroform extract was dried over anhydrous sodium sulphate and purified by preparative thin layer chromatography to yield phorate sulphone.

^{1}H NMR ($CDCl_3$): δ4.28(S, 2H), δ1.28(6H, t, $-OCH_2CH_3$ × 2) and δ4.15 (4H, m, $-OCH_2CH_3$ × 2) MS: $-$m/e at 292. The peak at δ4.28(S, 2H) characteristic of the ($-S-CH_2-S-$) group which appears at lower field than that of phorate sulphoxide compound.

RESULTS AND DISCUSSION

Phorate(I) was rapidly degraded under the experimental conditions used. A 5 ppm solution of Phorate in methanol water (60:40) exhibits first order Kinetics and has a rate constant of disappearance $4.9 \times 10^{-5}\ S^{-1}$. The first order Kinetics curve for the photolysis of Phorate(I) is shown in Figure (1).

Figure (2) shows the photodegradation kinetics of Phorate(I) on glass surface under ultraviolet light. The half-life of Phorate(I) on glass surface exposure was 5 hours.

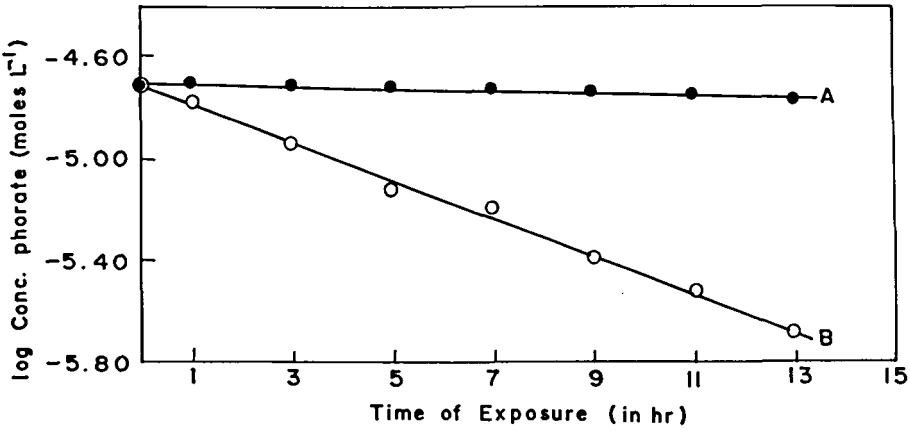

Figure 1 Rate of photodegradation of Phorate(I) in methanol-water (60:40). (A) Dark; (B) UV light.

The various photodegradation products which have been isolated are shown in Figure (3). The product-II was identified as phorate sulphoxide by co-tlc and comparison of its nmr and mass spectra with the authentic sample prepared as above. The product III was identified as phorate sulphone by co-tlc and comparison of its nmr and mass spectrum with the authentic sample.

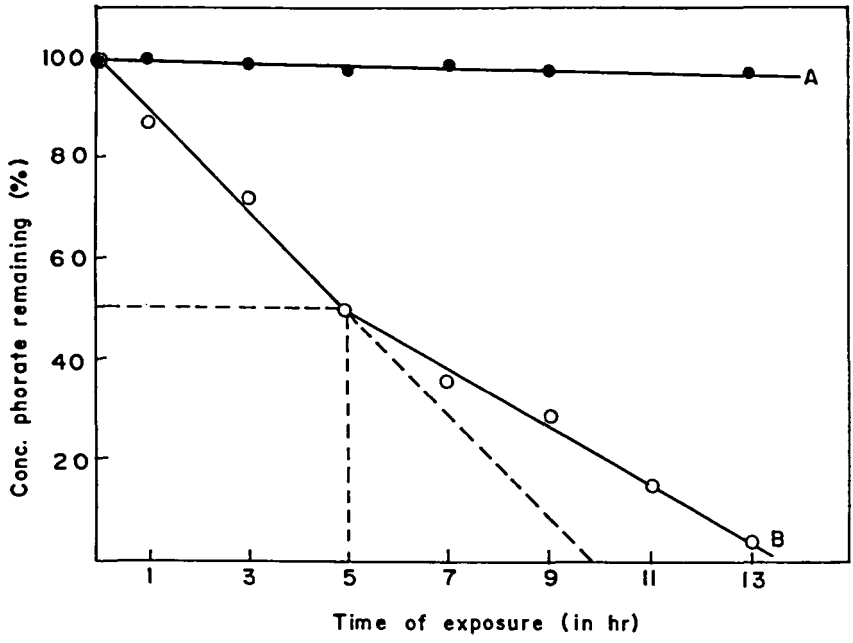

Figure 2 Loss of Phorate(I) from glass surface under. (A) Dark; (B) UV light.

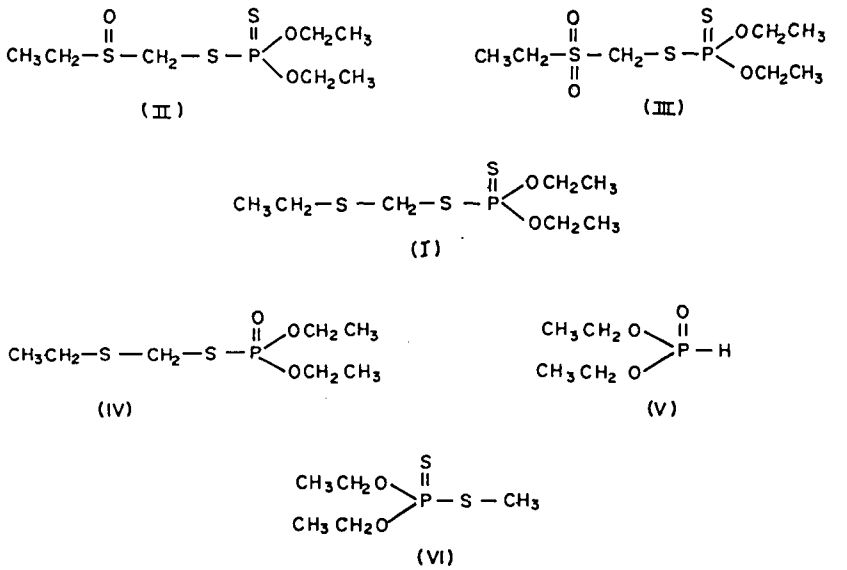

Figure 3 Photoproducts of 'Phorate'.

The infrared spectrum of tlc band (IV) revealed a strong band at 1265 cm^{-1} typical for the P=O group. The ^1H NMR spectra of the product was similar to that of Phorate(I) except (—OCH_2CH_3) protons which were present at δ4.4(q) and its mass spectrum showed a molecular ion peak at 244. This was identified as phorate oxon, formed by the conversion of P=S to P=O.

The ^1H NMR spectra of (V) showed a triplet at δ1.38 (6H, t, J = 6.8 Hz), δ4.17(4H, q, $^3J_{P-H}$ = 10.6 Hz) and singlet at δ6.82(IH). Its mass spectrum showed (($M^+ - 138$), it was assigned the structure O,O-diethyl phosphonate. The ^1H NMR ($CDCl_3$) of (VI) showed a triplet at δ1.4(6H, t) at low field, δ4.15(m for 4H) and δ2.17(3H, S) $M^+ - 200$, it was assigned the structure O,O-diethyl *S*-methyl phosphorodithioate.

CONCLUSION

These studies indicate that Phorate is rapidly degraded under the influence of ultra-violet light. It undergoes oxidation, P=S to P=O, and cleavage of P—S— bond to produce various types of degradation products. This is the first report on the photodecomposition of Phorate yielding different types of toxicologically-significant degradation products under laboratory controlled conditions.

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